

FUNDAMENTAL INVESTIGATION OF
THE BOSCH REACTION

by

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of the Requirements for

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at the

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ABSTRACT

"Fundamental Investigation of the Bosch Reaction"

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Richard B. Wilson

Submitted to the Department of Chemical Engineering on August 1, 1971, in partial fulfillment of the requirements for the degree of Master of Science.

The Bosch reaction, i. e., hydrogen reduction of carbon dioxide to yield solid carbon plus water, has received considerable study as a feasible method for oxygen reclamation on long duration space flights. The major goal of this research effort was to obtain a better general understanding of the reaction of the oxides of carbon plus hydrogen over an iron catalyst. A secondary aim was to answer some of the critical questions, the answers to which are needed to help evaluate the Bosch reactor system for space applications.

Studies using a mixture of carbon dioxide, carbon monoxide and hydrogen over an iron rod at 600°C and atmospheric pressure showed that the Bosch reaction ($\text{CO}_2 + 2\text{H}_2 \rightleftharpoons \text{C} + 2\text{H}_2\text{O}$) does not occur. The major reaction contributing to the formation of the filamentous carbon deposit was the Boudouard ($2\text{CO} \rightleftharpoons \text{CO}_2 + \text{C}$). Hydrogen was found to be a very active promoter for this reaction. The results indicated that the 2-3% water which was produced resulted from the reverse water gas shift reaction. ($\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$) An autocatalytic effect was observed, but its importance decreased with longer times for reaction. This autocatalytic effect resulted from the small iron particles found on the ends of the carbon filaments.

Studies of the reaction over the carbon product showed a gradual decreasing rate as more carbon deposited. Reaction continued until the iron concentration fell below 0.5%. Electronmicrographs of the carbon showed small ribbon-like threads with dense crystals of iron or a high carbide at the ends. It was postulated that the metal crystals have two active surfaces for carbon growth. These crystals seemed to disintegrate and disperse throughout the carbon when reacted for longer times.

It is suggested that the rate of reaction was controlled by the active surface area of the iron available for chemisorption. Thus, at long reaction times, the rate would be controlled by the reaction over the carbon product. Results showed that the Bosch reaction(s) are controlled more by kinetic and mechanistic factors than by equilibrium considerations. The results suggest that in a Bosch reactor system, the carbon dioxide provides (via hydrogen reduction) the carbon monoxide which decomposes to the filamentous carbon product via the Boudouard reaction.

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Professor E. Neal Hartley
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Dear Professor Hartley:

In accordance with the regulations of the Faculty, I herewith submit a thesis, entitled "Fundamental Investigation of the Bosch Reaction", in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering at the Massachusetts Institute of Technology.

Respectfully submitted,

R. Barry Wilson

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The author wishes to express his gratitude to Professor Robert C. Reid and Professor Herman P. Meissner for their encouragement and thoughtful guidance of this project. A special thankyou is expressed to Professor Reid for his concerned and challenging direction and his warm friendship.

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The author wishes to express his appreciation to his parents whose help and encouragement have made his education a rewarding experience. Finally, his wife Janet deserves a special thankyou for her tireless support in the typing and preparation of this thesis, and most of all for her understanding and love.

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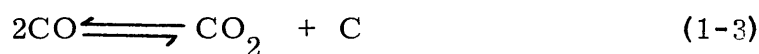
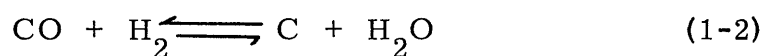
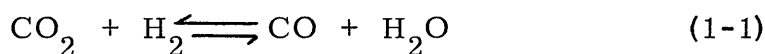
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I. SUMMARY

The hydrogen reduction of carbon dioxide to yield solid carbon plus water (Bosch Reaction) has received considerable attention during the past ten years. This has stemmed from NASA's desire to develop a closed loop oxygen cycle. One method currently being studied as a feasible means for oxygen reclamation on long duration space flights utilizes a Bosch reactor system. After separation of the exhaled carbon dioxide and addition of hydrogen, the gas mixture would be passed through a "Bosch Reactor," where carbon would be deposited and water condensed. The water would then be electrolyzed to yield oxygen which would be stored for later astronaut consumption and hydrogen which would be recycled.

No reference has been found which suggests that the Bosch reaction ($\text{CO}_2 + 2\text{H}_2 \rightleftharpoons \text{C} + 2\text{H}_2\text{O}$) actually occurs over an iron catalyst. If the overall reaction were written as above, a series of sequential reactions would be logical.



Over an iron catalyst there is the possibility of the products reacting further to yield such species as methane and iron carbides. Considering only the three reactions above, numerous contradictions were found in the literature as to the active catalyst species, important operating parameters, mechanism of reaction and nature of the carbon product. Consequently, it was the purpose of this research to obtain a better general understanding of the reactions when passing mixtures of carbon oxides plus hydrogen over an iron surface.

A tubular reactor, furnace and gas flow system were designed

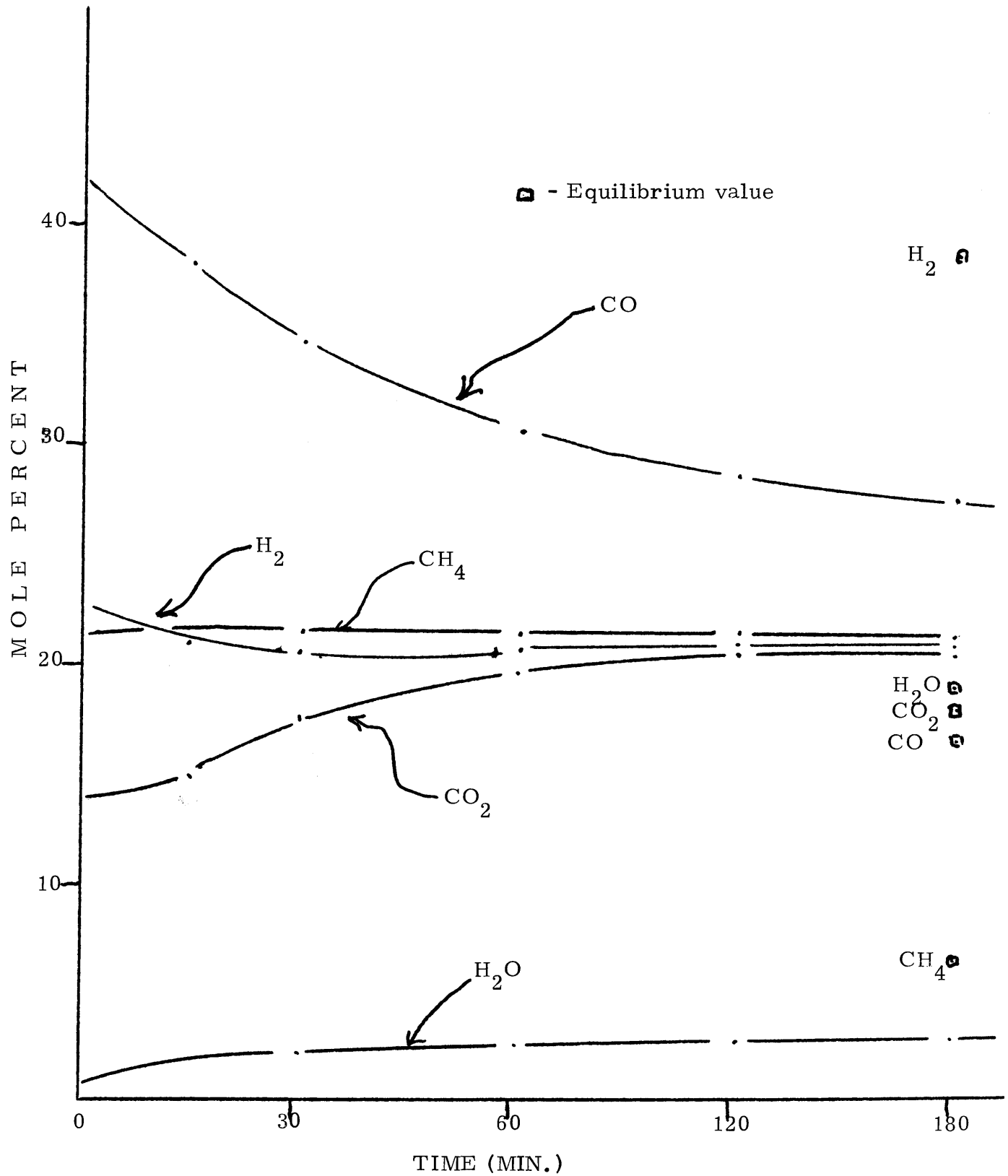
with flexibility and simplicity in mind. The reaction was performed by passing the preheated gas mixture over a concentrically supported rod. A residence time of 20 seconds and an average Reynolds number of 2 was maintained over the rod. Operating temperatures varied between 500°C-700°C, but all experiments were performed at atmospheric pressure. The rate of reaction was determined from inlet and exit gas compositions and flow rates. The deposited carbon was observed under a transmission electron microscope.

In runs with only carbon dioxide and hydrogen passing over the iron rod, small amounts of carbon monoxide and water were produced. The conversion increased as the temperature was raised from 500°C to 700°C. However, no carbon was deposited. These results indicated that only the reverse water-gas shift was occurring, Equation (1-1). Changing the feed to one of 50% hydrogen and 25% carbon monoxide and carbon dioxide, led to a large carbon deposit formed on the iron rod after only a few hours. When substituting helium for hydrogen, negligible carbon was deposited, and no water was detected. However, if only carbon monoxide and hydrogen were fed, carbon was deposited after a very short time. Carbon dioxide and water were also detected which indicated that both the Boudouard reaction, Equation (1-3), and the hydrogen reduction reaction, Equation (1-2), were responsible for the carbon.

Various recycle gas compositions have been used in studies for NASA, but typical values were: 25% hydrogen, 20% methane, 40% carbon monoxide and 15% carbon dioxide. Using this approximate composition, studies over the iron rod showed some notable results. A plot of the gas composition as a function of time (refer to Figure 1-A) showed large decreases in carbon monoxide and a measureable increase in carbon dioxide. The concentration of water increased with increasing time of reaction but remained fairly constant after two hours. The symmetrical shape of the carbon monoxide and carbon

FIGURE 1-A

GAS COMPOSITION OVER IRON
ROD AS A FUNCTION OF TIME



dioxide curves indicates that nearly all of the carbon deposit resulted from the Boudouard reaction. This further suggested that the water must have been produced via the reverse water-gas shift reaction.

Using these data, the rate of carbon formation was determined as a function of the time of reaction. Figure 1-B shows a definite increase in the rate of carbon deposition, although the rate of increase decreases with time. The reaction appears to be autocatalytic.

Analysis of the carbon showed it to contain over 9.0% iron. This raised the possibility that the autocatalytic effect could have resulted from the iron in the carbon product. Also, at longer reaction times, when appreciable carbon had deposited, it was possible that the rate might be controlled by the reaction over carbon.

In order to determine the validity of these postulates, an experiment was performed by replacing the carbon deposit in the reactor and using the same NASA gas composition. The exit gas composition over the carbon was plotted in Figure 1-C. From these results it was apparent that even the carbon product was catalytic. Again, the symmetry of the carbon monoxide and carbon dioxide curves indicated that further carbon deposition resulted from the Boudouard reaction, Equation 1-3. A carbon balance as a function of time (see Figure 1-D) showed a maximum in the rate of deposition followed by a gradual decrease. No explanation was forwarded to account for this observed maximum in the rate. However, the gradual decrease in the rate of deposition over the carbon probably resulted from a disintegration of the iron crystal "heads."

A series of experiments were performed on replaced carbon to determine the minimum concentration of iron necessary to elicit reaction. This would also permit an observation of changes in the carbon for longer reaction times. A given weight of carbon was reacted then reweighed. A small amount of this re-reacted carbon was replaced in the reactor and the same procedure followed. These

FIGURE 1-B

RATE OF CARBON DEPOSITION ON IRON ROD
AS A FUNCTION OF TIME

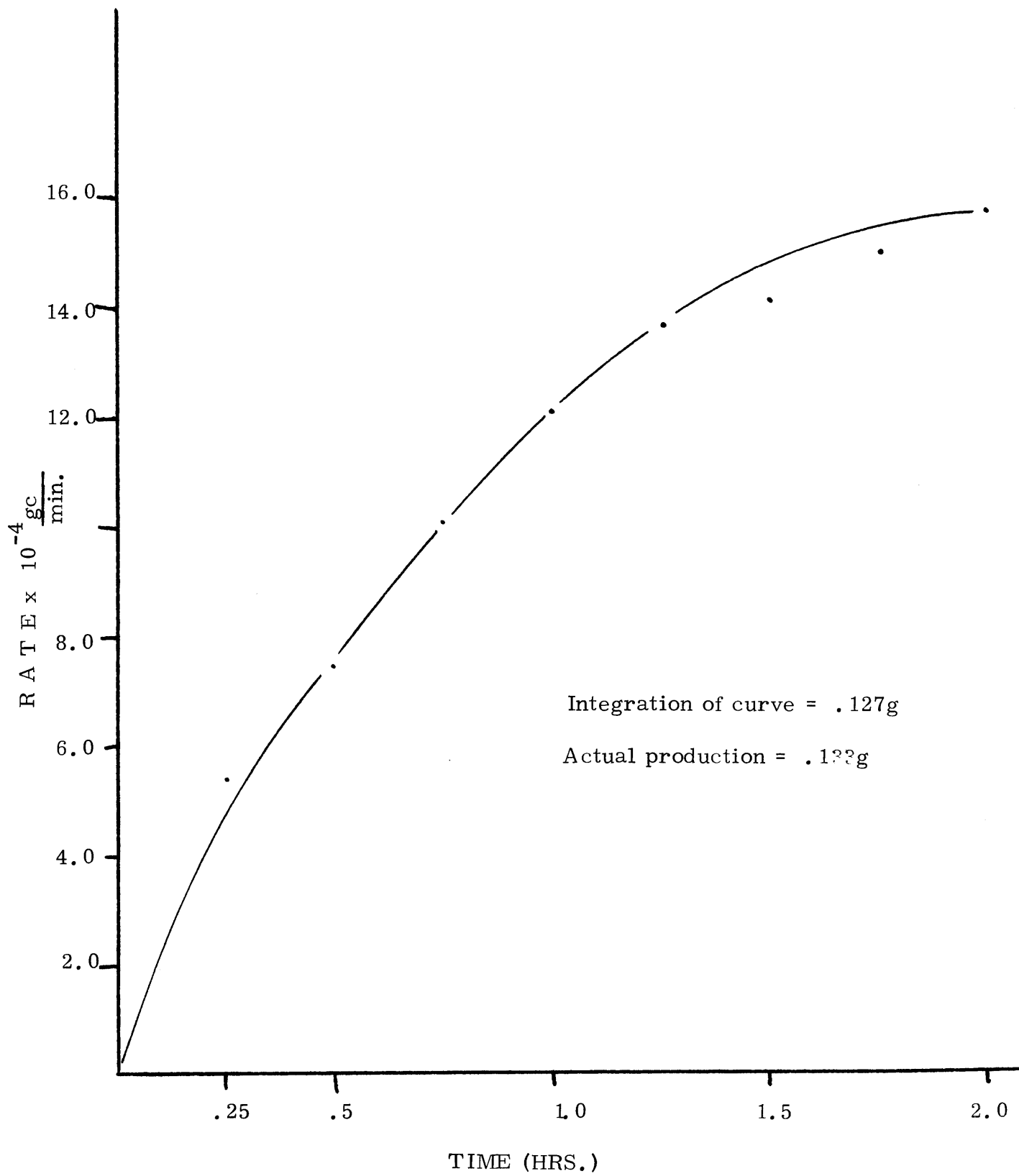


FIGURE 1-C
GAS COMPOSITION OVER CARBON
AS A FUNCTION OF TIME

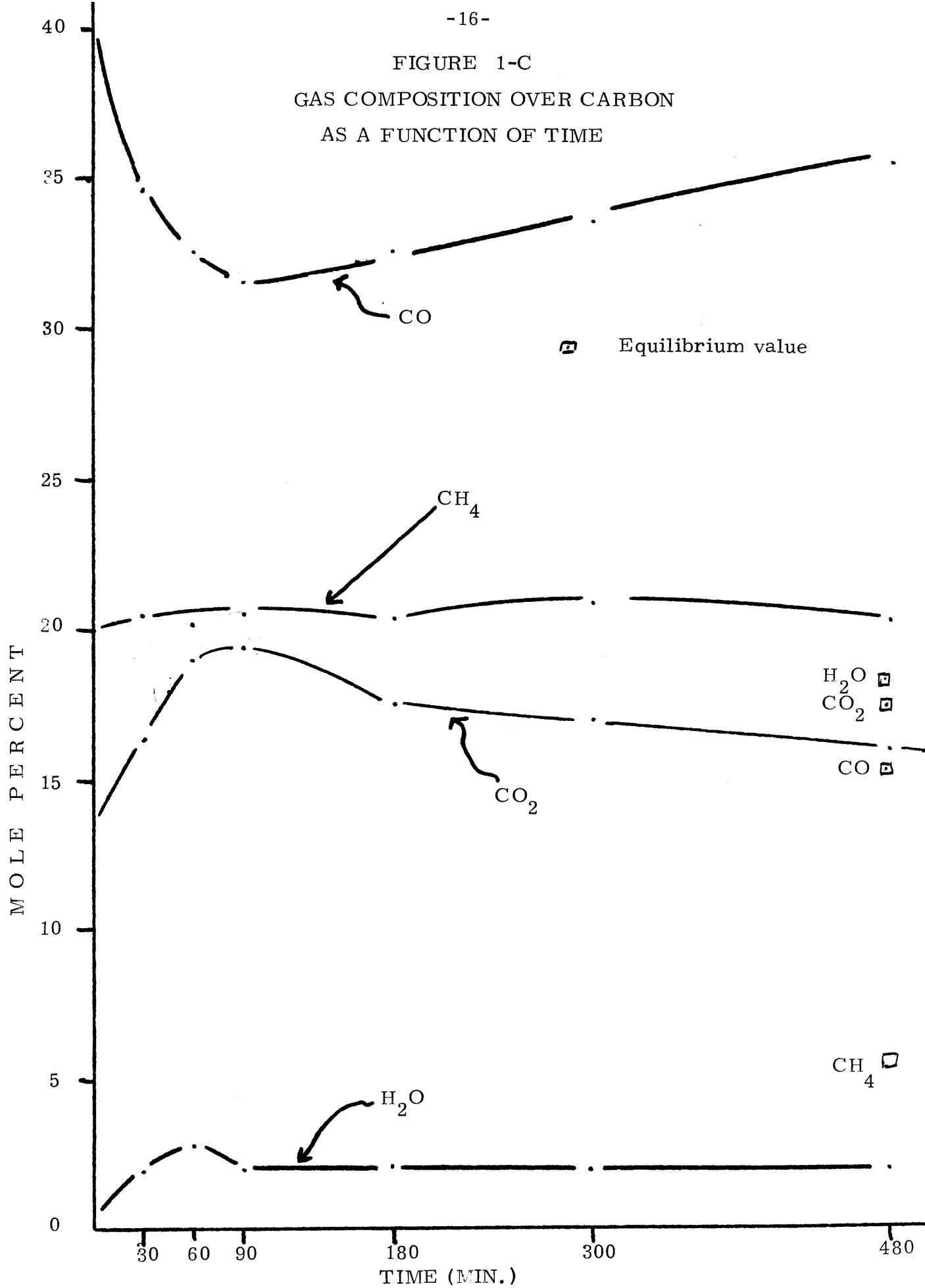
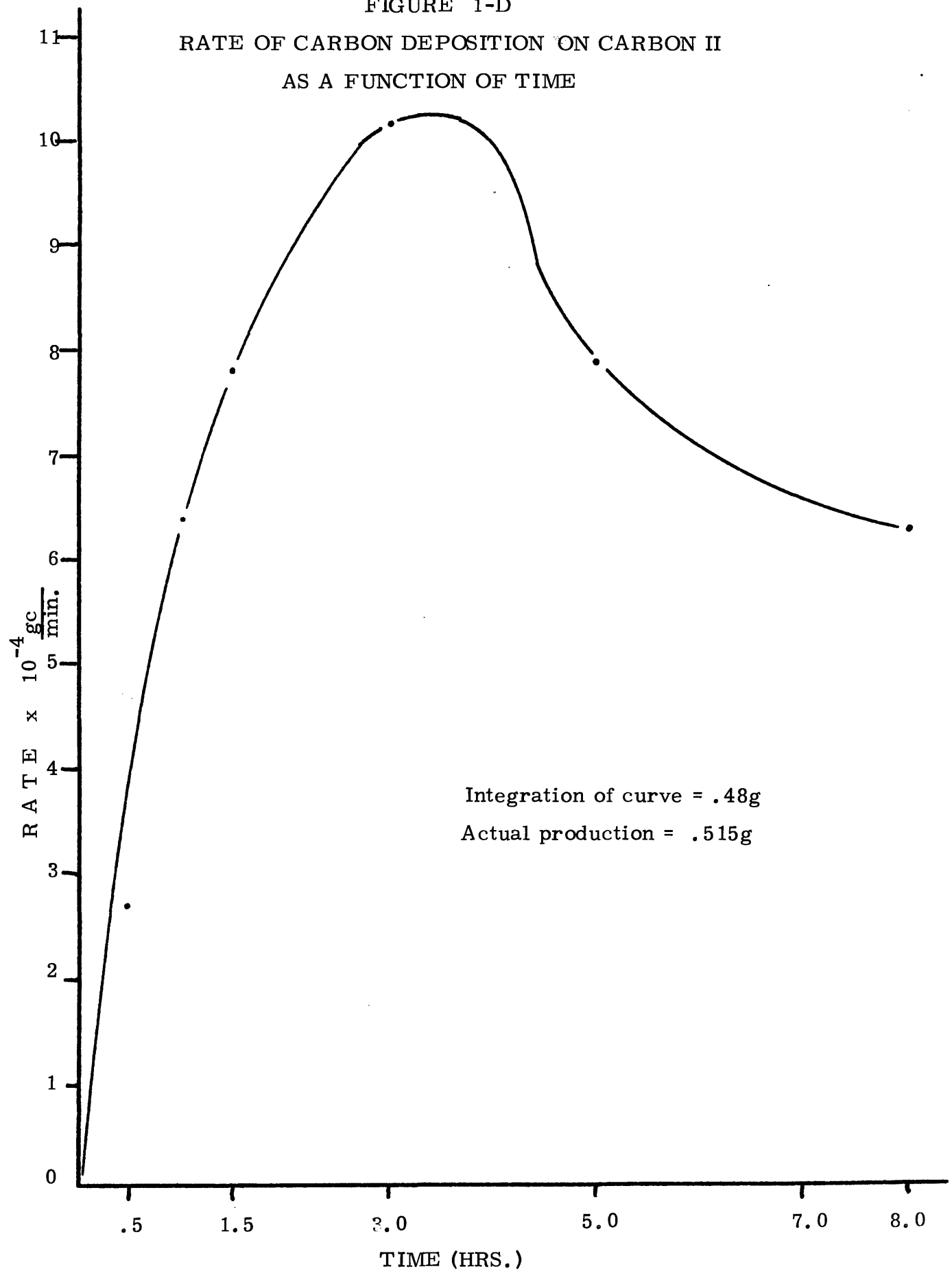


FIGURE 1-D
RATE OF CARBON DEPOSITION ON CARBON II
AS A FUNCTION OF TIME



successive replacements were continued until little or no reaction was observed. The initial carbon had an iron concentration of 9.6% but decreased to 0.5% before the reaction rate was negligible. A summary of this data can be found in Table I-A.

Observation of the carbon deposits showed characteristic thread-like fibers about 1μ in length and between $0.1-0.2\mu$ in width. A dark, dense crystal of iron or an iron carbide was distinguishable at the ends of the fibers and frequently within its length. This suggests that the crystal may have two active surfaces for further carbon growth. Figure 1-E, shows typical carbon formations. Another characteristic structure was a dense granular appearance in some of the carbon fibers. It was hypothesized that these electron-rich kernels have resulted from disintegrating crystal "heads." Previous investigators have found similar carbon formations from carbon monoxide, methane, acetylene and carbon monoxide-hydrogen mixtures over iron and other transition metal catalysts. They have referred to the carbon fibers as filaments, which suggests a cylindrical shape. Results from this study show that under high magnification, a ribbon-like structure was apparent, having a thickness of $100\text{\AA}$. See Figure 1-F. Electron micrographs of the carbon which has been further reacted showed a decrease in the number of distinct crystal "heads." The disintegrated "heads" seem to have resulted in dark bands or dense kernels along the length of the carbon ribbon. Refer to Figure 1-G.

Equilibrium calculations predict that the production of water should be maximized at an oxygen to hydrogen ratio of 0.5, and the production should increase with decreasing temperature. Neither this study nor any previous investigation has found the equilibrium predictions to be justified by experimental evidence.

DATA FOR SUCCESSIVE REPLACEMENTS OF CARBON

TABLE I-A

	Carbon I*	Carbon II	Carbon III	Carbon IV
Weight of Carbon Initially (grams)	0.0	.262	.168	.205
Weight of Carbon after Reaction (grams)	.346	.777	.784	.238
Increase in weight of Carbon (grams)	.346	.515	.616	.034
Time for Reaction (hours)	4.0	8.0	16.0	14.0
Percentage Iron in Carbon* (after reaction)	9.58%	3.07%	.551%	.30%
Calculated Percentage Iron (from dilution)	_____	3.23%	.645%	.43%
Rate $\frac{\text{g Carbon Formed}}{\text{hr} - \text{g Initial Carbon}}$	.0865***	.245	.230	.012
Rate $\frac{\text{g Carbon Formed}}{\text{hr} - \text{g Iron}}$	.00108	2.56	7.48	2.15

*Deposition of carbon on iron rod

**All values have a precision of $\pm 0.05\%$

***Units for carbon I are $\frac{\text{g carbon formed}}{\text{hr}}$

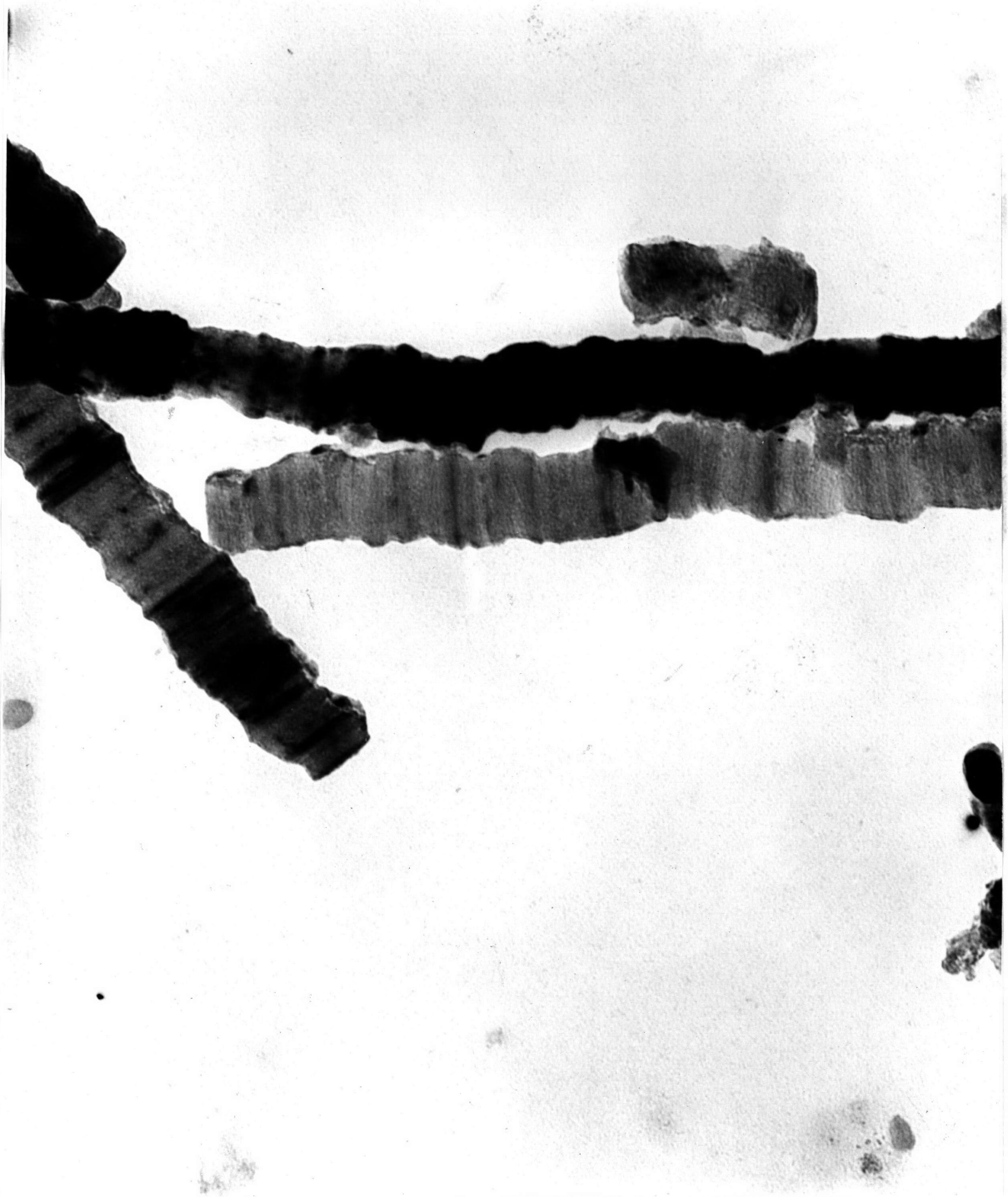
FIGURE 1-E



Carbon Electronmicrograph - typical formations
(31,000X)

0.5 μ

FIGURE 1-F



Carbon Electronmicrograph - Ribbon-like structures

(189,500X)

500 Å
—|—

FIGURE 1-G



Carbon Electronmicrograph - disintegrated iron heads

(70,500X)

1430 Å

As a result of this study, the following conclusions were drawn:

- The Bosch reaction, as written $\text{CO}_2 + 2\text{H}_2 \rightleftharpoons \text{C} + 2\text{H}_2\text{O}$, does not occur over iron at 600°C and atmospheric pressure. Instead, the results indicate a stepwise sequence initiated by the reverse water-gas shift reaction, $(\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O})$ followed by the decomposition $(2\text{CO} \rightleftharpoons \text{CO}_2 + \text{C})$ or hydrogen reduction of carbon monoxide $(\text{CO} + \text{H}_2 \rightleftharpoons \text{C} + \text{H}_2\text{O})$.
- Under the conditions of this study, the Boudouard reaction, carbon monoxide decomposition, is the major source of the carbon.
- The water resulted from the reverse water-gas shift reaction.
- The Bosch reaction(s) is controlled more by kinetic and mechanistic factors than by equilibrium considerations.
- The autocatalytic nature of these reactions resulted from the appreciable amount of iron contained in the carbon product.
- The rate of reaction was probably controlled by the active surface area of iron available for chemisorption. This suggests that for long reaction times, the rate was controlled by the reaction over carbon.
- The decrease in the rate of deposition over carbon resulted from a slow disintegration of the catalytic iron particles.
- The carbon fibers appear to be ribbon-like rather than cylindrical filaments.

The naïve reader might assume that as a result of this study, great strides have been made toward a better understanding of the reactions of the carbon oxides plus hydrogen over an iron

catalyst. Such thinking is far from the truth. Although progress has been made, the pathway to a complete understanding has been barely travelled. Thus, a significant number of recommendations for future studies can be made:

- A detailed investigation of the reaction mechanism could be performed using radioactive gases. By using Carbon-14 labelled carbon dioxide over iron and analyzing for the amount of radioactive carbon monoxide, the extent of the reverse water-gas shift reaction could be determined. Labelling carbon monoxide and analyzing carbon dioxide would indicate the importance of the Boudouard reaction.
- Notable results should be obtained by studying the reactivity of the carbon after extracting the iron with acid.
- Further studies to identify the iron particle found in the carbon and also a determination of the growth mechanism for the carbon ribbons are suggested.
- Surface area and absorption characteristics of the carbon are also warranted.

II. INTRODUCTION

The scope of this research effort involved an investigation of the Bosch reaction, i. e., the hydrogen reduction of carbon dioxide over an iron catalyst to yield solid carbon and water as the primary products. The National Aeronautics and Space Administration is interested in utilizing this process on long duration space flights. Following a separation of the exhaled carbon dioxide, the gas (after addition of an appropriate amount of hydrogen) would be passed through a "Bosch Reactor," where the solid carbon product remains in the reactor and the water is condensed. The water would then be electrolyzed to yield oxygen, which would be stored for later use by astronauts, and hydrogen for recycle. NASA has supported a number of studies to determine the feasibility of using a Bosch process for oxygen reclamation. (1), (2), (3), (4), (5), (6), (7). Although a Bosch reduction unit for processing the carbon dioxide output from a four man crew has been successfully demonstrated (8), some fundamental questions still remain unanswered.

It was the aim of this research to:

- (1) Determine how the rate of reaction is influenced by changes in such operating parameters as: reactant gas composition; temperature; and nature of the catalyst.
- (2) Elucidate the probable mechanism for the overall reaction.
- (3) Investigate the nature of the carbon formed.
- (4) Identify the species performing the role of the catalyst.

As a result of these fundamental studies, it was hoped that a contribution could be made toward the better understanding of the reaction between the oxides of carbon and hydrogen over an iron catalyst. A further aim of this research was to draw conclusions and make recommendations which would aid in developing and evaluating the Bosch reactor system as a method for oxygen reclamation on long-duration space flights.

To accomplish these goals a tubular reactor and associated gas flow system was designed with simplicity and maximum flexibility in mind so that reliable and meaningful data could be obtained with a minimum of cost and time. It was decided that a differential reactor utilizing a solid iron rod concentrically supported in the tubular reactor would serve the above purpose. The reaction rate would then be easily calculated by monitoring (via a gas chromatograph) the inlet and exit gas concentrations as a function of the various operating parameters.

This type of system was also very amenable to studying the carbon formed as a product. After carrying out the reaction for a given length of time, the iron rod could be withdrawn and the carbon studied via an electron microscope.

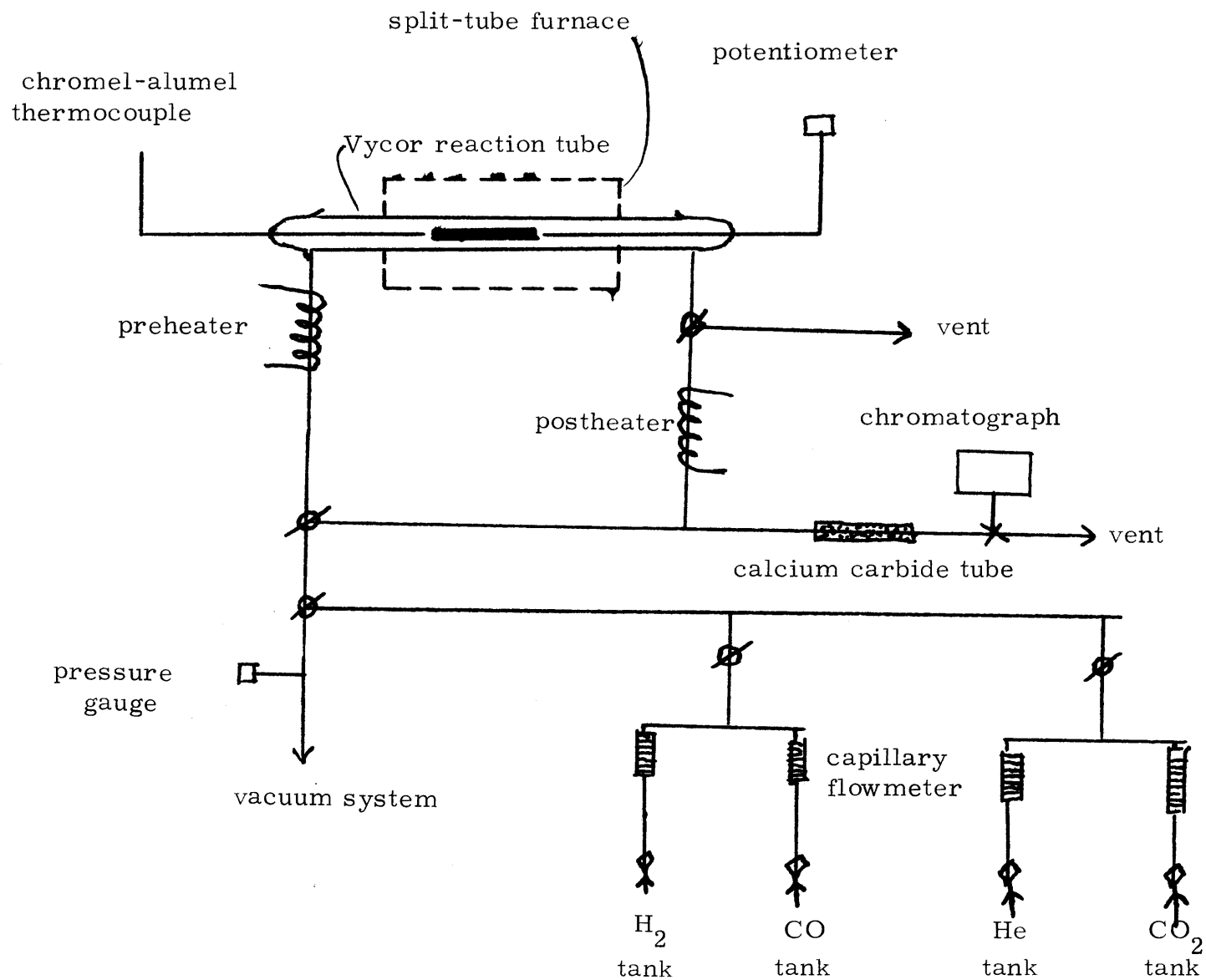
There is a voluminous amount of information in the literature pertaining to the reactions involved in this process and related areas. Numerous contradictions exist in the literature concerning the active catalyst species, type and structure of the carbon product, and the mechanism of reaction. For a detailed review of the past research in this and related areas, the reader is requested to refer to Appendix A.

III. APPARATUS and EXPERIMENTAL PROCEDURE

A. Apparatus

The reactor consisted of a 12mm Vycor glass tube in which a 5mm by 15cm electrolytic iron rod was supported concentrically in the center of the tube. For details of the apparatus and procedure, refer to Appendix B. A preheater section was necessary so that the reacting gases would be at the desired temperature when they reached the front of the iron rod. The reactor was placed in a tubular electric furnace which was thermostatically controlled to within $\pm 5^{\circ}\text{C}$. Chromel-alumel thermocouples were placed in the gas stream at either end of the iron rod to monitor temperature changes. The exit tubing from the reactor to the chromatograph sampling valve was wrapped with a silicone heating tape to prevent water from condensing in the line before it could be measured. The gas feed system was constructed to provide a constant composition and flow rate to the reactor. Refer to Figure 1 for a schematic of the gas flow apparatus. Each of the reaction gases was throttled through a Hoke needle valve, and the flow rate of each gas was correlated with the pressure drop across a glass capillary tube. All of the gases (carbon dioxide, carbon monoxide, hydrogen, and methane) were obtained from Matheson Gas Products and had a minimum purity of 99.5%. A thermal conductivity gas chromatograph with an on-line gas sampling valve permitted easy monitoring of the inlet and exit gas compositions. The 12 ft. by 1/4 in. separation column filled with Poropak-Q was operated at room temperature for most of the measurements. Ultrahigh purity helium was used as a carrier gas at a flow rate of 30cc per minute and an inlet pressure of 50 psi. The output of the chromatograph detector was converted to peaks on a moving chart by a millivolt recorder.

GAS FLOW APPARATUS



B. Experimental Procedure

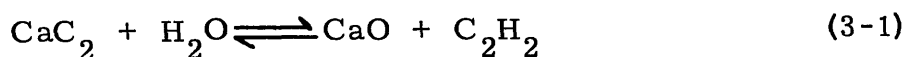
1. Reaction over iron rod

The procedure followed in performing an experimental run was not complicated but required careful attention to the order in which the various steps were initiated. After placing the solid iron rod in the reactor section of the tube, the reactor was supported in the furnace and sealed. The reactor assembly was evacuated to 10^{-4} torr and purged with helium several times to eliminate oxygen and other gas impurities inside the reactor system. Helium was passed through the reactor while the furnace temperature was raised to 800°C. Hydrogen was then admitted at a flow rate of 15cc per minute for six hours. This was necessary to eliminate any oxides on the rod by reduction to the α -iron form. Helium was again passed through the reactor as the temperature was lowered to reaction conditions (usually around 600°C). Observation of the rod showed it to be a dull silver color after reduction. At this time the reacting gases were premixed, heated and passed through the reactor. Hydrogen was always the first gas passed over the iron rod before the other reactive gases were added to make the desired gas composition. This would insure that no pre-carbiding or other reaction with the α -iron would occur before the gas mixture entered the reactor. In each run the total gas flow was between 40-50cc per minute. Assuming "plug-flow" conditions, a residence time of 20 seconds and an average Reynolds number of approximately 2 was maintained over the rod. All runs were carried out at atmospheric pressure. After a given length of reaction time, the furnace was allowed to cool as helium was passed over the rod and the deposited carbon. After removing the reactor unit from the apparatus,

the rod was taken out by turning the reactor on its end and withdrawing the rod slowly, using a magnet attached to a stiff wire. In this way, very little of the deposited carbon was disturbed. Most of the carbon was removed from the rod by means of a small camel hair brush and placed in a vacuum dessicator for later analysis.

2. Gas Analysis

Exit gas compositions were measured about every 15 minutes as this was the length of time necessary for all the gases to elute from the chromatograph column. During the few initial runs the water vapor in the exit gas presented a number of problems. In order that the water retention time be shortened, it was necessary to temperature program the column manually at a higher temperature. Also, a standard calibration of the chromatograph for water was difficult and precision poor. This made a mass balance impossible. To circumvent these problems, a 6 in. by 1/2 in. Pyrex column packed with calcium carbide was inserted between the reactor outlet and the chromatograph sampling valve. The calcium carbide reacted quantitatively with the water vapor to yield acetylene according to:



The acetylene elutes from the Poropak-Q column easily in 15 minutes and standardization is simple and accurate.

One other problem in the gas analysis was the low sensitivity of the thermal conductivity detector for hydrogen. If argon is used as the carrier gas, the sensitivity for hydrogen is greatly increased at the expense of a decrease in sensitivity of the other reaction gases. It was decided that the best

solution to this conflict was to determine the hydrogen concentration by difference from the other gases.

Actual gas compositions were easily determined by comparing the areas under the peaks of the exit gases with the areas for a known standard mixture. Fortunately, all of the gas peaks were sharp and symmetrical, thus a geometrical method of calculating the areas was used. (Height of peak multiplied by the width at half the height.) Refer to Appendix C for details of the gas analysis.

3. Reaction over carbon

In a few experimental runs the carbon was removed from the iron rod and placed back in the reactor. For each of these runs the carbon sample was carefully weighed (.1-.2g) and put into a heavy aluminum foil boat. The aluminum boat was non-catalytic (9) and was convenient for holding the carbon. The boat was placed in the reactor in the same position in which the rod had been supported. The pre-reaction technique with carbon was identical to that using the iron rod. A gas composition similar to the one which was passed over the iron rod was also passed over the carbon. Exit gas compositions were measured before cooling the reactor and reweighing the carbon sample. A small portion of this carbon was again weighed and replaced in the reactor where the same procedure as above was followed for the new carbon sample. The technique of taking a small portion of each successively reacted carbon and placing it back in the reactor was repeated until no further reaction was noted.

For each carbon sample a small amount was retained for later electron microscope analysis. The remaining amount was sent to the analytical laboratory of MIT's Materials Research

Center for a determination of the iron concentration in the carbon.

4. Electron Microscopy

The microscopy analysis was performed on a Phillips EM-200 transmission electron microscope which permitted a maximum magnification power of approximately 300,000. Each sample was prepared by suspending a small amount of the water on an electron microscope grid with an eye dropper. The water was evaporated, leaving the finely dispersed carbon for viewing. Pictures were taken of representative and/or interesting carbon formations.

IV. RESULTS

A. Reaction of Carbon Dioxide and Hydrogen Over the Iron Rod

1. Effect of Gas Composition

With a reactor temperature of 600°C, operations at atmospheric pressure, and total gas flow rate of 50cc/min., the inlet ratio of hydrogen to carbon dioxide was varied from 0.5 to 2.0. In all runs the exit gas showed no appreciable change in composition of carbon dioxide and hydrogen except for the production of approximately 0.5% carbon monoxide. A lower inlet H_2/CO_2 ratio gave only a very slight increase in carbon monoxide in the exit gas. No other gases such as methane or ethane were detected; in these early runs the water concentration was not measured. Observation of the iron rod after 24 hours of reaction showed no sign of carbon deposited on, nor any other visible change in the iron rod.

2. Effect of Temperature on the Reaction of Carbon Dioxide and Hydrogen Over the Iron Rod

With a hydrogen to carbon dioxide ratio of approximately 1.5 and atmospheric pressure, the temperature of the reactor was varied from 525°C to 725°C. As the temperature was increased, the concentration of carbon monoxide in the exit gas increased from approximately 0.5% at 525°C to 5.5% at 725°C. There was a small but measurable decrease in carbon dioxide concentration with the increasing temperature. Again water was not measured, but condensation in the exit lines indicated a definite increase in water production accompanied an increase in temperature. No other gases were detected in the exit gas, and after 15 hours of operation at the highest temperature

the rod had no carbon deposit nor was it visibly changed.

B. Reaction of Carbon Dioxide, Carbon Monoxide and Hydrogen Mixtures Over the Iron Rod

Unless otherwise stated, all runs were performed under conditions of one atmosphere and 600°C.

A feed composition of approximately 50% hydrogen and 25% of both carbon monoxide and carbon dioxide was passed over the iron rod. The exit gas composition showed a significant decrease in carbon monoxide concentration with a smaller decrease in carbon dioxide. Water was also noted condensing in the cooler glass tubing near the exit of the reactor.

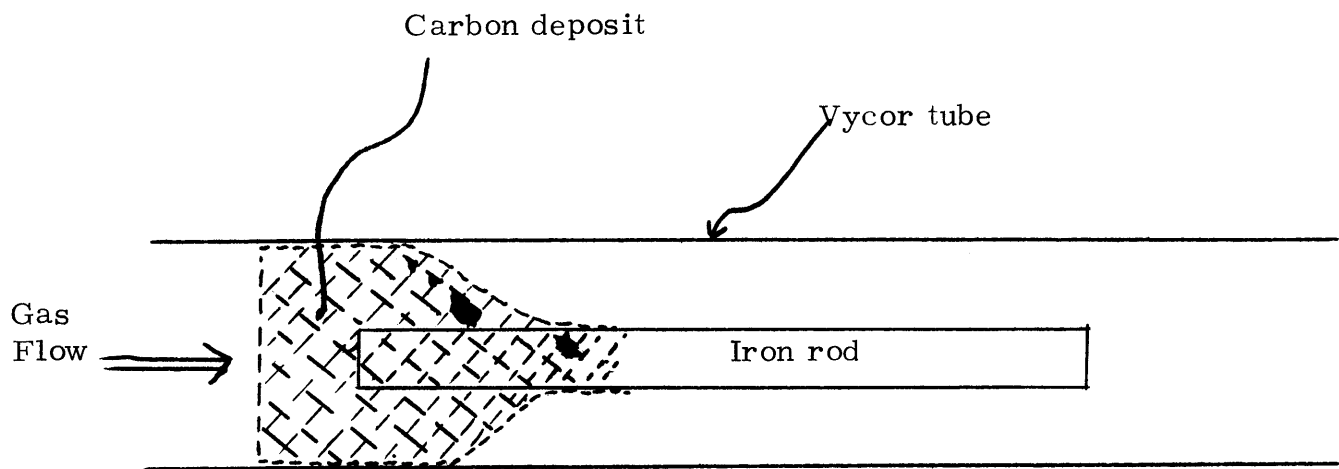
After ten hours of operation, a significant pressure drop was evident across the reactor. Inspection showed that the front of the rod was plugged with a black carbon deposit. Refer to Figure 2. However, the section of the rod furthest removed from the inlet was still a bright silver color, indicating that it was still in the completely reduced form. A large portion of the carbon plug had formed in front of the iron rod, and a very small amount of carbon had been deposited on the back end of the rod. After withdrawing the iron rod and removing the deposited carbon, it was found that a magnetic field strongly attracted the carbon sample. The carbon deposit was viewed under a low power optical microscope where it was noticed that the carbon which had been formed in front of the iron rod had a coarse granular appearance whereas the carbon which had been brushed off the iron rod had a fine powdery texture.

C. Reaction of Carbon Dioxide and Carbon Monoxide Over the Reduced Iron Rod

In this run a composition of approximately 20% carbon dioxide and 20% carbon monoxide was passed over the reduced iron rod at 610°C. Helium was substituted for the hydrogen. There was no

FIGURE 2

CARBON DEPOSIT ON IRON ROD



detectable change noticed in the exit gas composition, and after 48 hours of operation the iron rod showed no appreciable deposit of carbon. However, the surface of the iron rod had a dark mottled appearance rather than the usual bright silver color of the reduced form.

D. Reaction of Carbon Monoxide and Hydrogen Over the Iron Rod

A feed mixture of approximately 50% hydrogen, 25% carbon monoxide and 25% helium was passed over the reduced iron rod at a temperature of 600°C. The exit gas showed a significant decrease (40%) in the carbon monoxide concentration with measureable quantities of both carbon dioxide and methane produced. Water condensed in the exit tubing from the reactor but no measurement of its concentration in the exit gas was made. After only one hour of operation, a large plug of carbon had formed in the reactor. This carbon deposit seemed identical to that formed using a mixture of carbon dioxide, carbon monoxide and hydrogen. Refer to Figure 2. The carbon was also strongly magnetic.

E. Reaction of Carbon Monoxide Passed Over the Predeposited Carbon

Approximately 1g of the carbon which had been deposited on the iron rod using the carbon monoxide and hydrogen gas mixture was replaced in the reactor. Passing a gas composition of approximately 35% carbon monoxide in helium over the carbon at 625°C resulted in a significant decrease in the carbon monoxide concentration with the resulting production of a measureable quantity of carbon dioxide (4.0%). No water or other gases were detected. After 12 hours of operation it was visually apparent that more carbon had been formed. The carbon was still strongly magnetic.

F. Reaction of Carbon Monoxide and Hydrogen Over the Predeposited Carbon

A gas feed of approximately 40% hydrogen, 35% carbon monoxide

and the balance being helium was passed over 1g of carbon. The exit gas composition showed a 40% decrease in carbon monoxide concentration and a significant (7%) production of carbon dioxide. Approximately 0.5% methane was detected in the exit gas. Although the water concentration was not measured, its presence was noted by the appearance of water droplets in the cool exit tubes of the reactor. An increase in the amount of carbon was readily apparent by inspection of the reactor after six hours of operation.

G. Reactions Using NASA's Recycle Gas Composition

In NASA's Bosch reaction system, various recycle gas compositions have been used. (10) (11) (12) Typical values are:

(dry basis)

H_2	25%
CH_4	20%
CO	40%
CO_2	15%

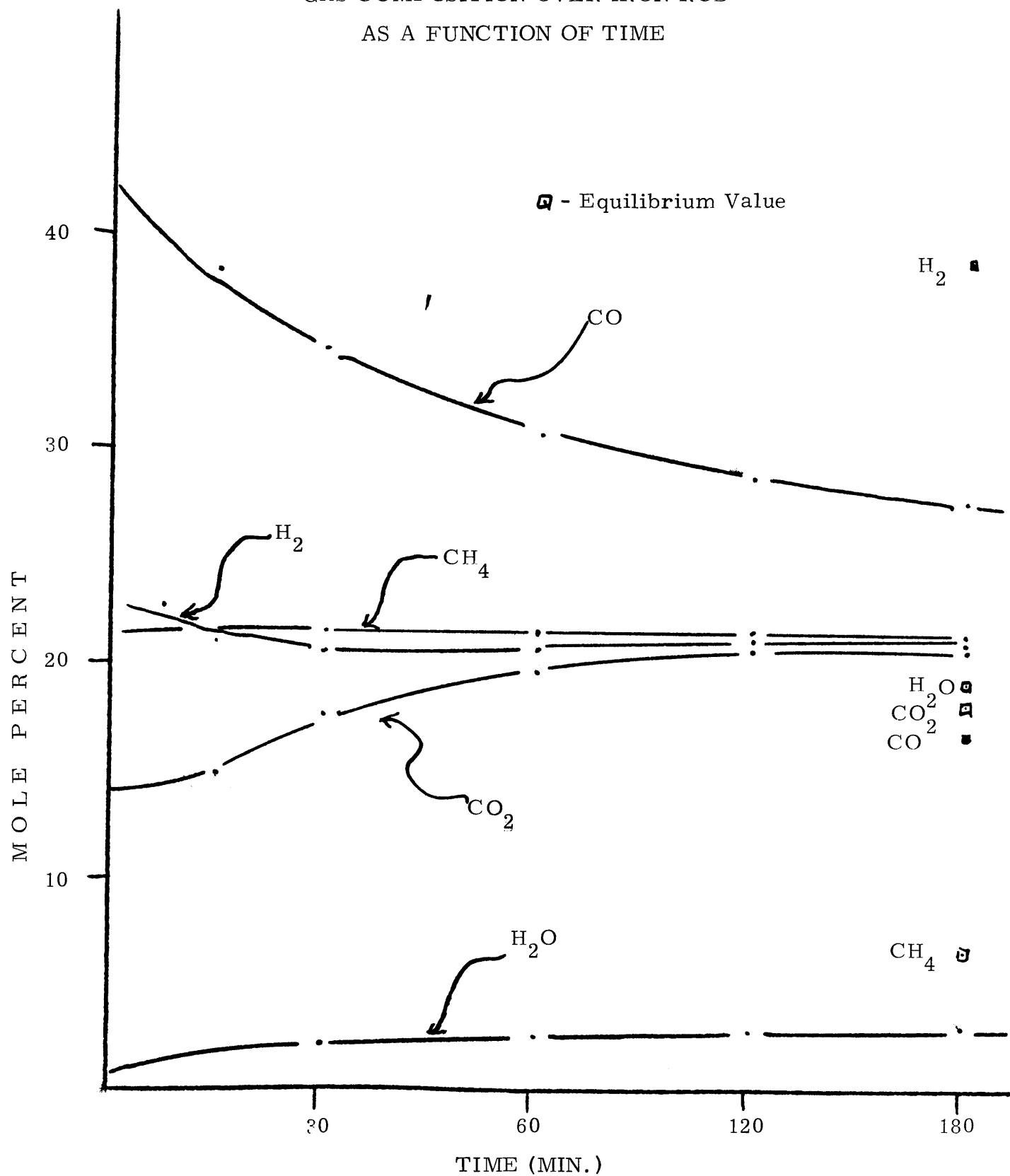
The final series of experimental runs were performed using a feed gas of approximately the above composition with a total flow rate of 55cc/min.

1. Reaction Over Iron Rod at 615°C and Atmospheric Pressure

The exit gas from the reactor was monitored every 15 minutes in order that changes in the rate could be observed as a function of time. Also, unsteady state phenomena would be readily apparent. The data are plotted in Figure 3. A very definite decrease in carbon monoxide concentration with increasing time of reaction is accompanied by an increase in carbon dioxide concentration. The curves for both gases appear to level off at a constant value after approximately two hours of operation. Hydrogen and methane concentrations, although

FIGURE 3

GAS COMPOSITION OVER IRON ROD
AS A FUNCTION OF TIME



unsteady during the first hour of operation, appeared to have stabilized at a constant value after two hours. The water vapor concentration in the exit gas increased with increasing time of operation; however, the rate of increase for water production decreased to a very small value after about two hours.

Chemical analysis of the carbon deposited during the two hours showed it to contain 9.58% by weight of iron. A mass balance was performed on the reactor and showed less than 5% difference in the oxygen and hydrogen between inlet and exit. A balance on the carbon in the inlet and exit gases showed the exit gas to be lower in carbon by about 7%. This was to be expected since there was deposition of carbon on the iron rod. All of the carbon could not be scraped off the rod, and some of the carbon probably existed as carbides which made an independent carbon balance impossible.

2. Reaction Over Product Carbon at 615°C and Atmospheric Pressure

When a gas mixture similar to NASA's recycle composition was passed over carbon which had previously been deposited on the iron rod, the exit composition showed approximately a 9% decrease in carbon monoxide and a 3% increase in carbon dioxide. The water concentration increased and the hydrogen concentration decreased slightly. The methane concentration remained approximately the same as the inlet, 20%. A mass balance for hydrogen and oxygen showed less than 1% difference between inlet and exit. As expected, the carbon balance indicated a small decrease in the amount of carbon exiting from the reactor. The above compositions were measured between the second and third hours of operation. Refer to Table I for an example of a "typical" gas composition for the reaction over the replaced carbon.

TABLE I

Typical Gas Compositions Over Carbon III

615°C

Atmospheric Pressure

Inlet*		Exit
CO	41.7	33.87
CH ₄	19.98	20.67
CO ₂	13.53	16.47
H ₂ O	0.47	1.90
H ₂	24.35	21.79

*Total Inlet Gas Flow Rate was 55cc/min.

3. A Series of Reactions Over Product Carbon at 620°C
and Atmospheric Pressure

In this group of experiments carbon was deposited on the iron rod after which the carbon was replaced and reacted further. These successive replacements of carbon were continued until little or no reaction occurred. A summary of this data can be found in Table II. This data shows clearly that the carbon continues to catalyze the deposition of carbon. The concentration of iron in the carbon decreases with further carbon deposition until there is a sharp decrease in the rate of reaction. This decrease in the rate occurred when the iron concentration in the carbon had diminished to approximately 0.5%.

4. Gas Composition as a Function of Time for Reaction of
Carbon II.

Referring to Figure 4, the carbon monoxide concentration decreases sharply at the beginning followed by a gradual increase.

DATA FOR SUCCESSIVE REPLACEMENTS OF CARBON

TABLE II

	Carbon I*	Carbon II	Carbon III	Carbon IV
Weight of Carbon Initially (grams)	0.0	.262	.168	.205
Weight of Carbon after Reaction (grams)	.346	.777	.784	.238
Increase in weight of Carbon (grams)	.346	.515	.616	.034
Time for Reaction (hours)	4.0	8.0	16.0	14.0
Percentage Iron in Carbon** (after reaction)	9.58%	3.07%	.551%	.30%
Calculated Percentage Iron (from dilution)	—	3.23%	.646%	.43%
Rate $\left[\frac{\text{g Carbon Formed}}{\text{hr} - \text{g Initial Carbon}} \right]$	.0865***	.245	.230	.012
Rate $\left[\frac{\text{g Carbon Formed}}{\text{hr} - \text{g Iron}} \right]$	.00108	2.56	7.48	2.15

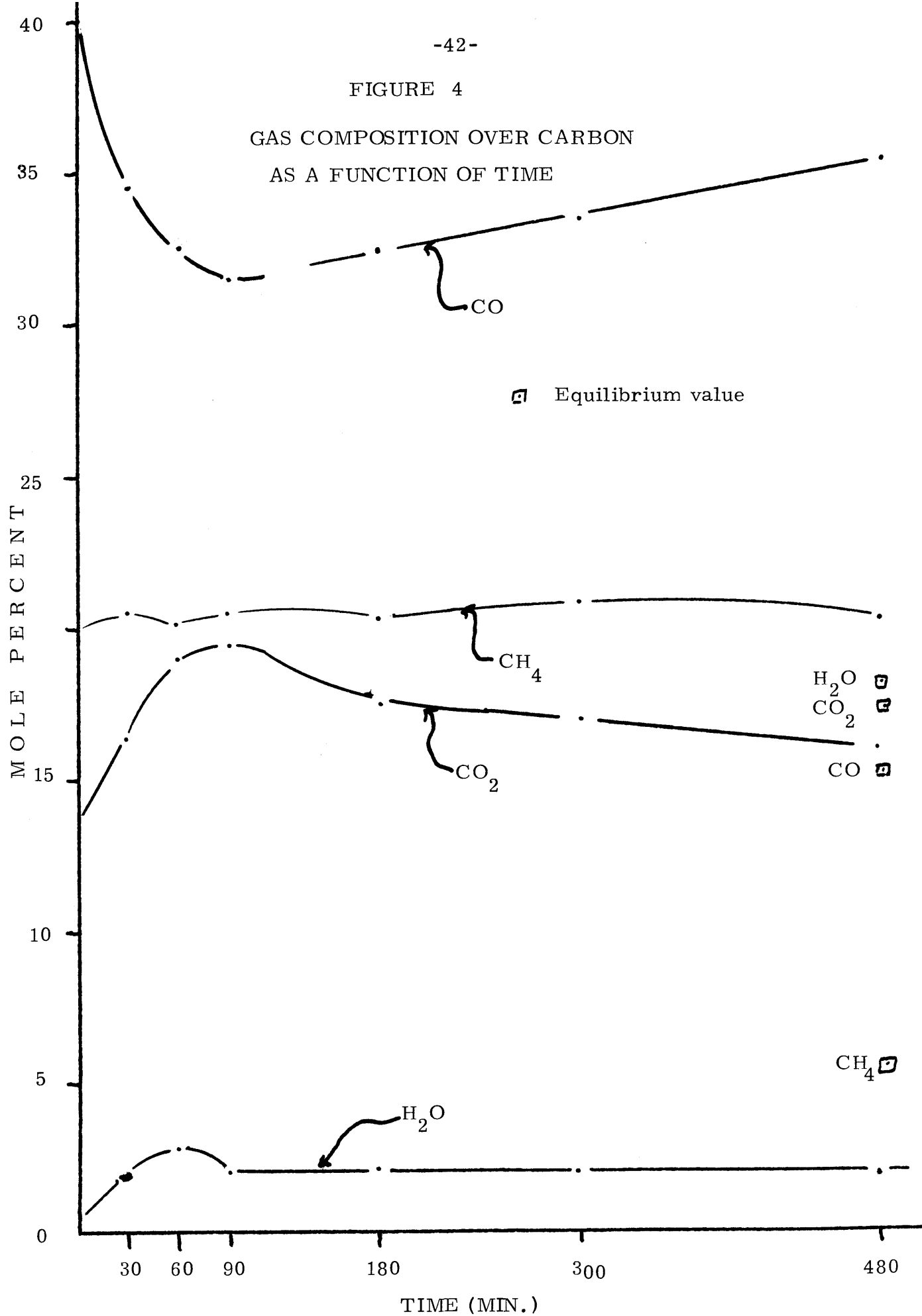
*Deposition of carbon on iron rod

**All values have a precision of $\pm 0.05\%$

***Units for carbon I are $\frac{\text{g carbon formed}}{\text{hr}}$

FIGURE 4

GAS COMPOSITION OVER CARBON
AS A FUNCTION OF TIME



The carbon dioxide concentration increases rapidly and reaches a maximum at the same time in which the carbon monoxide reaches a minimum. After this point the carbon dioxide decreases gradually. The water concentration reaches a maximum and then decreases to a value of approximately 2.0% where it remains constant with increasing time. These data seem to indicate that the major reaction occurring is the Boudouard, and that the rate is decreasing with increasing time.

H. Electronmicrographs of Carbon

1. Deposited on Iron Rod

Many previous investigators have studied the carbon formed from carbon monoxide, methane, acetylene and carbon monoxide-hydrogen mixtures over iron and other metal catalysts. (13) (14) (15) (16) (17) In these studies, the most characteristic structure was a carbon filament (sometimes twisted like a rope) about 1μ in length and between $0.1-0.5\mu$ in diameter. A small crystal of the metal or metal carbide was usually located at the ends of the carbon filaments. Referring to the electronmicrographs from this research (Figures 5-12), there is easily distinguishable a dark dense crystal at the ends and frequently within the length of the carbon filaments. The width of the filaments was in the range of $0.1-0.2\mu$ with the length varying between 0.5 and 2.0μ . Although there is a variation in width between filaments, there is a remarkably constant width along each filament. Refer to Figures 5, 8, and 9. In most respects, it is difficult to distinguish between a literature photograph of the carbon (18) (19) (20) (21) and those obtained in this study. The dense crystal structures on the carbon filaments have a relatively constant width of $1000\text{\AA}$ and are usually slightly larger than the width of the filament.

See Figures 5, 6, 7, 8, and 9. There does not appear to be an identifiable shape common to all of the crystals. However, in some cases (Figure 7), a hexagonal crystal structure can be distinguished, and in others an almost oval shape is apparent. In most photographs (Figures 6, 7, 10 and 13) the carbon filaments have a series of dark bands along the filament length. Whether this consists of the same material as the crystal "heads" is not known. The chemical structure of these crystals has not been determined in this research. However, a recent investigator (22) has identified them as being Fe_7C_3 .

Another characteristic structure in some of the carbon filaments was a granular appearance. See Figures 6, 9, 10 and 11. Other investigators (23) have referred to these regions as electron rich kernels. It seems reasonable that these dense areas are metal or metal carbides which have resulted from disintegrating crystal "heads." However, this was not elucidated in this research.

In the literature this particular carbon structure is always referred to as filaments. This would imply a cylindrical shape. However, when observed under high magnification, a ribbon-like structure is apparent with a thickness of approximately $100\text{\AA}$. See Figures 12, 13, 14 and 15. Located in the center of Figure 12 is an area which appears to be an overlapping of two carbon "filaments." This overlapping section appears to be an area of relatively constant density. If the filaments were cylindrical in shape, the outer edges and corners should be lighter in color (less dense) and get progressively darker toward the center. This has not been observed.

2. Re-reacted Carbon

Electronmicrographs of the carbon which had been further reacted show some distinct differences from the carbon removed from the rod. The most noticeable change is that there is a definite decrease in the number of distinct crystal "heads" of iron or iron carbide. See Figures 12, 14, and 18. The crystals seem to have disintegrated and mixed throughout the carbon ribbons. Good examples of this can be seen in Figures 11, 13, 17, and 19. In some ribbons the disintegrated heads seem to have resulted in a series of dark bands. (See Figure 17) In other ribbons the carbon appears to be dispersed in dense kernels throughout the length. (See Figures 11 and 19)

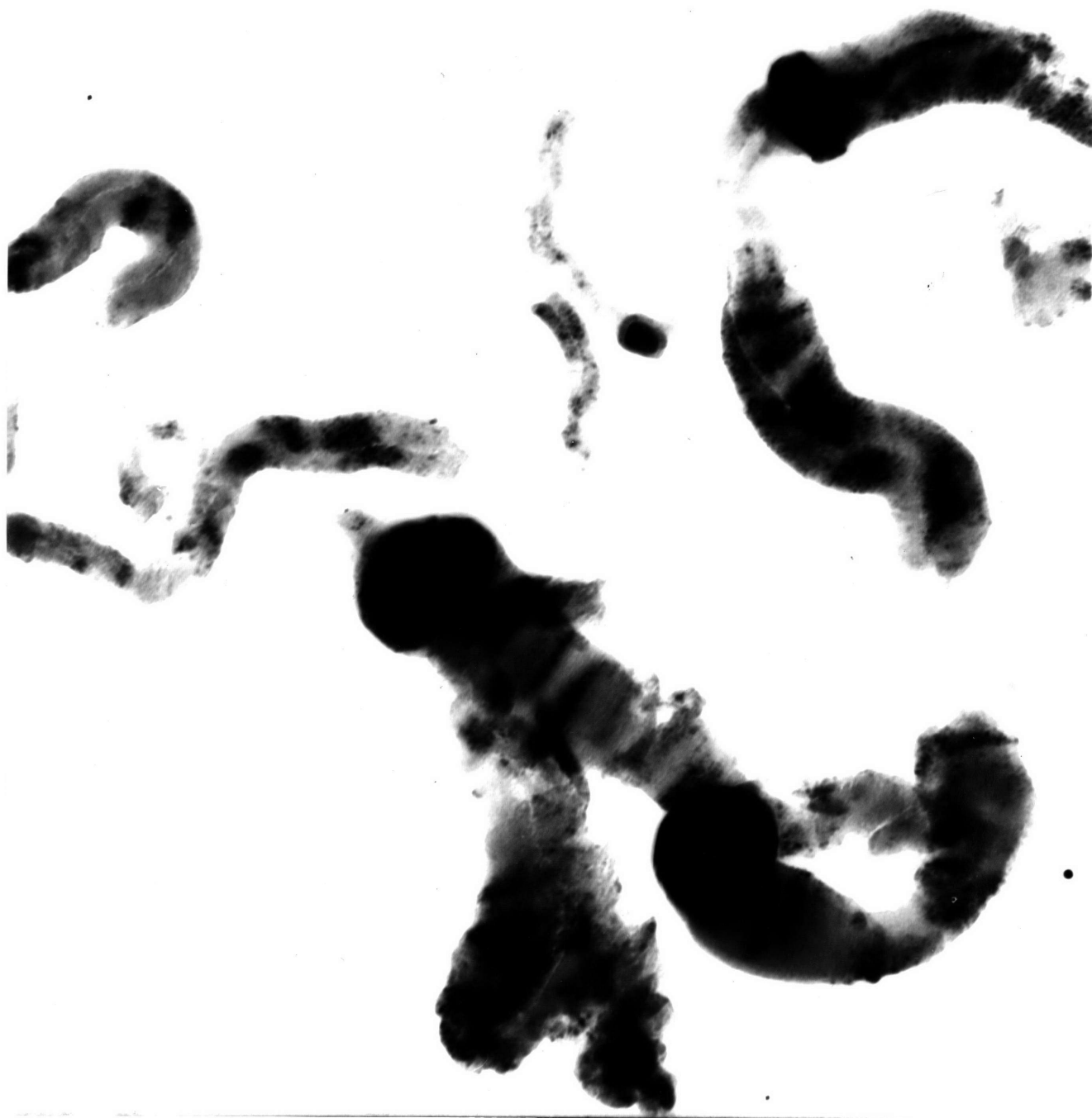
FIGURE 5



Carbon Filaments - typical formations
(31,000X)

—|—
0.5 μ

FIGURE 6

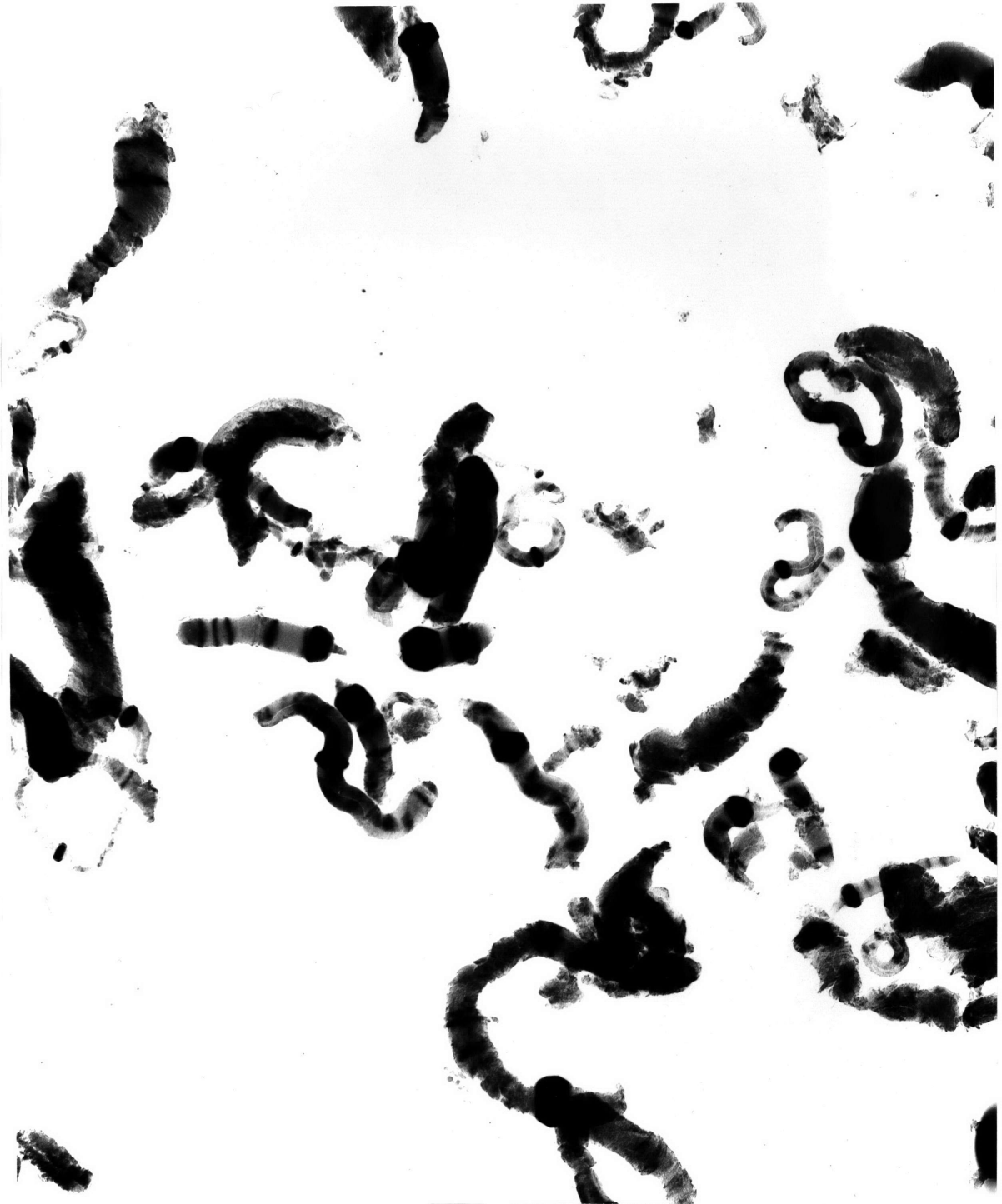


Carbon Filaments - crystal heads, granular and banded appearance

(124,000X)

800 Å

FIGURE 7



Carbon Filaments- hexagonal crystal
(40,600X)
500X)

0.5 μ

FIGURE 8



Carbon Filaments - showing constant width
(63,600X)


.25μ

FIGURE 9



Carbon Filament - showing iron crystal in middle of filament

(243,000X)

400 Å

FIGURE 10



Carbon Filaments - showing bands

(63,600X)

300 A. 25 μ

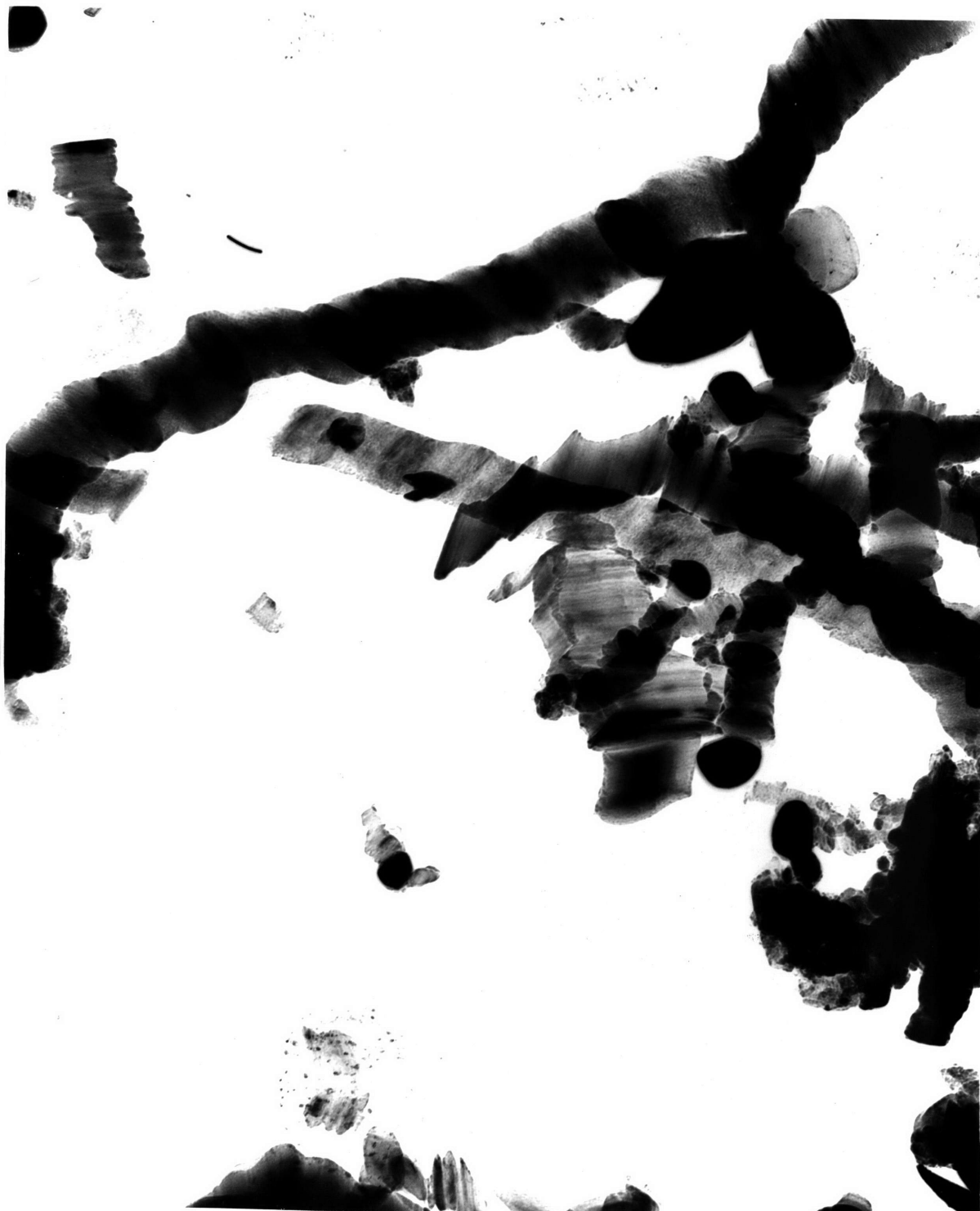
FIGURE 11



Carbon Filament - granular appearance
(189,500X)

—|—
500 Å

FIGURE 12

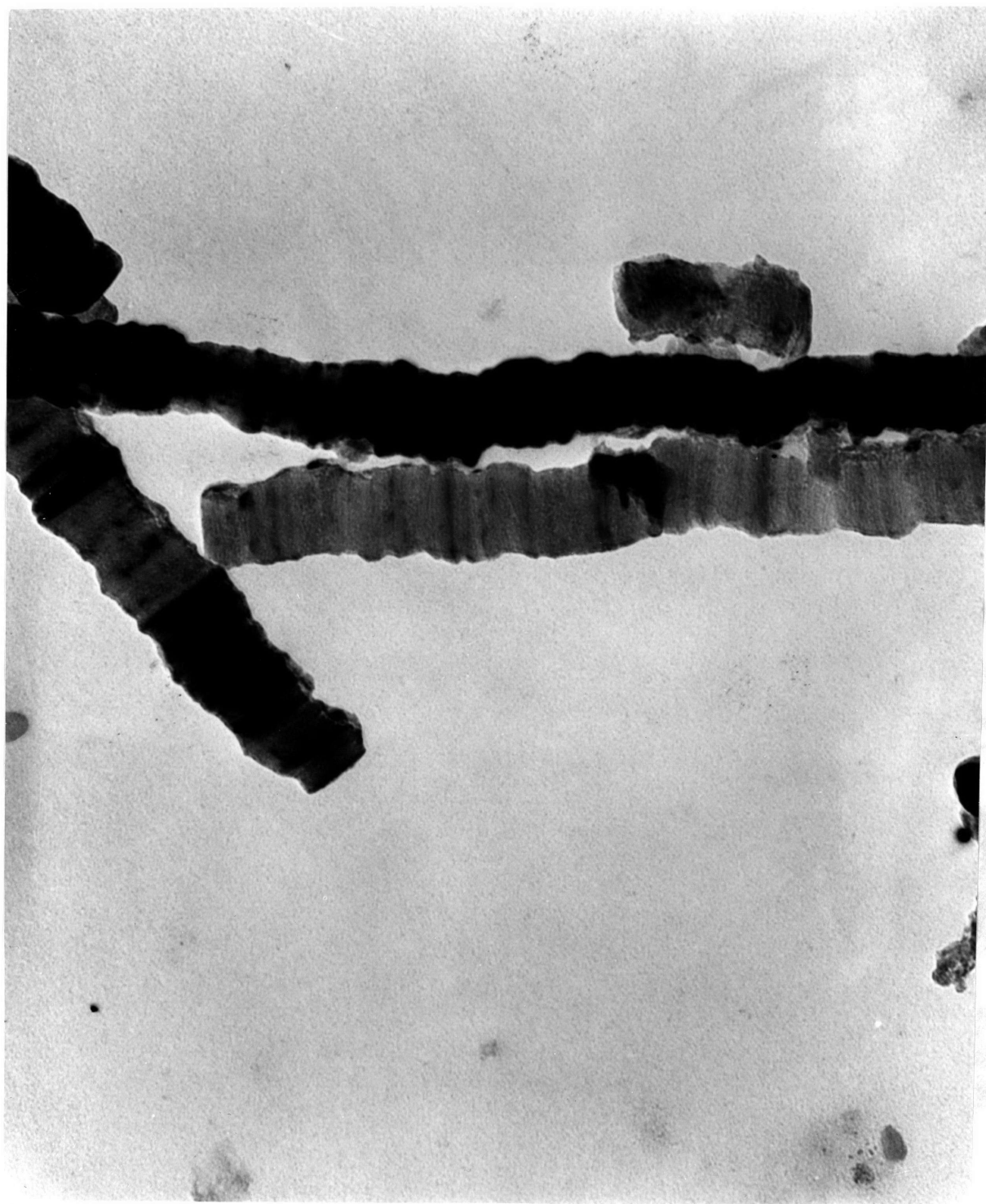


Carbon Filaments - ribbon-like appearance

(83, 600X)

—|—
.25 μ

FIGURE 13



Carbon Filaments - ribbon-like appearance
(189,500X)

—
500 Å

FIGURE 14



Carbon Filaments - after being reacted further
(63,600X)

—
.25 μ

FIGURE 15



Carbon Filament - ribbon-like appearance
(243,000X)

400 Å

FIGURE 16



Carbon Filament - showing metal crystal and bands
(147,000X)

650 Å

FIGURE 17



Carbon Filaments - after being reacted further
(83,600X)

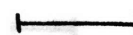
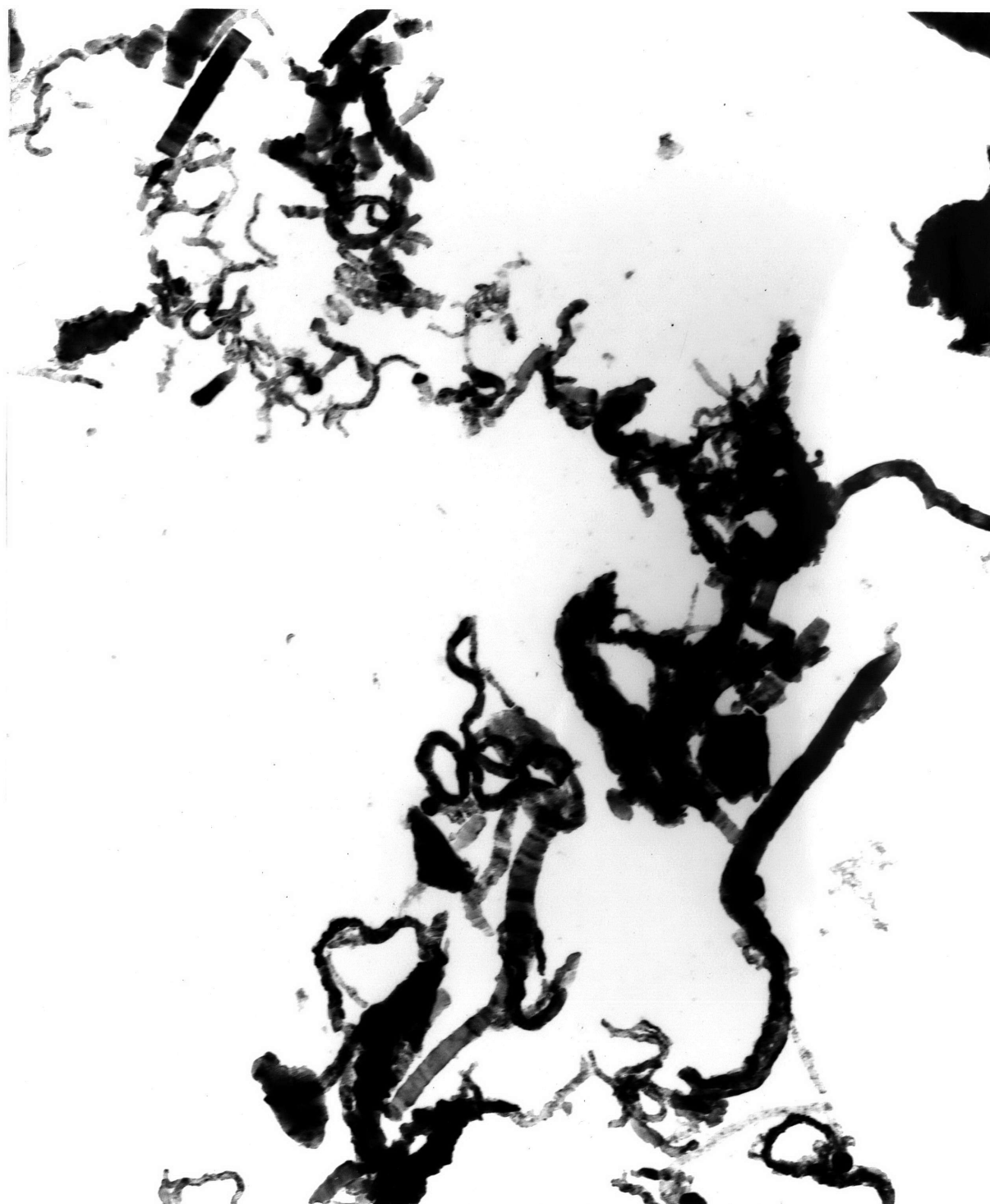
 .25 μ

FIGURE 18



Carbon Filaments - after being reacted further
(26,000X)


0.5 μ

FIGURE 19



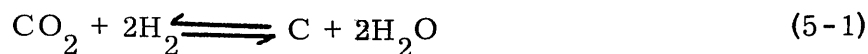
Carbon Filaments - granular appearance
(70,500X)

 1430 Å

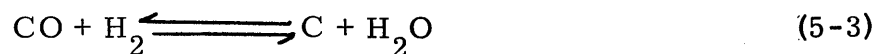
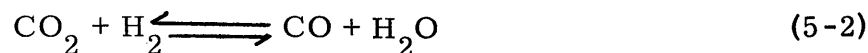
V. DISCUSSION OF RESULTS

A. General Remarks

When referring to the Bosch reaction, it is generally implied that the overall mechanism involves the reaction of two molecules of hydrogen with one molecule of carbon dioxide to yield solid carbon plus water.



However, the results of this investigation indicate that the actual mechanism involves at least three separate reactions. These are:



Thus, if carbon is deposited, it must result from reaction (5-3) and/or (5-4). From a thermodynamic viewpoint, reaction (5-2) is favored at a higher temperature relative to reactions (5-3) and (5-4). However, past studies of the Bosch reaction have revealed that this reaction over an iron catalyst is controlled more by kinetic and mechanistic factors than by equilibrium considerations. (23) (24) For example, equilibrium calculations (See Appendix D) predict an increase in water production with decreasing temperature. No studies, including this one, have found these calculations to be demonstrated in experimental results.

B. Reaction Over an Iron Rod

Viewing the experimental results from passing carbon dioxide and hydrogen over the iron rod, it was apparent that the only change in the gas composition resulted from the production of carbon monoxide. Since the conversion increased with increasing

temperature and no carbon was deposited, it is suggested that the only reaction which occurred was the reverse water-gas shift (Equation 5-2). This reaction has been studied extensively (25) and the investigator concluded that the conversion rate was controlled by mixing and diffusional resistances, i.e., not a chemically controlled reaction. Since no homogeneous gas phase reaction takes place below 800°C, the reverse water-gas shift reaction will only occur heterogeneously under the conditions used in this research. Even at 725°C the carbon monoxide concentration never rose higher than 3-4%. Equilibrium calculations showed that it was not possible to deposit carbon under these conditions. Furthermore, if any carbon were present, it would react with carbon dioxide to yield carbon monoxide.

To overcome this equilibrium limitation, the gas mixture was doped with 25% carbon monoxide. Under these conditions the reactor plugged with carbon in just a few hours. Water was detected in the exit gas, but it was not possible to determine if it resulted from reactions (5-2) and/or (5-3).

Since both reactions (5-3) and (5-4) are possible sources for carbon deposition, it was necessary to determine the relative importance of each to the carbon production. This was accomplished by keeping all variables constant, except replacing the hydrogen with helium. Using a reaction mixture of carbon monoxide and carbon dioxide, only a negligible amount of carbon formed on the iron rod. This would suggest that the Boudouard reaction, Equation 4, is not occurring at a significant rate. However, this conclusion cannot be extrapolated back to the original gas mixture which contained hydrogen. In the presence of hydrogen, the carbon monoxide decomposition reaction is very strongly accelerated. This reaction has been studied quite extensively by various investigators, (26) (27) (28), all of whom suggest acceleration by

both hydrogen and water. Another characteristic of the Boudouard reaction over metals is that the carbon product always contains appreciable amounts of the metal. The very definite magnetic character of the carbon produced in this study is further evidence that the Boudouard reaction is occurring.

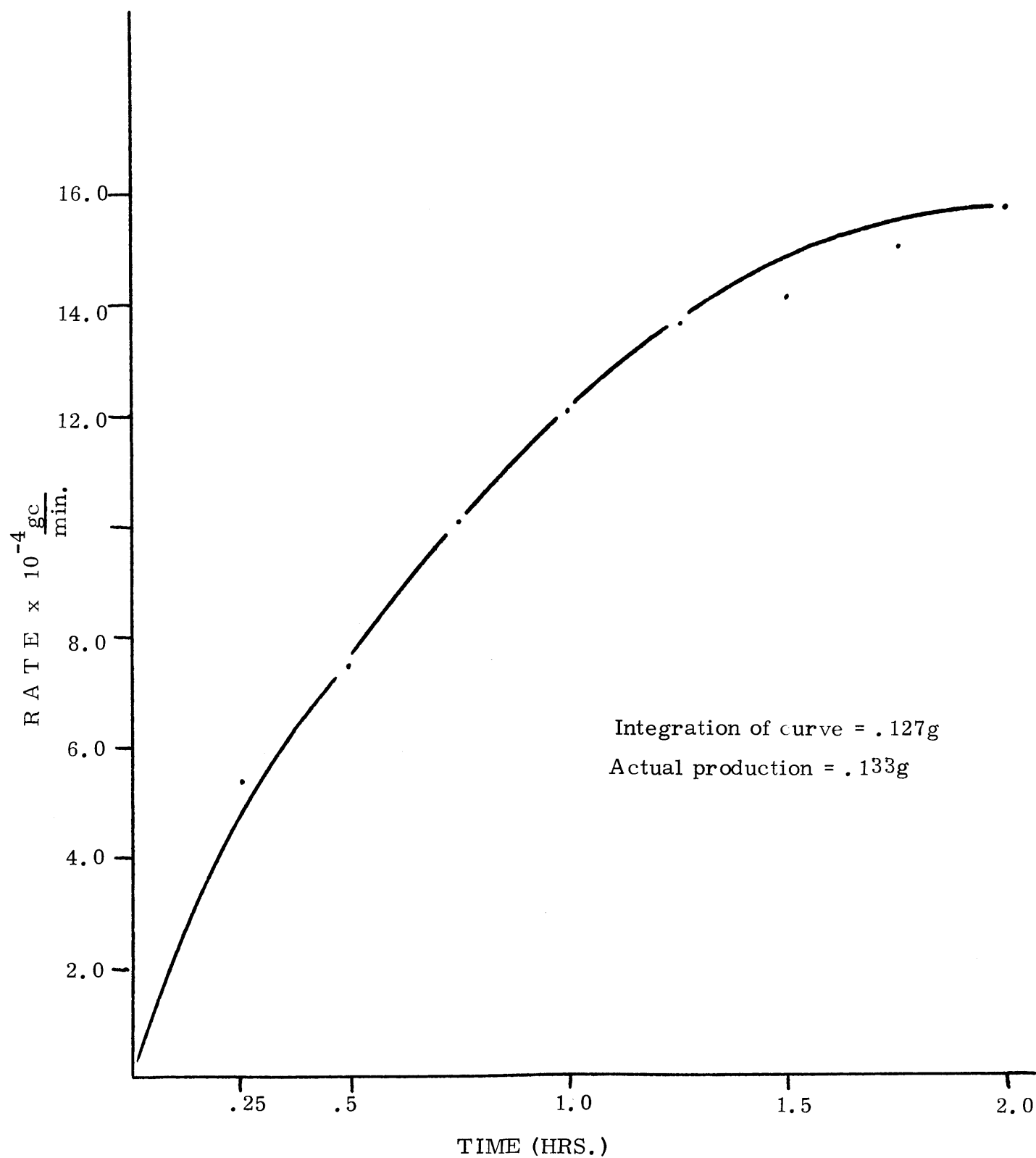
An experiment was performed using only carbon monoxide and hydrogen over the iron rod. The results showed almost a 50% decrease in carbon monoxide concentration with a small but significant production of carbon dioxide. Since the water-gas shift reaction was negligible under these conditions, and does not contribute to the carbon deposition, the results indicate that both carbon forming reactions, Equations 5-3 and 5-4, were proceeding over the iron rod. It is difficult to determine which of these reactions was more important to the carbon deposition because this depends on the experimental conditions, i.e., the partial pressures of hydrogen and carbon monoxide and the temperature. All of these factors determine the extent of their chemisorption and their subsequent reaction. Walker has found (29) that with a composition of 65% hydrogen and 35% carbon monoxide, the reduction of carbon monoxide to yield carbon plus water ($\text{CO} + \text{H}_2 \rightleftharpoons \text{C} + \text{H}_2\text{O}$) contributes more to the carbon deposition than the carbon decomposition reaction ($2\text{CO} \rightleftharpoons \text{C} + \text{CO}_2$). However, in this research the hydrogen concentration was much below 65%. Since carbon monoxide is so strongly adsorbed on iron when compared to hydrogen adsorption, it is expected that the Boudouard reaction was probably the source of most of the carbon deposited during runs with NASA's recycle composition.

Using NASA's recycle gas composition over the iron rod yielded some notable results. Referring to Figure 3, it was evident that the only concentrations which changed appreciably were carbon monoxide and carbon dioxide. The symmetry of the

decreasing carbon monoxide curve and resultant increasing carbon dioxide curve suggest that the major reaction occurring was the Boudouard. Since both curves remain constant after about two hours of reaction, it indicates that the rate of the Boudouard reaction has reached a maximum or steady state. An appreciable amount of carbon has been deposited during the two hours of reaction, and it is possible that the rate has been considerably influenced by the reaction over the carbon. By knowing the flow rate of gases into the reactor and the inlet and exit compositions, the exit flow rate can be calculated from an oxygen or hydrogen balance. From these calculations a total carbon balance was performed to determine how it compared with the actual amount of carbon deposited. Refer to Appendix E for a sample calculation. Figure 20 is a plot of the rate of carbon formation as a function of the time for reaction. The shape of the curve shows that the rate increased steadily over the first hour of reaction, but the rate of increase begins to decrease past one hour of operation. Integration of this curve yielded a total of .127g of carbon as compared to .133g actually produced. The 4% error between calculated and observed values was not unreasonable. The observed decrease in the rate of increase of deposition may result from the appreciable accumulation of carbon on the iron rod. As the carbon builds up on the front end of the rod, the flow pattern of gases over the rod may be interrupted in such a manner as to effect the rate. Also, because of the much higher surface area of the finely dispersed metal in the carbon, the gases will tend to react with it in preference to the iron rod. This suggests that the "carbon-metal" deposit was acting as a catalyst for the Bosch reaction. If this was true an autocatalytic effect should have been observed. Figure 20 shows a very definite autocatalytic effect, even though the effect

FIGURE 20

RATE OF CARBON DEPOSITION ON IRON ROD
AS A FUNCTION OF TIME



decreases with longer reaction times. It seems possible that at longer times of reaction the rate may be controlled entirely by the reaction over the carbon product. After only a small amount of carbon has formed, the surface area of the metal or metal carbide contained in the carbon will be much greater than the surface area of the iron rod.

These hypotheses can also explain the observation of the carbon plug at the front end of the reactor. If the carbon acts in an autocatalytic manner, it is reasonable to postulate that once a small amount of carbon is formed at the front end of the rod, it will grow very rapidly because the majority of the reaction is occurring over the carbon. Another investigator (30) noted that carbon deposition occurred on surfaces nearest the gas inlet but gave no explanation for this effect.

C. Reaction Over Carbon

In the initial runs over carbon, the results showed its very active catalytic nature. By passing only carbon monoxide over the carbon, this would eliminate the possibility of any reaction except the Boudouard. Since a measureable amount of carbon dioxide was produced under these conditions, it was apparent that the Boudouard reaction was occurring. When hydrogen was added to the carbon monoxide and passed over the carbon, about twice the amount of carbon dioxide was produced as was produced without it. This indicates that the hydrogen was a strong activator for the Boudouard reaction. Water was also detected in the exit gas which suggests that the reduction of carbon monoxide to carbon and water is occurring (Equation 5-3). All of these results gave definite proof for the catalytic nature of the deposited carbon.

In experimental runs using NASA's recycle gas composition over carbon, a large decrease in carbon monoxide, a

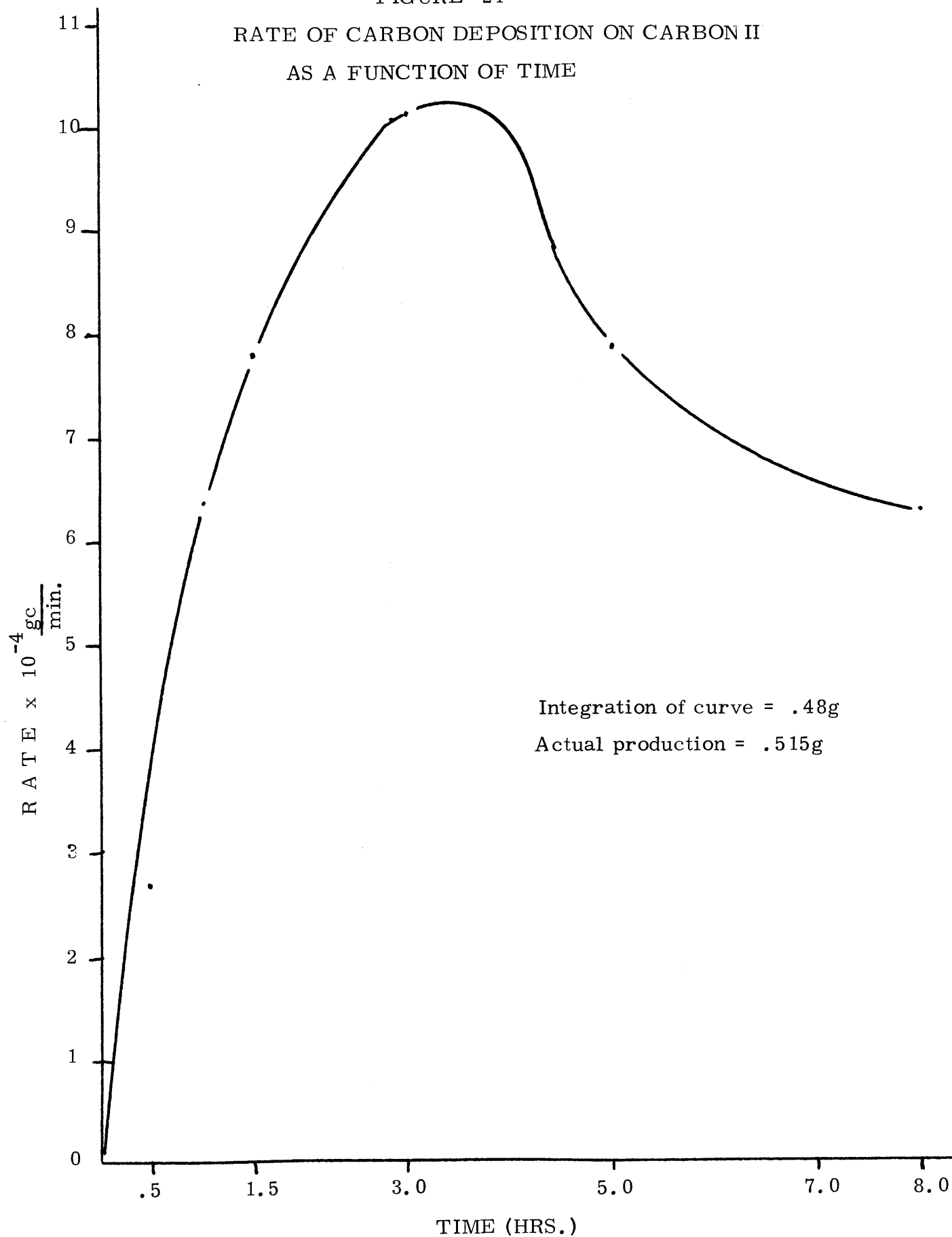
measurable increase in carbon dioxide and a 2% production of water were measured. Again, this is evidence that the carbon was acting as a catalyst for the decomposition reaction of carbon monoxide and possibly the reduction reaction as well. In this study when reference is made to the carbon deposit, it includes the iron that is dispersed through the carbon.

Changes in the gas composition passing over the carbon showed some interesting results. See Figure 4. The carbon monoxide concentration decreased rapidly during the first few hours of reaction and then gradually increased. The carbon dioxide concentration did just the opposite. Water reached a maximum concentration of 3% at approximately the same time that the carbon monoxide was at a minimum. It then decreased to 2% where it remained constant. These results seem to indicate that the Boudouard reaction is the major one contributing to the continued carbon deposition. The water in the exit gas could have been produced via the reverse water-gas shift and/or the reduction of carbon monoxide. However, since the decrease in carbon monoxide is matched almost exactly by the increase in carbon dioxide, this would indicate that the water probably resulted from the reverse water-gas shift reaction. If the source was a result of the hydrogen reduction of carbon monoxide, then the carbon monoxide and carbon dioxide curves would not be symmetrical.

By knowing the flow rate of gases into the reactor and the gas compositions in and out, the exit flow rate was calculated. This permitted a calculation for the rate of carbon deposition as a function of time. Integration of this curve (see Figure 21) yielded a value for the total amount of carbon produced. This curve showed a definite maximum occurring after three hours of reaction. At longer reaction times, the rate decreased, but appeared to level off somewhat after 8 hours of reaction.

FIGURE 21

RATE OF CARBON DEPOSITION ON CARBON II
AS A FUNCTION OF TIME



Integration of this curve gave a value of .48g of carbon. This calculated value was 7% below the .51g of carbon actually deposited. In calculations of this nature, the 7% error is not considered unreasonable.

A series of successive experiments were performed to determine how long the carbon could sustain the reaction. The results showed that further carbon deposition occurred with a steadily decreasing concentration of iron in the carbon. The iron concentration was initially 9.6% and decreased to about 0.5% at which point a small but measureable amount of carbon was still being deposited. It should be noted that if the concentration of iron is calculated on a purely dilution basis, the values are always higher than the chemical analysis shows. This is because not all of the iron can be extracted with acid used for the chemical analysis. Some iron evidently remains dispersed through the carbon. Walker (31) observed this same situation in which extraction with acid removed "heads" but some residual iron remained dispersed in the carbon filaments.

There are various ways in which the rate of carbon deposition over carbon can be expressed, not all of which are meaningful. Figure 21 showed that the rate increased during the first few hours of reaction and then gradually decreased with longer reaction times. If an average rate is calculated in terms of grams of carbon formed per unit time--per grams of carbon initially, the results show a sharp decrease when the iron content of the carbon fell below 0.5%. If it had remained constant, independent of the number of times the carbon was re-reacted, this would have suggested that it was the carbon and not the iron material which was responsible for the continued carbon deposition. The rate calculated in terms of grams of carbon formed per unit time--per gram of iron in the carbon yielded some confusing results.

Initially the rate was 2.6 but increased 3-fold before decreasing to the original value. These results lead to the conclusion that the weight of iron present in the carbon has no bearing on the rate of further deposition. It is felt that the only meaningful expression for the rate would be in terms of the active surface area of the iron. This would be almost impossible to determine and would undoubtedly vary during reaction.

D. Carbon Structure

Of all the aspects studied in this research, the various carbon formations proved to be the source of the most interest and fascination. Not only were they different from the carbon formations usually reported in the literature, but they also proved baffling when attempting to describe a mechanism for their formation, growth and catalysis. The only statement that can be made with confidence is that this carbon is black in color and is difficult to remove from white shirts, as are most other carbon formations.

When observing low resolution electronmicrographs of this carbon, there was a tendency for the observer to interpret the formations as cylindrical filaments. The dense crystals at the ends usually have a round shape which further biases the mind into thinking of filaments. Another source for the confusion originates in the literature. All the previous investigators speak of carbon "filaments" when referring to this particular type of carbon formation. It is the old story of "the eye sees what the mind expects it to see." However, when observed under high resolution, many of the carbon "filaments" have the appearance of a ribbon-like nature. (100Å thick and 1000Å wide) Support for this viewpoint comes from Figures 12, 13, 14, and 15. Again, it is easy to begin seeing all the carbon as "ribbons" if one looks

closely enough. In conclusion, it is felt that there was more evidence supporting the hypothesis of carbon "ribbons" than "filaments."

One other interesting but confusing observation was the location of the dense metal crystal. Many electronmicrographs show it on the end of the ribbons. However, it is also observed in many ribbons to be located somewhere along the length. This suggests that the crystal has at least one and possibly two specific crystal planes or faces which are catalytic. Thus each of the two catalytic crystal faces could support a ribbon-like carbon deposit. However, during the growth and interaction between the various filaments, the ribbon can break off at the point of growth leaving the crystal growth center on the end of one ribbon. It is apparent in the electronmicrographs that there are some ribbons which have no crystal head at all. These may have resulted from ribbons breaking.

Past investigators have never mentioned or hypothesized as to a growth mechanism for these "filaments." If it is the iron or iron carbide crystal which acts to catalyze further deposition of carbon (the results of this research support this hypothesis), it seems reasonable that growth would occur via:

- (1) Adsorption of carbon monoxide on the active crystal face(s).
- (2) Decomposition via the Boudouard reaction to yield carbon which keeps pushing out as more carbon is formed underneath. The result is a long and thin carbon ribbon.

Since this carbon is very porous, it should be easy for the carbon monoxide to reach the iron or iron carbide surface on which decomposition will occur.

It was observed that with increasing length of reaction the carbon ribbons slowly lost their activity to catalyze the deposition reactions. This could result from a gradual disintegration of the

metal crystal as small particles of the crystal were carried from its surface by the growing carbon ribbon. If this were true, the metal should be found within the carbon ribbon. Electronmicrographs give excellent support for this hypothesis by showing small, dense granules dispersed through the carbon ribbons. See Figures 11, 13, 17, and 19. Further support is received from electronmicrographs which show that with increasing length of reaction, there is a decrease in the number of distinct crystal heads. See Figures 12, 14, and 18.

Another possible explanation for the decreasing activity of the carbon with time is a poisoning of the metal or metal carbide catalyst. Sulfur and nitrogen compounds are good inhibitors of the Bosch reactions on iron because of their strong chemisorption. (32) (33) (34) (35) A past investigator (36) has found significant quantities of these compounds in gas cylinders of carbon dioxide, carbon monoxide and methane. Since none of these compounds were detected in this study, it is felt that poisoning is probably not the source of the decreasing rate.

Another interesting observation which warrants mention is the bent and twisted nature of the carbon ribbons. This phenomena can be explained in two ways. First, the activity of the catalytic crystal face(s) may not be uniform, resulting in different growth rates on the surface. This would obviously yield bent ribbons. If small particles of the metal are constantly being carried into the carbon ribbon, it seems reasonable to suspect that the surface of the metal crystal would not be uniform. The second possible source of the bent ribbons is the mechanical interaction resulting from the growing ribbons, i.e., the ribbons are bent and twisted from a purely physical interaction.

There remains one phenomenon to be explained, the source and formation of the metal crystal heads. Since the heads are

either iron or an iron carbide, it is not difficult to postulate that they originated from the iron rod. Since this study did not investigate the structure of the iron rod and the solid phases present during reaction, only speculative conclusions can be made, most of which are based on previous studies by other researchers. Most recent investigators (37) (38) are generally in agreement on the mechanism of carbon monoxide decomposition over an iron catalyst. They proposed that carbon monoxide chemisorbs on the iron surface followed by decomposition to carbon dioxide and carbon. The next step is interstitial diffusion of iron atoms through the iron matrix with precipitation of cementite (Fe_3C) when the surface region becomes supersaturated. At 600°C the cementite is only metastable and decomposes slowly to yield carbon and finely dispersed iron particles. The result is a large increase in the surface area. Since the small iron particles should be capable of chemisorption of carbon monoxide, it is not unreasonable to postulate that they are the growth sites for the carbon ribbons. It is also possible for these small iron particles to form higher carbides. Because of their small size they would be easily saturated with carbon with the formation of iron carbides.

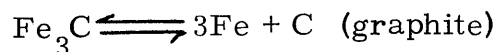
Although there was very little effort made in this research to study the solid phases of the iron rod, some relevant observations lend support to the above hypotheses. Hydrogen was noted to be a very active accelerator of the carbon deposition rate. The influence of hydrogen on the rate may result from two occurrences:

- (1) Acceleration in the rate of carbon monoxide decomposition.

This fact is well supported in the literature. (39) (40)

(41) (42) (43) Other investigations have also shown hydrogen will accelerate the deposition of carbon from methane and ethane on iron. (44)

- (2) Increase in the rate of cementite (Fe_3C) decomposition to yield the small iron particles.



This, too, is well supported in the literature (45) (46) and would obviously increase the rate by increasing the number of catalytic iron particles.

This research has provided no results which support or disprove Ruston's (47) hypothesis of Fe_7C_3 as being the catalytic metal crystal in the carbon. He states that this is the only carbide which is "truly" stable at 600°C . The other carbide which might be considered is cementite, Fe_3C . Although cementite is metastable and decomposes slowly, it has been suggested (48) that it could not possibly be catalytic because it will not adsorb carbon monoxide. The only other possibility is that the metal crystal is α -iron, i.e., in its completely reduced state. With such a strong reducing environment (hydrogen and carbon monoxide) this would not be an unreasonable hypothesis. However, since the presence of hydrogen has failed to inhibit the formation of Fe_3C in the initial carburization steps of iron, then it is felt that the formation of small particles of higher carbides is very probable.

E. Comments on NASA's Studies and Comparison with Results Obtained in This Investigation

One major problem in trying to compare NASA's results with those obtained in this study is the significant difference between NASA's recycle reactor (almost total recycle of all gases, with addition of hydrogen and carbon dioxide, and condensation of water) and the single pass reactor. Another difficulty was the extreme variation in recycle gas composition between different studies and also within each study. This was further complicated

by the fact that no data were presented in the NASA reports which show typical inlet and exit gas compositions. So it is impossible to determine how gas compositions changed in passing through the reactor.

One final problem in comparing results is that the NASA studies measured the rate of reaction in terms of either the water production or the volume of carbon dioxide fed to the reactor. This was a useful means of expressing the rate in NASA's work but not in this study.

In agreement with the results of this investigation, the NASA studies showed that the Bosch reaction is controlled more by kinetic factors than by equilibrium considerations. However, a study in 1967 (49) revealed that precise recycle gas composition was unnecessary because the rate of reaction was relatively insensitive to H_2/CO_2 over a range of 3.0 to 9.0. These results showed that the current investigation may lend support for this. In this study it was found that the major reaction occurring was the Boudouard and that the 2-3% water resulted from the reverse water-gas shift reaction. The NASA study also found a water concentration of 2-3% which seems to suggest that both measured approximately the same rate (in terms of water). If the rate is insensitive to the H_2/CO_2 , it means that the rate of the reverse water-gas shift must be insensitive too. Since carbon monoxide is so much more strongly adsorbed on iron surfaces than hydrogen or carbon dioxide, it is not surprising that the major reaction occurring is carbon monoxide decomposition. Another NASA study (50) showed no change in the rate of reaction by lowering the carbon dioxide concentration from 17% to 6%.

The most recent NASA study (51) indicated that satisfactory performance of the reactor system was obtained with gas compositions varying from .58 H_2 , .27 CH_4 , .13 CO , and .02 CO_2



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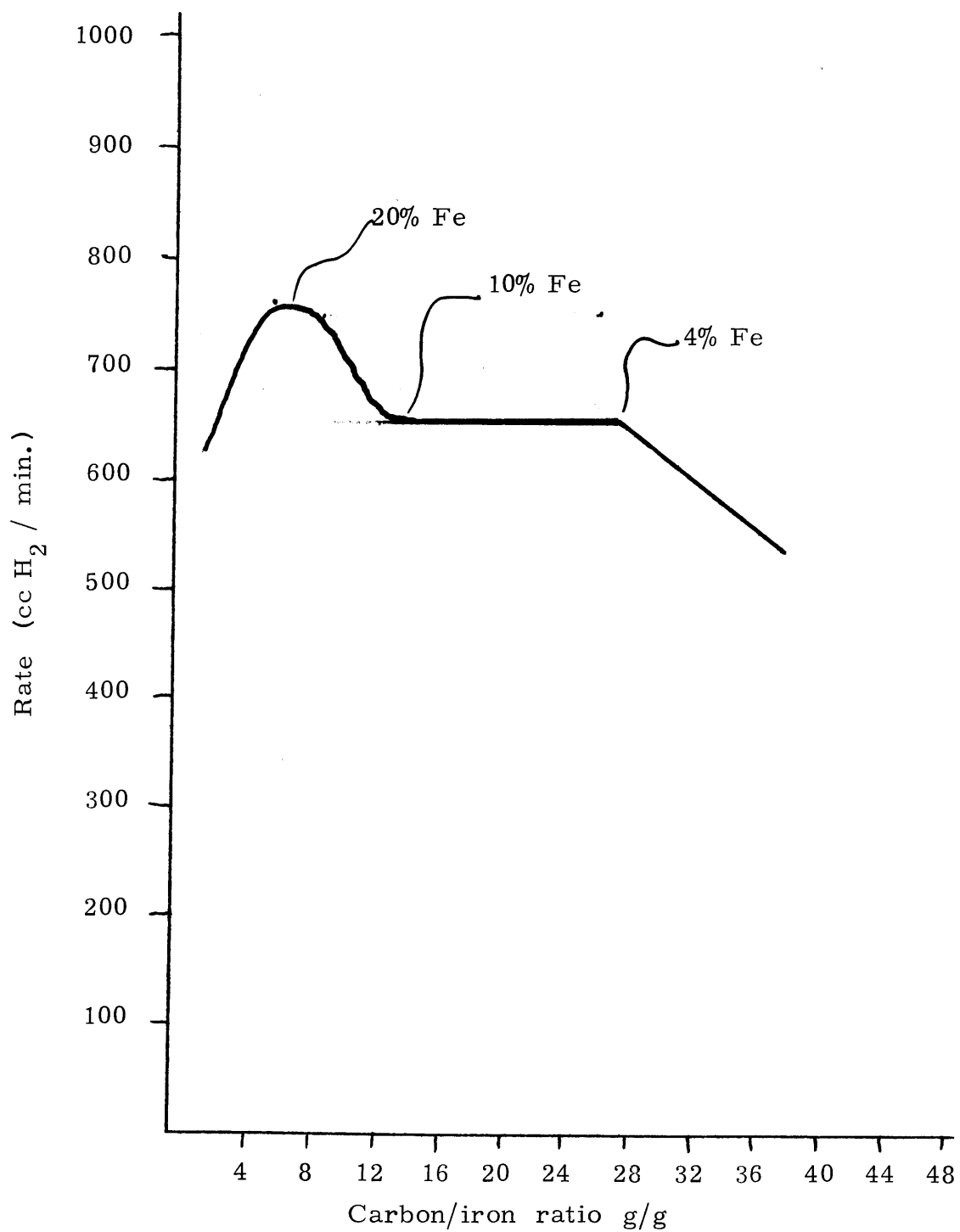
to .20 H₂, .20 CH₄, .40 CO, and .20 CO₂. Apparently the carbon dioxide can vary over a 10-fold range, however, carbon monoxide has only a 3-fold range. It seems that the carbon monoxide concentration is much more critical than carbon dioxide. This fact is well supported by the results from this study. The recent NASA study reported a water concentration in the exit gas of 3-4%, which is slightly higher than results from this study's 2-3%. However, this was probably due to the 660°C temperature (as opposed to 600°C in this study) used in the NASA study. The reverse water-gas shift is favored at higher temperatures and would account for the increased water.

One other interesting observation in the NASA studies was a plot showing the effect of the carbon to iron ratio on the rate of reaction (52). See Figure 22. This shows a region in which the rate was constant from an iron concentration of 10% to 4%. This does not appear to agree with the results in this study which show a decreasing rate with decreasing iron concentration. However, this is easily reconciled because the NASA rate is in terms of hydrogen fed per min and not grams of carbon deposited per min. Since the carbon forming reaction does not involve hydrogen, there should not necessarily be a correlation between the two.

The one disheartening fact which has been hard to explain was that all the NASA studies using a recycle reactor indicated that the carbon monoxide and methane concentrations remain constant while carbon dioxide and hydrogen are added to make up for that consumed by reaction. However, in the single pass reactor of this study, the carbon dioxide concentration increased as the carbon monoxide concentration decreased. In recent NASA studies, (53) the carbon dioxide was not added constantly. Only when a sensor in the recycle gas detected the concentration of carbon dioxide below a certain value did a valve open to admit more.

FIGURE 22

RATE OF BOSCH REACTION AS A
FUNCTION OF THE CARBON/IRON RATIO



The NASA reports indicated that the reactors were operating at steady state, but there may be some doubt. The only other possible explanation to account for the consumption rather than production of carbon dioxide was the higher temperature (660°C) used in the most recent NASA reactor. At this temperature the reverse water-gas shift reaction (this reaction consumes CO_2) is favored thermodynamically over the carbon deposition reaction (Boudouard). If the reactor were operating at steady state, the production of carbon monoxide via the reverse water-gas shift reaction must be equalled by the disappearance of carbon monoxide via the carbon deposition reactions. In this situation there would be a net carbon dioxide consumption.

However, the results from the experiments of this study suggest that at the temperature of 600°C the rate of the Boudouard reaction is much faster than the rate of the reverse water-gas shift reaction. Thus a net increase in carbon dioxide is observed.

VI. CONCLUSIONS AND RECOMMENDATIONS

A. Conclusions

An analysis of the results from this study yields the following conclusions:

- (1) The Bosch reaction, as written ($\text{CO}_2 + 2\text{H}_2 \rightleftharpoons \text{C} + 2\text{H}_2\text{O}$), does not occur over iron at 600°C and atmospheric pressure. The results show a stepwise sequence initiated by the reverse water-gas shift reaction ($\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$) followed by the decomposition ($2\text{CO} \rightleftharpoons \text{CO}_2 + \text{C}$) or hydrogen reduction ($\text{CO} + \text{H}_2 \rightleftharpoons \text{C} + \text{H}_2\text{O}$) of carbon monoxide.
- (2) Under the conditions used in this study, the Boudouard (carbon monoxide decomposition) reaction is the major source of the carbon. This reaction is accelerated by hydrogen.
- (3) The 2-3% water produced results from the reverse water-gas shift reaction.
- (4) The Bosch reaction(s) is controlled more by kinetic and mechanistic factors than by equilibrium considerations.
- (5) The carbon product always contains appreciable amounts of iron, probably in the form of a high iron carbide such as Fe_7C_3 .
- (6) An autocatalytic effect was apparent over the iron although the magnitude of the effect decreased with increasing carbon deposition.
- (7) The carbon product was catalytic due to the presence of iron. The carbon continued to be active until the iron concentration decreased below 0.5%.
- (8) For long reaction times, the rate was controlled by the reaction over carbon.

- (9) The rate of deposition over carbon decreases with time. This resulted from gradual disintegration of the catalytic iron particles.
- (10) The rate of reaction was probably controlled by the active surface area of the iron available for chemisorption.
- (11) Carbon "filaments" appear to be ribbons instead of cylindrical in shape.
- (12) The catalytic iron carbide crystal has two active surfaces for chemisorption and carbon growth.

B. Recommendations for Future Studies

1. Radioactive Studies

Some very useful results which would aid in the understanding of a reaction mechanism could be obtained with radioactive gases.

- (a) A mixture similar to NASA's recycle gas composition could be labelled with radioactive carbon dioxide (Carbon-14) and passed over the iron rod. By analyzing for the amount of radioactive carbon monoxide in the exit gas, the extent of the reverse water-gas shift reaction could be calculated.
$$C^*O_2 + H_2 \rightleftharpoons C^*O + H_2O$$
- (b) In another experiment, the same gas mixture as above could be used except the carbon monoxide would be labelled. Analysis for the amount of radioactive carbon dioxide produced would indicate the extent of the Boudouard (carbon monoxide decomposition) reaction.
$$2C^*O \rightleftharpoons C^* + C^*O_2.$$
- (c) A further experiment in which the oxygen atom in carbon monoxide was radioactively labelled would be advantageous. By measuring the amount of radioactive water produced, the extent of the hydrogen reduction of carbon monoxide could be calculated.
$$CO^* + H_2 \rightleftharpoons C + H_2O^*$$

2. Acid Treatment

Since it is the iron or iron carbide in the carbon which was suspected of being the catalytic agent for further carbon deposition, removal should show a noticeable difference in reactivity. Walker (54) has found that treatment of the carbon with HCL or HF removed nearly all the iron crystal heads from the carbon "filaments." It is suggested that an experiment be performed on carbon, from which the iron has been extracted, to determine the importance of the iron as a further catalyst.

3. Identification of Iron Species in Carbon

No conclusive identification has ever been made of the iron particle found in the carbon ribbons. Electron diffraction measurements would be a useful tool for this purpose. However, a means must first be developed for separating the iron species from the carbon. This would insure that reliable electron diffraction measurements would be correctly interpreted. One possible method for the separation might utilize a magnetic field to attract the iron particles after they are pulverized mechanically or ultrasonically.

4. Surface Area and Adsorptive Studies

The unique type of carbon formation found in this study may possess adsorptive properties which warrants further study. Although no measurements were performed in this research, past investigators (55) (56) have found the surface area to be between $120-160\text{m}^2/\text{g}$. The surface area was also found to increase with increasing length of reaction. (57) A rough calculation (See Appendix E) using the approximate dimensions of the carbon ribbons shows an external area for physical adsorption of $160\text{m}^2/\text{g}$. This calculation assumes a ribbon shape and does not consider the possibility of an internal pore structure. Since

this particular carbon formation may have useful applications for trace contaminant control in space vehicles, it is suggested that extensive studies be conducted to determine its absorptive properties.

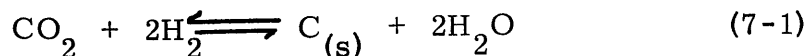
5. Method for Reducing Carbon Dioxide More Rapidly

The results of this study show that the Bosch reaction is composed of at least two or three interrelated but individual reactions. The rate of each reaction will be determined by a number of parameters including: temperature, pressure, gas composition and catalyst species. Since past studies have shown the rate to be relatively insensitive to gas composition, it is believed that the temperature is probably the most important variable. Thus there should be an optimum temperature at which the rate of water formation is a maximum. A higher concentration of both carbon dioxide and hydrogen should also tend to increase the rate of reduction. Since the concentration of both carbon monoxide and hydrogen is influential in the rate of the carbon deposition reactions, there may be an optimum composition.

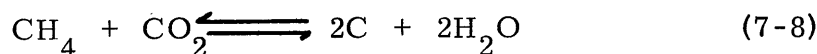
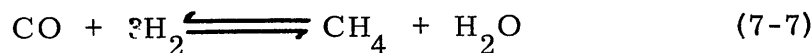
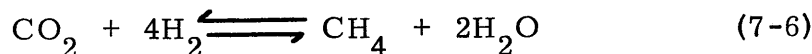
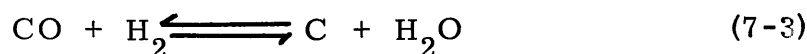
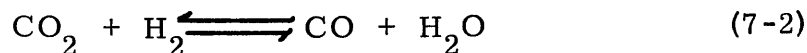
VIII. APPENDIX

A. Review of the Literature

In reviewing the literature of the past half century, no reference has been found which indicates that the Bosch reaction proceeds in one step with the formation of water and solid carbon.



If the reaction does not proceed in this manner, there are a number of reactions between carbon dioxide, hydrogen and the various products which might occur over an iron catalyst.



There are various other reactions which could yield oxygen and light hydrocarbons, however, under the conditions considered in this research (600°C and atmospheric pressure) only negligible quantities could be formed. Other reactions which must be considered are those between the metal (iron) and any of the products listed above. Thus there is the possibility of iron carbides being formed. The formation of any iron oxides would be unlikely in such a strong reducing atmosphere of hydrogen and carbon monoxide.

Of the above equations, it was doubted whether reactions (7-6) and (7-8) would occur over the iron because they are strongly inhibited by carbon monoxide. (58) Walker (59) has also found that reaction (7-7) was not significant at temperatures above 500°C.

Considering all the above reactions, only two have received considerable attention in the literature, these being the Boudouard and the water-gas shift reaction. (Equations (7-4) and (7-2) respectively.) The Boudouard reaction, carbon monoxide decomposition, will be considered first.

The work of Baukloh, Hieber, Spetzler, Henke, Chatterjee and Das over the period 1936-1955 represents the largest and most comprehensive research programs performed on carbon monoxide decomposition over metals (60) (61) (62) (63) (64) (65) (66). The reduced form of the metal was found to be the catalyst, and the rate was proportional to the amount of carbon monoxide adsorbed on the surface. The temperature range studied was between 300°C - 900°C with the maximum rate usually occurring around 500°C. The possibility of cementite (Fe_3C) acting as a catalyst was disproved.

Akamatsu (67) in 1949 assumed iron to be the catalyst with carbon resulting from carbide decomposition. In the period 1948-1950, Kummer (68) (69) reported some findings from studies on the Fischer-Tropsch synthesis catalysts. It was theorized that carbon could diffuse through iron and deposit in the lattice. Also, adsorption experiments showed that carbides do not adsorb carbon monoxide. In 1955, Royen (70) and Emmett (71) found metallic iron to catalyze the carbon monoxide decomposition in the temperature range 250°C - 450°C and 460°C - 600°C respectively.

Berry (72) reported Hagg carbide (Fe_5C_2) to be the catalyst from 400°C-565°C and cementite (Fe_3C) from 565°C-700°C. Iron and carbon were not considered to be catalytic. It is difficult to account for these discrepancies with other investigators. From 1962-1964, Cox (73) and Boule (74) both found metallic iron to be the catalyst. Various researchers have found that small amounts of sulfur compounds decrease and stop carbon monoxide decomposition over iron catalysts. (75) (76) (77) (78) Nitrogen compounds are also effective inhibitors (79) (80) (81) while hydrogen is a well-known promoter (82) (83) (84) (85). Water has been found to both retard and accelerate carbon monoxide decomposition (86) (87).

Extensive investigations were conducted by Walker, et. al., (88) on carbon monoxide decomposition in the presence of hydrogen. With the assumption that there was no carbon monoxide adsorption by cementite, they found the active catalyst to be iron. The carbon atoms were said to have a high mobility and will migrate across the surface to a nucleating center where they begin forming both free carbon and cementite. The production of free carbon would stop when the catalyst was completely carbided because chemisorption of carbon monoxide would cease. The temperature range of their study was 450°C-700°C.

In 1966 Ruston (89) reported on the decomposition of carbon monoxide at 550°C over electrolytic single crystals of iron. He proposed the mechanism of carburization resulting from interstitial diffusion of carbon atoms with precipitation of cementite when the solution becomes supersaturated. The formation of two types of carbon, lamellar and filamentous, was also noted. Small crystals of Fe_7C_8 were observed and

reported to be the growth centers for the filamentous carbon.

A recent study by Ratliff (90) on the reaction of carbon monoxide with iron single crystals resulted in the following conclusions. Carbon monoxide adsorbs and decomposes uniformly on a clean iron surface. The carbon atoms dissolve in the iron matrix. When the surface region becomes supersaturated, cementite will precipitate at dislocation sites. Thus a continuous precipitation process is initiated. However, there may be some critical supersaturation at which point the carbon penetration of the iron stops. The carbon monoxide decomposition is thus a function of the carbon content of the iron as well as the temperature and pressure. The onset of cementite decomposition with production of carbon and finely divided iron, results in a large increase in the surface area of iron and consequent increase in the rate of decomposition. Cementite, which precipitates early in the attack by carbon monoxide, precedes the nucleation and growth of graphite. He postulates that carbon nucleates at an active site (iron surface and the cementite-iron interface) just as cementite does. Ruston's (91) carbide crystal was not confirmed in Ratliff's study. Ratliff suggests that as the cementite decomposes to yield the finely divided iron particles, this fine form could easily form filaments of carbon and also higher carbides.

Many investigators have noted but not explained the reasons for the delayed catalytic activity of iron for carbon monoxide decomposition. Lo (92) has proposed that initially the iron adsorbs the carbon monoxide and hydrogen too strongly for the gases to react. The chemisorbed gas raises the energy level of the iron by reducing the number of vacant d-orbitals. After a lapse of time some of the chemisorbed carbon monoxide

decomposes to give free or carbidic carbon plus carbon dioxide. The carbon diffuses from the surface to the sublayer, allowing further chemisorption. The energy level of the iron electrons is lowered by the electrons from the carbon atoms, resulting in weakened chemisorption and greater reactivity of the gases. Lo suggested that the chemisorption of carbon monoxide was so strong it would tend to displace adsorbed hydrogen. However, it is felt that this is not completely true. It should be possible for carbon monoxide to adsorb on iron in which hydrogen has already adsorbed because of the different active sites for adsorption of gases.

Because of the industrial importance of the water-gas shift reaction, the literature contains volumes of research studies concerned with every conceivable aspect. However, little effort has been expended on studies of the reverse water-gas shift reaction. A recent and comprehensive study was performed by Robert Kunser (93). Using a packed bed flow reactor of porous 1/8 inch iron pellets operating at 635°C, he found that the conversion was controlled by mixing and diffusional resistances and was not chemically controlled. The homogeneous gas reaction does not become significant until 800°C. He also observed no significant amount of carbon deposited and a negligible amount of methane produced. His results showed conversions as high as 40% carbon monoxide, yet no carbon deposition. These results are surprising. With a carbon monoxide concentration this high, a large carbon deposit resulting from the Boudouard reaction would be expected.

A study by Hall (94) of the reaction between carbon dioxide and hydrogen over an iron foil at 900°C showed that the rate was proportional to the partial pressure of carbon dioxide to the first power and hydrogen to a power less than one.

A kinetic study of the Boudouard reaction, Equation (7-4), on Vycor glass showed that the forward reaction was much slower than the reverse. (95) The reaction rate was zero order on Vycor and proportional to the surface area.

Not only has carbon resulted from decomposition of carbon monoxide over iron, nickel and cobalt but also from pyrolysis of light hydrocarbons. Robertson (96) has reported two types of carbon being formed when methane is pyrolyzed over some transition metal surfaces at 650°C. A "flake" carbon having a perfect crystalline graphite structure was observed and also a fibrous polycrystalline deposit was noted. Evidence of the metal substrate within each form of carbon was given by microprobe analysis. Another investigator (97) has shown the formation of carbon fibers from the thermal decomposition of acetylene over nickel wire at 450°C-700°C. An autocatalytic acceleration was noted at the beginning, followed by a deceleration. The maximum rate occurred near 600°C and was promoted more than ten-fold with the addition of hydrogen to the gas. Another interesting observation was that the fibrous carbon itself acts as a catalyst, and the carbon adjacent to the wire has the same catalytic activity as the outer layer of carbon. Electron microscopy showed dark areas of metal or metal carbides in the carbon fibers. It was proposed that the two-step process is initiated by an activation of the metal surface followed by a growth of carbon fibers from the active sites. No hypothesis was made as to the active species, however, a carbide species seems probable.

Walker (98) has recently completed some studies on the chemisorption of hydrogen on activated charcoal. The amount of hydrogen adsorbed increased with both pressure and temperature. Four linear regions were identified as corresponding

to chemisorption on four different sites of the carbon. Carbon is also capable of adsorbing both carbon monoxide and carbon dioxide which suggests that a reaction between these gases is possible over carbon.

It is possible for the catalytic action of the iron particles to benefit from the large quantity of gas which would be physically adsorbed by the carbon. As the decomposition reactions occur over the iron catalyst, the carbon might act as a good store-house and supplier of reactive gases to the iron.

B. Details of Apparatus and Procedures

1. Tubular Reactor

The reactor consisted of a 12mm by 60cm Vycor glass tube. See Figure 23 for a detailed schematic. Vycor ground glass joints on each end of the tube permitted easy access to the interior of the reactor. Two thermocouple wells entered through ground glass joints from each end. Small dimples in the middle of the reactor tube acted as the cradle for supporting the iron rod.

2. Preheater

The inlet gas tube to the reactor was 8mm by 15cm. The entire length was packed with 3mm glass beads to make certain that the gases were well mixed. The heat was supplied by a number 22 gauge nichrome wire wound around the inlet tube and connected to a variable voltage transformer. Several layers of asbestos fiber mat were used as insulation.

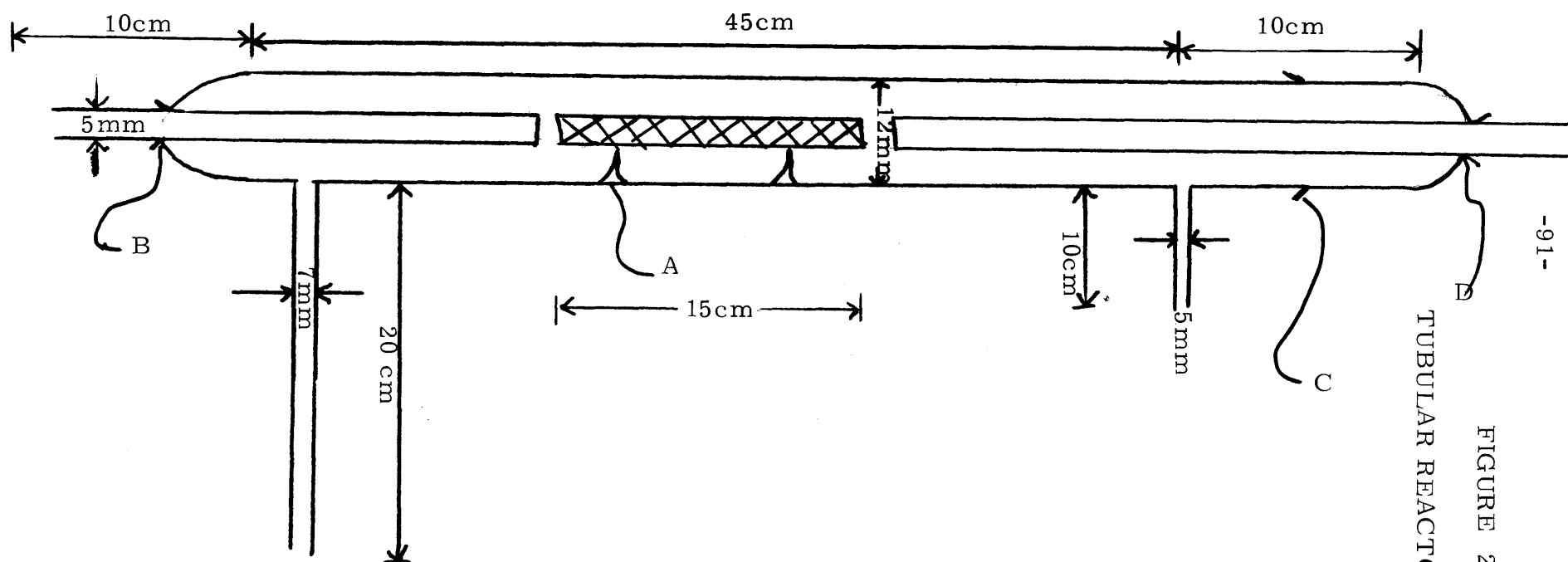
3. Flow Meters and Calibration

Each reactive gas was throttled through a Hoke needle valve, and the flow rate was correlated with the pressure drop across a glass capillary tube. Assuming that the entrance effects on the pressure drop in capillary tubes are negligible, the pressure drop is given by the well-known Poiseuille equation. *

$$\Delta P = \frac{8\mu LU}{d^2 g_c} \quad (7-10)$$

*NOMENCLATURE

μ viscosity	g_c gravitational constant
L capillary length	ΔP pressure drop
U average velocity	Q gas flow rate
d capillary diameter	



A - Dimple supporting the iron rod
 B - 10/30 Vycor joint

C - 14/35 Vycor joint
 D - 10/30 Pyrex joint

TUBULAR REACTOR DIMENSIONS

The volumetric flow rate is given by*:

$$Q = \frac{\pi d^4 g_c}{32 \mu L} \Delta P \quad (7-11)$$

Obviously the volumetric flow rate at constant temperature is a linear function of the pressure drop across a capillary tube. A monometer U-tube filled with colored diffusion pump oil ($\rho = .96$) was used to measure the pressure drop. This was correlated to the gas flow rate as measured by a Matheson #600 dual float rotometer.

4. Furnace

A 1000 watt, Lindberg Hevi-Duty, split tube furnace reached reaction temperature (600°C) in approximately two hours, after which the automatic temperature control would stabilize the temperature to within $\pm 5^\circ\text{C}$.

5. Iron Rods

The electrolytic iron rods were obtained from United Mineral and Chemical Corporation. A minimum purity of 99.95 was guaranteed by the supplier. Refer to Table III for a list of the impurity content of the electrolytic rod.

TABLE III

Impurity Content of the Electrolytic Iron Rod Used in
the Carbon Deposition Experiments

	ppm
C	60
S	60
P	40
Si	40
Cu	2
Mn	8
Gases	<u>Balance</u>
	< 500 ppm

6. Reaction Gases

All gases were obtained from Matheson Gas Products. The tanks contained approximately 100 cubic feet of gas. Refer to Table IV for a listing of the impurity content of the gases.

TABLE IV

Gas	Purity %	Maximum Impurity Content (ppm)						
		O ₂	N ₂	CO ₂	H ₂	CH ₄	CO	C ₂ -C ₆
CO	99.5	20	75	200	5	2		
CO ₂	99.5	900	3000				50	
H ₂	99.5	8	400	1		1		
CH ₄	99.8		6000	2000				1500

C. Details of Gas Analysis

Exit gas compositions were measured by a Hewlett-Packard, 700 Laboratory Chromatograph. Gas samples were collected via an on-line, 1/2 cc gas sampling valve. The gas sample was swept from the sample loop with ultra-high purity helium at a flow rate of 30cc/min. A 12 foot by 1/4 inch column of Poropak-Q was used for separating the gases. The output of the thermal conductivity detector was connected to a millivolt recorder. Figure 24 shows a typical gas chromatogram. Because the peaks were sharp and symmetrical, the areas under the peaks were determined by a geometrical method (height times width at 1/2 the height). The area for each gas in a sample was compared to the area for a standard gas sample. See Table V for an analysis of the standard sample.

FIGURE 24

TYPICAL GAS CHROMATOGRAM

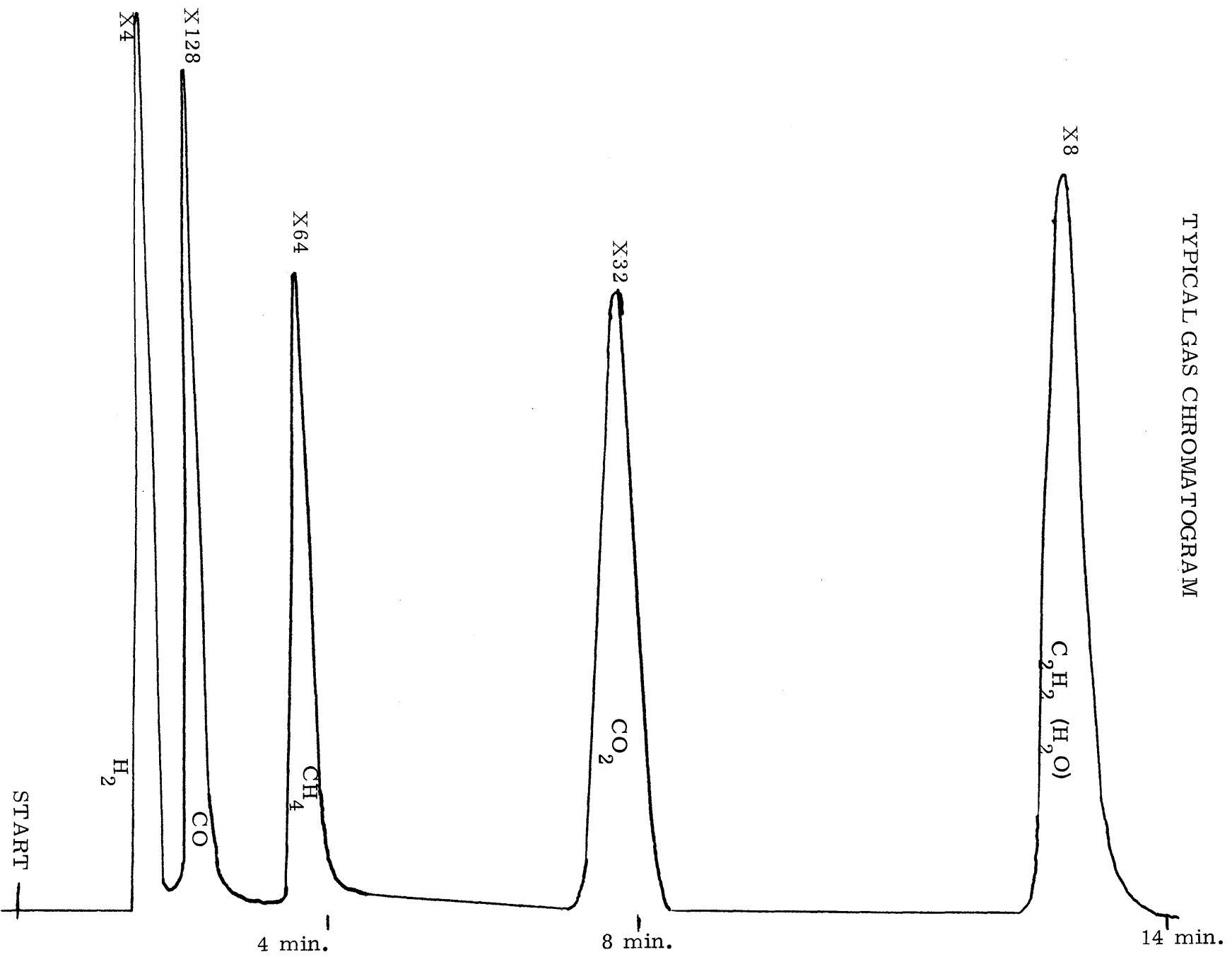


TABLE V

Analysis of Standard Gas Sample*

<u>Gas</u>	<u>Composition (%)</u>
H ₂	29.1%
CO ₂	14.8%
CO	29.4%
CH ₄	21.4%
C ₂ H ₂	5.3%

*Provided by Matheson Gas Products

It should be mentioned that in many samples hydrogen traced a double peak. A possible explanation for this phenomenon is suggested by considering the operating principle of the thermal conductivity detector.

If a gas component with a higher thermal conductivity than the carrier gas passes through the sensing cell, the temperature of the thermistor falls, and a negative peak is traced. Just the opposite occurs with a gas of low thermal conductivity. With helium as the carrier gas, hydrogen should show a negative peak. The thermal conductivities of various gases are listed in Table VI.

TABLE VI

Thermal Conductivities of Gases

<u>Gas</u>	<u>k_o</u>	<u>Gas</u>	<u>k_o</u>
Hydrogen	4160	Methane	721
Helium	3480	Ethylene	419
Argon	398	Ethane	436
Carbon Monoxide	563	Nitrogen	581
Carbon Dioxide	352	Oxygen	589
		Air	583

In the actual chromatogram, hydrogen showed a single positive peak if its concentration was below about 30%. With higher concentrations, the peak was split. This negative peak first appeared as a mere shoulder on the positive peak but grew in the negative direction with increasing hydrogen concentration.

The occurrence may be explained by the presence of oxygen as an impurity in commercial helium. The oxygen combines with hydrogen over the surface of the thermistor, because the thermistor acts as a catalyst. As the hydrogen band passes through the sensing cell, the concentration varies gradually from zero through a maximum to zero again. At the initial low concentration, the exothermic effect of the reaction overshadows the cooling effect of the hydrogen, and the pen moves in a positive direction. At high concentrations, the heat conducted away by the hydrogen is more than the heat of reaction, and the pen moves in the negative direction. At the low concentration in the tail end of the hydrogen band, the exothermic reaction is again dominant, and a second positive peak results.

The double peaks did not occur if argon was the carrier gas because the difference in thermal conductivities is so great that the cooling effect of the hydrogen always dominates.

Nevertheless, helium and not argon was used as the carrier gas. If argon was used, the sensitivity for the other reaction gases would be poor. Therefore, with helium, the hydrogen concentration was determined by difference.

D. Thermodynamic and Equilibrium Considerations

Chemical equilibrium exists when the rates of the forward and reverse reactions are equal. Given a typical gas phase reaction, $aA + bB \rightleftharpoons cC + dD$, where the ideal gas law is assumed valid, the equilibrium constant, K , is defined:

$$K = \frac{(X_C)^c (X_D)^d}{(X_A)^a (X_B)^b} (\pi)^{c+d-a-b} \quad (7-12)$$

where:

π is the total system pressure

A + B are reactant species

C + D are product species

a, b, c, + d are the stoichiometric coefficients

X's are the volume fractions

K is related to the Standard Gibbs free energy by:

$$\Delta G^\circ = -RT \ln K \quad (7-13)$$

where:

ΔG° is the Gibbs free energy change between products and reactants in their standard states

T is the reaction temperature

R is the universal gas constant

G° can be evaluated via: (7-14)

$$\frac{\Delta G^\circ}{T} = \sum_{\text{Products}} \left[\left(\frac{G^\circ_T}{T} - \frac{H^\circ_O}{T} \right) + \frac{G^\circ_f}{T} \right] - \sum_{\text{Reactants}} \left[\left(\frac{G^\circ_T}{T} - \frac{H^\circ_O}{T} \right) + \frac{G^\circ_f}{T} \right]$$

where:

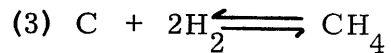
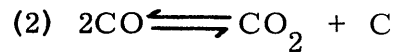
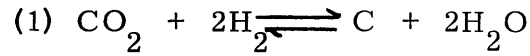
G_T° is the standard Gibbs free energy at temperature T

H_O° is the enthalpy of chemical species at 0°K

H_f° is the standard heat of formation at 0°K

The system under consideration is carbon dioxide reacting with hydrogen and all subsequent products of this reaction. The compounds which must be considered at equilibrium include: carbon monoxide, carbon dioxide, water, hydrogen, methane, and solid carbon. Reaction conditions are in the temperature range 500°K to 1100°K and approximately atmospheric pressure.

Three independent reactions may be written to represent all the relationships of the above compounds:



All other possible reactions of these compounds can be formed by a linear combination of the three above reactions.

The equilibrium equations corresponding to the above reactions can be represented:

$$K_1 = \frac{(X_{\text{H}_2\text{O}})^2}{(X_{\text{H}_2})^2 (X_{\text{CO}_2}) (\pi)} \quad (7-15)$$

$$K_2 = \frac{(X_{\text{CO}_2})}{(X_{\text{CO}})^2 (\pi)} \quad (7-16)$$

$$K_3 = \frac{(X_{CH_4})}{(X_{H_2})^2 (\pi)} \quad (7-17)$$

For a given temperature and pressure, the K's can be calculated via equations (7-13) and (7-14). We have three equations and five unknowns. The two other equations can be derived from an atom balance and a relationship between the volume fractions. The ratio of oxygen to hydrogen atoms in the initial feed is identical to the equilibrium mixture.

$$O/H = \frac{2X_{CO_2} + X_{CO} + X_{H_2O}}{2X_{H_2} + 2X_{H_2O} + 4X_{CH_4}} \quad (7-18)$$

The volume fractions are related by

$$X_{CO_2} + X_{CO} + X_{H_2O} + X_{H_2} + X_{CH_4} = 1.0$$

By specifying the system temperature, pressure and oxygen to hydrogen atom ratio, the five equations in five unknown volume fractions can be calculated. A computer program was developed (99) to solve the five equations and plot the volume fractions of each species as a function of oxygen to hydrogen ratio. A listing of this program is found in Figure 25. Figures 26, 27, and 28 are examples of calculated equilibrium gas composition for conditions used in this research. (600°C and atmospheric pressure) Comparing these equilibrium values with typical values for the exit gas compositions measured during experiments in this research shows that in every case the gas mixture was still far removed from equilibrium.

Referring to Figures 26, 27, and 28, it is evident that if only equilibrium considerations are important, then the production of water is maximized at an O/H ratio equal to 0.5, and that the production increases with decreasing temperature. These results agreed with the conclusions of Remus (100).

The NASA studies used slightly higher pressures than these studies. Figure 29 shows a plot of the equilibrium gas composition versus temperature for NASA's pressure conditions and an O/H ratio of 0.4 (typical value in the most recent NASA studies). The equilibrium concentration of hydrogen and carbon monoxide rise with increasing temperature (over the temperature range 530°C - 710°C). However, the water, carbon dioxide and methane concentrations decreased with increasing temperature.

In the most recent NASA study (101) the results showed that as the temperature was decreased below the optimum (660°C) the recycle gas composition was higher in methane and lower in carbon monoxide. This is in agreement with equilibrium predictions.

Another NASA study (102) found that an increase in the carbon dioxide recycle concentration resulted in an increased carbon monoxide concentration and decreased methane concentration. An increase in the carbon dioxide recycle composition is equivalent to an increased O/H ratio. Referring to Figure 27, the equilibrium calculations predict the same results which were observed in the NASA study.

PAGE 1

// JOB

LOG DRIVE CART SPEC CART AVAIL PHY DRIVE
0000 03CE 03CE 0000

V2 MOR ACTUAL BK CONFIG BK

// FOR

*LIST ALL

*ONE WORD INTEGERS

*IOCS(CARD, 1132 PRINTER)

REAL K1,K2, K3

DIMENSION SF(5),X(5), A(25), F(5)

DIMENSION PL(306)

READ (2,50) NRUNS, NOH, TOL

50 FORMAT (10X,I3,12X,I3,12X,F10.2)

N=5

MAX= 500

NOH1= NOH+1

XNOH= NOH

XNOH1= NOH1

DO 20 KRUN=1,NRUNS

READ (2,51) T,P,(X(I),I=1,5)

51 FORMAT (2(10X,F10.1),10X,5F5.2)

WRITE (3,60)

60 FORMAT ('1', 28X,'EQUILIBRIUM VOLUME FRACTIONS -- RICHARD FREEDMAN

1 ' ,//)

WRITE(3,53) T,P

53 FORMAT (' TEMPERATURE =' ,F9.2, ' DEGK PRESSURE =' ,F9.5,

1' ATM.,' ,//,5X,'O/H RATIO',10X,'X(CO2)',11X,'X(H2)',10X,'X(H2O)',

211X,'X(CO)',10X,'X(CH4)',//)

CALL EQCON(T,K1,K2,K3)

DELTA= (ALOG(10.) -ALOG(0.1))/XNOH

G= EXP(ALOG(0.1) -DELTA)

DO 25 IG= 1,NOH1

G= EXP(ALOG(G) +DELTA)

ITER= 0

10 X1= X(1)

X2= X(2)

X3= X(3)

X4= X(4)

X5= X(5)

F(1)= 1. -(X1+X2+X3+X4+X5)

FN= 2.*X4+X2+X3

FD= X1+X2+2.*X5

F(2)= -0.5*FN/FD +G

F(3)= -X2**2/(X1**2 *X4+P) +K1

F(4)= -X3**2 *P/X4 +K2

F(5)= -X5/(X1**2 *P) +K3

F11= 1.

F12= 1.

F13= 1.

F14= 1.

F15= 1.

F21= -0.5*FN/(FD**2)

F22= -0.5*(FN -FD)/(FD**2)

F23= 0.5/FD

F24= 1.0/FD

F25= -FN/(FD**2)

FIGURE 25a

FIGURE 25b

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```

1000 PL(I) = G
      I = NOH1 + IG
      PL(I) = X(4)
      I = 2 * NOH1 + IG
      PL(I) = X(1)
      I = 3 * NOH1 + IG
      PL(I) = X(2)
      I = 4 * NOH1 + IG
      PL(I) = X(3)
      I = 5 * NOH1 + IG
      PL(I) = X(5)
25   CONTINUE
      CALL DATSW (0, I)
      GO TO (1001, 20), I
1001 WRITE (3, 150)
150   FORMAT ('1')
      WRITE (3, 61) T, P
71   FORMAT ('1' TEMPERATURE = '1, F9.2, ' DEGK PRESSURE = '1, F9.5,
      1' ATM, '1, //, 5X, 'O/H RATIO', 10X, 'X(CO2)=1 X(H2)=2 X(H2O)=3
      2X(CO)=4 X(CH4)=5')
      CALL PLOD (KRUN, PL, NOH1, 6, NOH1, 0)
20   CONTINUE
      CALL EXIT
      END

```

VARIABLE ALLOCATIONS

SF(R) = 0008-0000	X(R) = 0012-000A	A(R) = 0044-0014	F(R) = 004E-0046	PL(R) = 02B2-0050	K(R) = 02B4
K2(R) = 02B6	K3(R) = 02B8	TOL(R) = 02BA	XNOH(R) = 02BC	XNOH1(R) = 02BE	T(R) = 02C0
P(R) = 02C2	DELTA(R) = 02C4	G(R) = 02C6	X1(R) = 02C8	X2(R) = 02CA	X3(R) = 02CC
X4(R) = 02CE	X5(R) = 02D0	FN(R) = 02D2	FD(R) = 02D4	F11(R) = 02D6	F12(R) = 02D8
F13(R) = 02DA	F14(R) = 02DC	F15(R) = 02DE	F21(R) = 02E0	F22(R) = 02E2	F23(R) = 02E4
F24(R) = 02E6	F25(R) = 02E8	F31(R) = 02EA	F32(R) = 02EC	F33(R) = 02EE	F34(R) = 02F0
F35(R) = 02F2	F41(R) = 02F4	F42(R) = 02F6	F43(R) = 02F8	F44(R) = 02FA	F45(R) = 02FC
F51(R) = 02FE	F52(R) = 0300	F53(R) = 0302	F54(R) = 0304	F55(R) = 0306	NRUNS(I) = 030C
NOH(I) = 030D	N(I) = 030E	MAX(I) = 030F	NOH1(I) = 0310	KRUN(I) = 0311	I(I) = 0312
IG(I) = 0313	ITER(I) = 0314	KS(I) = 0315	L(I) = 0316		

STATEMENT ALLOCATIONS

50 = 033A	51 = 0341	60 = 0349	53 = 0369	101 = 03A9	100 = 03BB	150 = 03BE	61 = 03C1	10 = 049B	3 = 06B0
2 = 06C7	7 = 06F1	8 = 06FD	6 = 0702	1000 = 072F	25 = 07A3	1001 = 07B6	20 = 07CA		

FEATURES SUPPORTED

ONE WORD INTEGERS
19CS

CALLED SUBPROGRAMS

EGCON	FALOG	FEXP	SIMQ	FABS	DATSW	PLOD	FADD	FADDX	FSUB	FMPY	FDIV	FLD	FLDX	FSTO
FSTOX	FSBR	FDVR	FAXI	FLQAT	CARDZ	PRNTZ	SRED	SWRT	SCOMP	SF10	SIOFX	SIOF	SIOI	SUBS
SNR														

REAL CONSTANTS

.100000E 02=0326	.100000E 00=0328	.100000E 01=032A	.200000E 01=032C	.500000E 00=032E	.000000E 00=0330
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INTEGER CONSTANTS

2=0332	5=0333	500=033A	1=0335	3=0336	0=0337	4=0338	6=0339
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CORE REQUIREMENTS FOR

COMMON	0 VARIABLES	806 PROGRAM	1198
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FIGURE 25c

PAGE 2

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F31= -2.*X2**2/(X1**3 *X4*P)
F32= 2.*X2/(X1**2 *X4*P)
F33= 0.
F34= -(X2**2)/((X1*X4)**2 *P)
F35= 0.
F41= 0.
F42= 0.
F43= 2.*X3*P/X4
F44= -(X3**2)*P/(X4**2)
F45= 0.
F51= -2.*X5/(X1**3 *P)
F52= 0.
F53= 0.
F54= 0.
F55= 1.0/(X1**2 *P)
A(1)= F11
A(2)= F21
A(3)= F31
A(4)= F41
A(5)= F51
A(6)= F12
A(7)= F22
A(8)= F32
A(9)= F42
A(10)=F52
A(11)=F13
A(12)=F23
A(13)=F33
A(14)=F43
A(15)=F53
A(16)=F14
A(17)=F24
A(18)=F34
A(19)=F44
A(20)=F54
A(21)=F15
A(22)=F25
A(23)=F35
A(24)=F45
A(25)=F55
DO 3 I=1,N
SF(I)= -F(I)
3 CONTINUE
CALL SIMQ(A,F,N,KS)
L=KS
DO 2 I=1,N
2 X(I)= X(I) +F(I)
DO 6 I=1,N
IF (ABS(SF(I)) -TOL) 6,6,7
7 ITER= ITER +1
IF (ITER -MAX) 10,10,8
8 WRITE (3,101)
101 FORMAT ('0***** NO CONVERGENCE *****')
CALL EXIT
6 CONTINUE
WRITE (3,100) G,X(4),X(1),X(2),X(3),X(5)
100 FORMAT (6E16,3)
CALL DATSW (0,I)
GO TO (1000,25),I

```

PAGE 3

```
// FOR
*LIST ALL
*ONE WORD INTEGERS
SUBROUTINE EQCON (T,K1,K2,K3)
REAL K1,K2,K3
DIMENSION GIBBS(6,12), HEAT(6),FREE(6), X(12)
DO 100 I=1,12
XI=I*100
X(I)= 200. +XI
100 CONTINUE
GIBBS(1,1)= -24.465
GIBBS(1,2)= -26.422
GIBBS(1,3)= -27.950
GIBBS(1,4)= -29.203
GIBBS(1,5)= -30.265
GIBBS(1,6)= -31.186
GIBBS(1,7)= -32.004
GIBBS(1,8)= -32.738
GIBBS(1,9)= -33.402
GIBBS(1,10)= -34.012
GIBBS(1,11)= -34.576
GIBBS(1,12)= -35.098
GIBBS(2,1)= -37.221
GIBBS(2,2)= -39.508
GIBBS(2,3)= -41.295
GIBBS(2,4)= -42.768
GIBBS(2,5)= -44.026
GIBBS(2,6)= -45.131
GIBBS(2,7)= -46.120
GIBBS(2,8)= -47.018
GIBBS(2,9)= -47.842
GIBBS(2,10)= -48.605
GIBBS(2,11)= -49.318
GIBBS(2,12)= -49.989
GIBBS(3,1)= -0.5227
GIBBS(3,2)= -0.8245
GIBBS(3,3)= -1.1460
GIBBS(3,4)= -1.4770
GIBBS(3,5)= -1.8100
GIBBS(3,6)= -2.1380
GIBBS(3,7)= -2.4590
GIBBS(3,8)= -2.7710
GIBBS(3,9)= -3.0730
GIBBS(3,10)= -3.3650
GIBBS(3,11)= -3.6470
GIBBS(3,12)= -3.9190
GIBBS(4,1)= -40.391
GIBBS(4,2)= -42.393
GIBBS(4,3)= -43.947
GIBBS(4,4)= -45.222
GIBBS(4,5)= -46.308
GIBBS(4,6)= -47.254
GIBBS(4,7)= -48.097
GIBBS(4,8)= -48.860
GIBBS(4,9)= -49.554
GIBBS(4,10)= -50.196
GIBBS(4,11)= -50.789
GIBBS(4,12)= -51.345
GIBBS(5,1)= -43.601
```

FIGURE 25d

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GIBBS(5,2)= -45.928
GIBBS(5,3)= -47.663
GIBBS(5,4)= -49.239
GIBBS(5,5)= -50.634
GIBBS(5,6)= -51.895
GIBBS(5,7)= -53.047
GIBBS(5,8)= -54.109
GIBBS(5,9)= -55.096
GIBBS(5,10)= -56.018
GIBBS(5,11)= -56.888
GIBBS(5,12)= -57.706
GIBBS(6,1)= -36.510
GIBBS(6,2)= -38.860
GIBBS(6,3)= -40.750
GIBBS(6,4)= -42.390
GIBBS(6,5)= -43.860
GIBBS(6,6)= -45.210
GIBBS(6,7)= -46.470
GIBBS(6,8)= -47.650
GIBBS(6,9)= -48.780
GIBBS(6,10)= -49.860
GIBBS(6,11)= -50.890
GIBBS(6,12)= -51.880
HEAT(1)= 0.0
HEAT(2)= -57.107
HEAT(3)= 0.0
HEAT(4)= -27.2019
HEAT(5)= -93.9686
HEAT(6)= -15.987
R= 1.9872/1000.
XT = T/100.
I1 = XT -3.
IF (I1 -111.1,2
1 I1 = 1
GO TO 4
2 IF (I1 - 10) 4,3,3
3 I1 = 9
4 CONTINUE
I4 = I1 +3
DO 8 N=1,6
FREE(N)= 0.0
DO 7 L=I1,I4
PROD= 1.0
DO 6 J=I1,I4
IF (J-L) 5,6,5
5 PROD = PROD*(T -X(J))/(X(L) -X(J))
6 CONTINUE
FREE(N) =FREE(N) +PROD*GIBBS(N,L)
7 CONTINUE
FREE(N) = FREE(N)/1000.
8 CONTINUE
DGOT=2.*FREE(2) +2.*HEAT(2)/T +FREE(3) -(FREE(5) +HEAT(5)/T
1 +2.*FREE(1))
K1 = EXP(-DGOT/R)
DGOT= FREE(5) +HEAT(5)/T +FREE(3) -(2.*FREE(4) +2.*HEAT(4)/T)
K2= EXP(-DGOT/R)
DGOT= FREE(6) +HEAT(6)/T -(FREE(3) +2.*FREE(1))
K3= EXP(-DGOT/R)
RETURN

```

FIGURE 25e

PAGE 5

END

VARIABLE ALLOCATIONS

GIRRS(R)=008E-0000	HEAT(R)=009A-0090	FREE(R)=00A6-009C	X(R)=00BE-00A8	XI(R)=00C0	R(R)=00C2
XT(R)=00C4	PROD(R)=00C6	DGOT(R)=00C8	I(I)=00D0	I(I)=00D1	I4(I)=00D2
N(I)=00D3	L(I)=00D4	J(I)=00D5			

STATEMENT ALLOCATIONS

100 =01BD 1	=03FF 2	=0405 3	=040B 4	=040F 5	=0434 6	=0450 7	=046F 8	=0480
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FEATURES SUPPORTED

ONE WORD INTEGERS

CALLED SUBPROGRAMS

FEXP	FADD	FADDX	FSUB	FSUBX	FMPY	FMPYX	FDIV	FLD	FLDX	FSTC	FSTOX	FSBR	FDVR	IFIX
FLOAT	SUBSC	SNR	SUBIN											

REAL CONSTANTS

.200000E 03=00F6	.244650E 02=00E8	.264220E 02=00FA	.279500E 02=00EC	.292030E 02=00EE	.302650E 02=00F0
.311860E 02=00F2	.320040E 02=00F4	.327380E 02=00F6	.334020E 02=00F8	.340120E 02=00FA	.345760E 02=00FC
.350980E 02=00FE	.372210E 02=0100	.395080E 02=0102	.412950E 02=0104	.427680E 02=0106	.440260E 02=0108
.451310E 02=010A	.461200E 02=010C	.470180E 02=010E	.478420E 02=0110	.486050E 02=0112	.493180E 02=0114
.499890E 02=0116	.522700E 00=0118	.524500E 00=011A	.514600E 01=011C	.5147700E 01=011E	.5181000E 01=0120
.213800E 01=0122	.245900E 01=0124	.277100E 01=0126	.307300E 01=0128	.336500E 01=012A	.364700E 01=012C
.391900E 01=012E	.403910E 02=0130	.423930E 02=0132	.439470E 02=0134	.452220E 02=0136	.463080E 02=0138
.472540E 02=013A	.480970E 02=013C	.488600E 02=013E	.495540E 02=0140	.501960E 02=0142	.507690E 02=0144
.513450E 02=0146	.436010E 02=0148	.458280E 02=014A	.476630E 02=014C	.492390E 02=014E	.506340E 02=0150
.518950E 02=0152	.530470E 02=0154	.541090E 02=0156	.550960E 02=0158	.560180E 02=015A	.568680E 02=015C
.577060E 02=015E	.365100E 02=0160	.388600E 02=0162	.407500E 02=0164	.423900E 02=0166	.438000E 02=0168
.452100E 02=016A	.464700E 02=016C	.476500E 02=016E	.487800E 02=0170	.498600E 02=0172	.508900E 02=0174
.518800E 02=0176	.000000E 00=0178	.571070E 02=017A	.272019E 02=017C	.939686E 02=017E	.159670E 02=0180
.198720E 01=0182	.100000E 04=0184	.100000E 03=0186	.300000E 01=0188	.100000E 01=018A	.200000E 01=018C

INTEGER CONSTANTS

1=018E	12=018F	100=0190	10=0191	9=0192	3=0193	6=0194
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CORE REQUIREMENTS FOR EQCON

COMMON 0 VARIABLES 230 PROGRAM 1070

RELATIVE ENTRY POINT ADDRESS IS 0195 (HEX)

END OF COMPILATION

FIGURE 25f

PAGE 1

// JOB

LOG DRIVE	CART SPEC	CART AVAIL	PHY DRIVE
0000	03CF	03CE	0000

V2 M08 ACTUAL BK CONFIG 8K

// FOR

*LIST ALL

*ONE WORD INTEGERS

SUBROUTINE PLOD(N0,A,N,M,NL,NS)

DIMENSION OUT(101),YPR(11),ANG(9),A(1)

DATA BLANK/' ',ANG/'1','2','3','4','5','6','7','8','9'/

MX=3

MY=4

1 FORMAT (///,60X,7H CHART ,I3//)

2 FORMAT (1X,F11.4,5X,101A1)

3 FORMAT (2X)

5 FORMAT(10A1)

7 FORMAT(16X, 100H.)

8 FORMAT (///,9X,11F10.4)

NLL=NL

IF(NS) 16, 16, 10

10 DO 15 I=1,N

DO 14 J=I,N

IF(A(I)-A(J)) 14, 14, 11

11 L=I-N

LL=J-N

DO 12 K=1,M

L=L+N

LL=LL+N

F=A(L)

A(L)=A(LL)

12 A(LL)=F

14 CONTINUE

15 CONTINUE

16 IF(NLL) 20, 18, 20

18 NLL=50

20 WRITE(MX,1)NO

XSCAL=(A(N)-A(1))/(FLOAT(NLL-1))

M1=N+1

M2=M*N

YMIN=A(M1)

YMAX=YMIN

DO 40 J=M1,M2

IF(A(J)-YMIN) 28,26,26

26 IF(A(J)-YMAX) 40,40,30

28 YMIN=A(J)

GO TO 40

30 YMAX=A(J)

40 CONTINUE

YSCAL=(YMAX-YMIN)/100.0

XB=A(1)

L = 1

MX = M-1

I=1

45 F=1-1

XPR=A(1)

FIGURE 25g

PAGE 2

```

      IF(A(L)-XPR) 50,50,70
50 DO 55 IX=1,101
55 OUT(IX)=BLANK
      DO 60 J=1,MYX
      LL=L+J*N
      JP=((A(LL)-YMIN)/YSCAL)+1.0
      OUT(JP)=ANG(J)
60 CONTINUE
      WRITE(MX,2) XPR,(OUT(IZ),IZ=1,101)
      L = L + 1
      GO TO 80
70 WRITE(MX,3)
80 I=I+1
      IF(I-NLL)45,84,86
84 XPR=A(N)
      GO TO 50
86 WRITE(MX,7)
      YPR(1)=YMIN
      DO 90 KN=1,9
90 YPR(KN+1)=YPR(KN)+YSCAL*10.0
      YPR(11)=YMAX
      WRITE(MX,8)(YPR(IP),IP=1,11)
      RETURN
      END

```

VARIABLE ALLOCATIONS

OUT(R) =00C8-00D0	YPR(R) =00DE-00CA	ANG(R) =00F0-00E0	F(R) =00F2	XSCAL(R) =00F4	YMIN(R) =00F6
YMAX(R) =00F8	YSCAL(R) =00FA	XP(R) =00FC	XP(R) =00FE	BLANK(R) =0100	MX(I) =0106
MY(I) =0107	NLL(I) =0108	I(I) =0109	J(I) =010A	L(I) =010B	LL(I) =010C
K(I) =010D	V(I) =010E	M(I) =010F	MYX(I) =0110	IX(I) =0111	JP(I) =0112
IZ(I) =0113	KN(I) =0114	IP(I) =0115			

UNREFERENCED STATEMENTS

5

STATEMENT ALLOCATIONS

1	=0127	2	=0134	3	=013A	5	=013C	7	=013F	8	=0174	10	=0186	11	=01D3	12	=0203	14	=0212
15	=021R	16	=0224	18	=0228	20	=022C	26	=0276	28	=0284	30	=028F	40	=0298	45	=02BD	50	=02D9
55	=02DD	60	=031C	70	=0346	80	=034A	84	=0358	86	=0363	90	=0371						

FEATURES SUPPORTED

ONE WORD INTEGERS

CALLED SUBPROGRAMS

FADD	FADDX	FSUR	FSURX	FMPI	FDIV	FLD	FLDX	FSTO	FSTOX	FDVR	IFIX	FLOAT	SWRT	SCOMP
SIOFX	SIOF	SIOI	SURSC	SUBIN										

REAL CONSTANTS

.100000E 03=011A .100000E 01=011C .100000E 02=011E

INTEGER CONSTANTS

3=0120 4=0121 1=0122 50=0123 101=0124 9=0125 11=0126

CORE REQUIREMENTS FOR PLOD

COMMON 0 VARIABLES 282 PROGRAM 660

RELATIVE ENTRY POINT ADDRESS IS 017A (HEX)

END OF COMPILE

FIGURE 25h

EQUILIBRIUM VOLUME FRACTIONS -- RICHARD FREEDMAN

TEMPERATURE = 873.00 DEGK		PRESSURE = 1.05000 ATM.			
O/H RATIO	X(CO ₂)	X(H ₂)	X(H ₂ O)	X(CO)	X(CH ₄)
0.100E 00	0.247E-01	0.615E 00	0.126E 00	0.472E-01	0.186E 00
0.125E 00	0.353E-01	0.591E 00	0.144E 00	0.564E-01	0.172E 00
0.158E 00	0.495E-01	0.563E 00	0.163E 00	0.668E-01	0.156E 00
0.199E 00	0.681E-01	0.532E 00	0.181E 00	0.784E-01	0.139E 00
0.251E 00	0.918E-01	0.498E 00	0.196E 00	0.910E-01	0.122E 00
0.316E 00	0.121E 00	0.460E 00	0.209E 00	0.104E 00	0.104E 00
0.398E 00	0.155E 00	0.421E 00	0.216E 00	0.118E 00	0.873E-01
0.501E 00	0.195E 00	0.380E 00	0.219E 00	0.132E 00	0.711E-01
0.630E 00	0.240E 00	0.339E 00	0.216E 00	0.147E 00	0.565E-01
0.794E 00	0.287E 00	0.298E 00	0.208E 00	0.161E 00	0.438E-01
0.100E 01	0.336E 00	0.259E 00	0.196E 00	0.174E 00	0.331E-01
0.125E 01	0.385E 00	0.222E 00	0.180E 00	0.186E 00	0.244E-01
0.158E 01	0.433E 00	0.189E 00	0.162E 00	0.197E 00	0.176E-01
0.199E 01	0.477E 00	0.159E 00	0.143E 00	0.207E 00	0.124E-01
0.251E 01	0.518E 00	0.132E 00	0.124E 00	0.216E 00	0.863E-02
0.316E 01	0.554E 00	0.109E 00	0.106E 00	0.223E 00	0.589E-02
0.398E 01	0.586E 00	0.898E-01	0.897E-01	0.230E 00	0.396E-02
0.501E 01	0.613E 00	0.732E-01	0.748E-01	0.235E 00	0.264E-02
0.630E 01	0.637E 00	0.594E-01	0.619E-01	0.239E 00	0.173E-02
0.794E 01	0.656E 00	0.480E-01	0.508E-01	0.243E 00	0.113E-02
0.999E 01	0.672E 00	0.387E-01	0.441E-01	0.246E 00	0.738E-03

FIGURE 26a

TEMPERATURE = 873.00 DEGR PRESSURE = 1.05000 ATM.
O/H RATIO X(CO2)=1 X(H2)=2 X(H2O)=3 X(CO)=4 X(CH4)=5

CHART 4

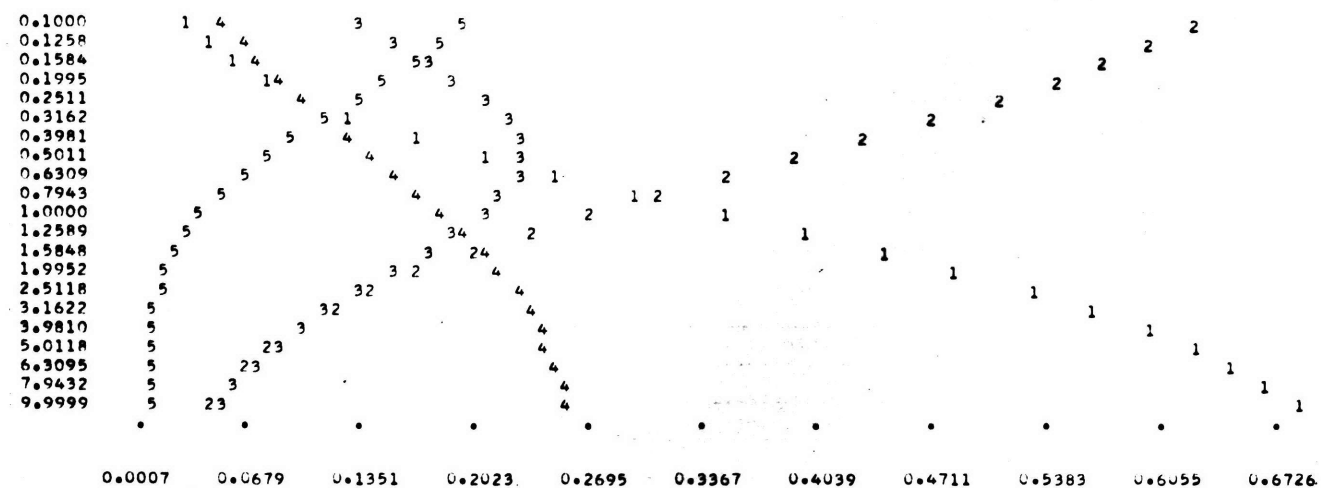


FIGURE 26b

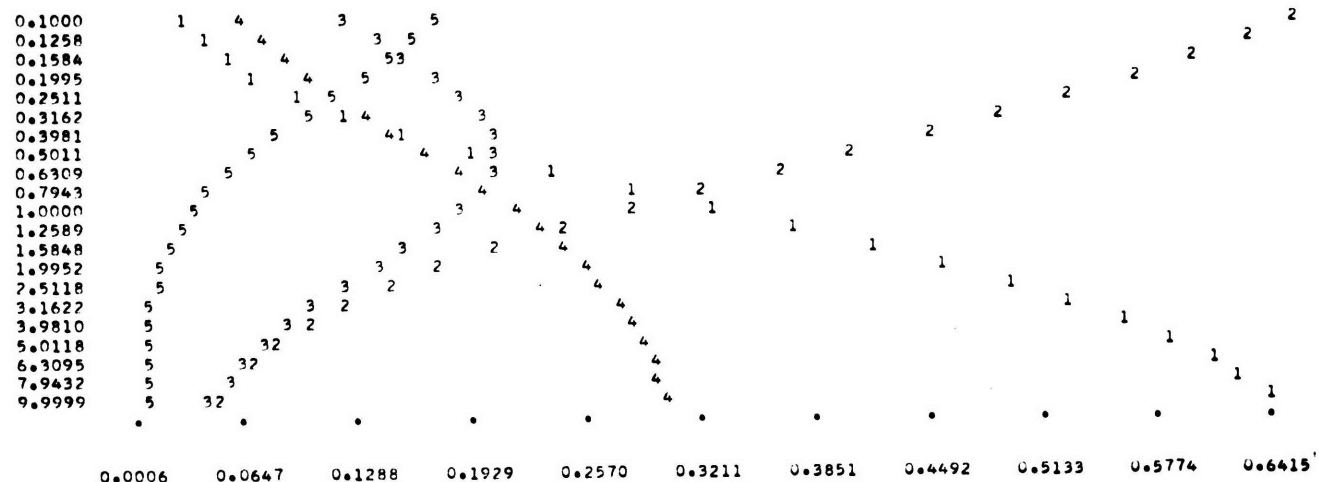
EQUILIBRIUM VOLUME FRACTIONS -- RICHARD FREEDMAN

TEMPERATURE = 888.00 DEGR		PRESSURE = 1.05000 ATM.			
O/H RATIO	X(CO2)	X(H2)	X(H2O)	X(CO)	X(CH4)
0.100E 00	0.234E-01	0.641E 00	0.114E 00	0.561E-01	0.164E 00
0.125E 00	0.334E-01	0.616E 00	0.130E 00	0.670E-01	0.152E 00
0.158E 00	0.464E-01	0.587E 00	0.147E 00	0.793E-01	0.138E 00
0.199E 00	0.643E-01	0.555E 00	0.163E 00	0.930E-01	0.123E 00
0.251E 00	0.866E-01	0.519E 00	0.177E 00	0.107E 00	0.108E 00
0.316E 00	0.114E 00	0.480E 00	0.188E 00	0.123E 00	0.926E-01
0.398E 00	0.146E 00	0.439E 00	0.195E 00	0.140E 00	0.774E-01
0.501E 00	0.184E 00	0.397E 00	0.197E 00	0.157E 00	0.632E-01
0.630E 00	0.225E 00	0.354E 00	0.195E 00	0.174E 00	0.502E-01
0.794E 00	0.269E 00	0.312E 00	0.188E 00	0.190E 00	0.390E-01
0.100E 01	0.315E 00	0.271E 00	0.177E 00	0.206E 00	0.294E-01
0.125E 01	0.361E 00	0.233E 00	0.162E 00	0.220E 00	0.217E-01
0.158E 01	0.405E 00	0.198E 00	0.146E 00	0.233E 00	0.157E-01
0.199E 01	0.447E 00	0.166E 00	0.129E 00	0.245E 00	0.111E-01
0.251E 01	0.485E 00	0.138E 00	0.112E 00	0.255E 00	0.771E-02
0.316E 01	0.519E 00	0.114E 00	0.960E-01	0.264E 00	0.526E-02
0.398E 01	0.549E 00	0.941E-01	0.810E-01	0.271E 00	0.355E-02
0.501E 01	0.574E 00	0.768E-01	0.676E-01	0.278E 00	0.236E-02
0.630E 01	0.596E 00	0.623E-01	0.559E-01	0.283E 00	0.155E-02
0.794E 01	0.614E 00	0.504E-01	0.459E-01	0.287E 00	0.101E-02
0.999E 01	0.630E 00	0.406E-01	0.374E-01	0.291E 00	0.661E-03

FIGURE 27a

TEMPERATURE = 888.00 DEGR PRESSURE = 1.05000 ATM
O/H RATIO X(CO2)=1 X(H2)=2 X(H2O)=3 X(CO)=4 X(CH4)=5

CHART 1



// *ENDJOB

FIGURE 27b

EQUILIBRIUM VOLUME FRACTIONS -- RICHARD FREEDMAN

TEMPERATURE = 903.00 DEGR		PRESSURE = 1.05000 ATM.			
O/H RATIO	X(CO2)	X(H2)	X(H2O)	X(CO)	X(CH4)
0.100F 00	0.218E-01	0.665E 00	0.102E 00	0.657E-01	0.145E 00
0.125F 00	0.311E-01	0.639E 00	0.117E 00	0.785E-01	0.134E 00
0.158E 00	0.436E-01	0.609E 00	0.132E 00	0.929E-01	0.121E 00
0.199F 00	0.599E-01	0.575E 00	0.146E 00	0.108E 00	0.108E 00
0.251F 00	0.805E-01	0.538E 00	0.158E 00	0.126E 00	0.952E-01
0.316F 00	0.105E 00	0.498E 00	0.168E 00	0.144E 00	0.816E-01
0.398F 00	0.136E 00	0.456E 00	0.174E 00	0.164E 00	0.683E-01
0.501E 00	0.170E 00	0.412E 00	0.176E 00	0.183E 00	0.557E-01
0.630E 00	0.209E 00	0.367E 00	0.174E 00	0.203E 00	0.444E-01
0.794E 00	0.250E 00	0.324E 00	0.168E 00	0.222E 00	0.344E-01
0.100E 01	0.297E 00	0.281E 00	0.158E 00	0.240E 00	0.260E-01
0.125F 01	0.335E 00	0.242E 00	0.145E 00	0.257E 00	0.192E-01
0.158E 01	0.376E 00	0.205E 00	0.131E 00	0.272E 00	0.139E-01
0.199E 01	0.414E 00	0.173E 00	0.115E 00	0.286E 00	0.984E-02
0.251F 01	0.449E 00	0.144E 00	0.100E 00	0.298E 00	0.683E-02
0.316F 01	0.481E 00	0.119E 00	0.859E-01	0.308E 00	0.467E-02
0.398F 01	0.508E 00	0.979E-01	0.725E-01	0.317E 00	0.314E-02
0.501E 01	0.532F 00	0.799E-01	0.605E-01	0.324E 00	0.209E-02
0.630E 01	0.552E 00	0.649E-01	0.500E-01	0.330E 00	0.138E-02
0.794F 01	0.569E 00	0.525E-01	0.411E-01	0.335E 00	0.904E-03
0.999E 01	0.583E 00	0.423E-01	0.335E-01	0.339E 00	0.587E-03

FIGURE 28a

TEMPERATURE = 903.00 DEGR PRESSURE = 1.05000 ATM.
O/H RATIO X(CO2)=1 X(H2)=2 X(H2O)=3 X(CO)=4 X(CH4)=5

CHART 1

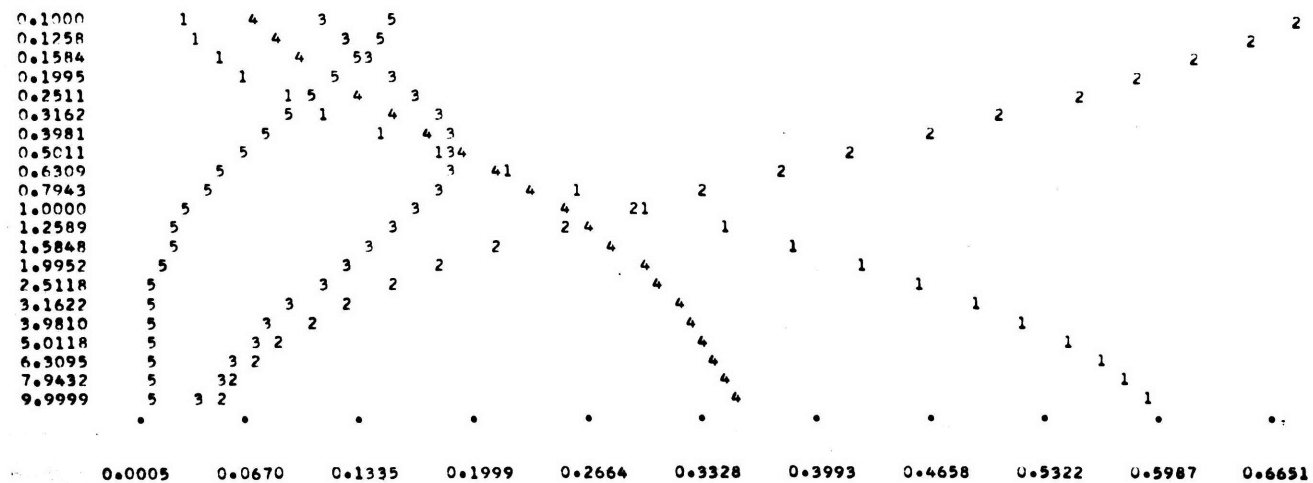
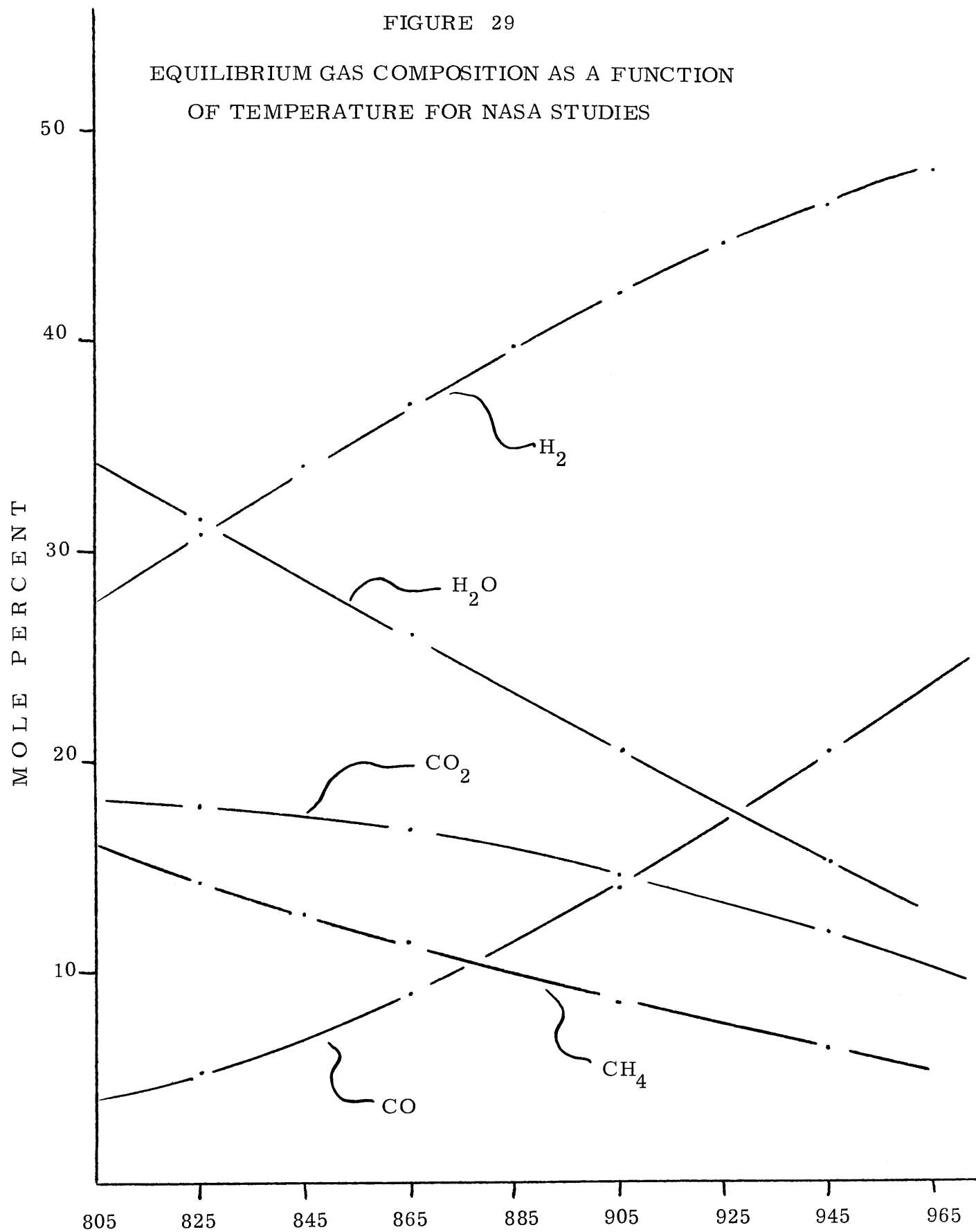


FIGURE 28b

FIGURE 29

EQUILIBRIUM GAS COMPOSITION AS A FUNCTION
OF TEMPERATURE FOR NASA STUDIES



E. Data Compilation and Sample Calculations

1. Experimental Data Compilation

- (A) $\text{CO}_2 + \text{H}_2$ over Fe at 525°C, 1 atm.
- (B) $\text{CO}_2 + \text{H}_2$ over Fe at 600°C, 1 atm.
- (C) $\text{CO}_2 + \text{H}_2$ over Fe at 620°C, 1 atm.
- (D) $\text{CO}_2 + \text{H}_2$ over Fe at 625°C, 1 atm.
- (E) $\text{CO}_2 + \text{H}_2$ over Fe at 725°C, 1 atm.
- (F) $\text{CO}_2 + \text{H}_2 + \text{CO}$ over Fe at 610°C, 1 atm.
- (G) $\text{CO}_2 + \text{CO} + \text{He}$ over Fe at 610°C, 1 atm.
- (H) $\text{CO} + \text{H}_2 + \text{He}$ over Fe at 610°C, 1 atm.
- (I) $\text{CO} + \text{He}$ over carbon at 615°C, 1 atm.
- (J) $\text{CO} + \text{H}_2 + \text{He}$ over carbon at 615°C, 1 atm.

A summary of the experimental conditions for each run is listed above.

2. Sample Calculations

a. Rate of Carbon Deposition

--Calculate exit flow rate from oxygen balance

$$\left(\frac{50 \text{ cc}}{\text{min.}} \right) (2 \text{ CO}_2 + \text{CO} + \text{H}_2\text{O}) = \frac{\text{X}_{\text{cc}}}{\text{min.}} (2 \text{ CO}_2 + \text{CO} + \text{H}_2\text{O})_{\text{Exit}}$$

$$\left(\frac{50 \text{ cc}}{\text{min.}} \right) (2 \times 14.19 + 41.7 + .47) = \frac{\text{X}_{\text{cc}}}{\text{min.}} (2 \times 19.48 + 30.65 + 2.53)$$

$$\frac{\text{X}_{\text{cc}}}{\text{min.}} = \left(\frac{50 \text{ cc}}{\text{min.}} \right) \frac{70.55}{72.14}$$

$$\frac{X_{cc}}{\text{min.}} = 48.9$$

--Carbon balance

$$\frac{50_{cc}}{\text{min.}} (\text{CO}_2 + \text{CO} + \text{CH}_4)_{\text{inlet}} = \frac{48.9_{cc}}{\text{min.}} (\text{CO}_2 + \text{CO} + \text{CH}_4)_{\text{out}} = \text{rate of carbon deposition}$$

$$\frac{50_{cc}}{\text{min.}} (.18 + .345 + .20) = \frac{48.9_{cc}}{\text{min.}} (.193 + .315 + .205) = \text{rate of carbon deposition}$$

$$\frac{36.0_{cc}}{\text{min.}} - \frac{34.86_{cc}}{\text{min.}} = \text{rate of carbon deposition}$$

$$\frac{1.14_{cc}}{\text{min.}} \times \left(\frac{1 \text{ mole}}{22400_{cc}} \right) \times \frac{12g}{\text{mole}} = 6.1 \times 10^{-4} \frac{g}{\text{min.}}$$

b. Surface Area of Ribbon-Like Carbon

Assuming the ribbon to be $1000\text{\AA}$ wide and $125\text{\AA}$ thick the volume of the filament can be calculated.

$$V = L \times 1.25 \times 10^{-6} \times 10^3 \times 10^{-8} \text{ cm}^3$$

$$V = 1.25 \times 10^{-1} \times L \text{ cm}^3$$

Assuming a sample of 1g, having a density of $1g/cc^3$, the equivalent length can be calculated.

$$V \times P = \text{Mass}$$

$$V = 1 = 1.25 \times 10^{-11} \times L$$

$$L = 8 \times 10^{10} \text{ cm}$$

$$\text{Area} = 8 \times 10^{10} \times 10^3 \times 10^{-8} \times 2 \text{ cm}^2$$

$$\text{Area} = 160 \frac{\text{m}^2}{g}$$

COMPOSITION (%)

Experiment	<u>In</u>					<u>Out</u>				
	H ₂	CO	CO ₂	CH ₄	H ₂ O	H ₂	CO	CO ₂	CH ₄	H ₂ O
(A)	~55	.005	45.5	0.0	0.0	*	0.5	42.6	0.0	—
(B)	~55	.005	43.8	0.0	0.0	*	2.56	39.8	0.0	—
(C)	~66.0	.005	35.0	0.0	0.0	*	2.85	33.3	0.0	—
(D)	~62.0	.005	41.0	0.0	0.0	*	2.87	35.8	0.0	—
(E)	~55	.005	44.0	0.0	0.0	*	5.57	36.8	0.0	—
(F)	~49.0	27.6	21.7	0.0	0.0	*	26.4	21.0	0.0	—
(G)	0.0	22.3	21.7	0.0	0.0	*	22.3	21.7	0.0	—
(H)	~53.0	22.3	0.0	0.0	0.0	*	13.2	2.5	0.0	—
(I)	~ 0.0	35.8	0.0	0.0	0.0	*	29.9	3.6	0.0	—
(J)	~40.0	35.8	0.0	0.0	0.0	*	18.3	8.6	0.0	—

— did not measure

* calculated by difference

GAS COMPOSITIONS OVER Fe ROD AS A FUNCTION OF TIME

	<u>Inlet</u>	<u>Exit</u>							
CO	41.7	39.18	34.59	32.28	30.65	29.42	29.00	28.49	28.00
CH ₄	21.13	20.87	21.50	21.70	21.36	21.23	21.36	21.22	21.31
CO ₂	14.19	14.37	17.39	18.30	19.43	20.01	20.27	20.37	20.43
H ₂ O	.47	1.72	2.05	2.45	2.53	2.63	2.67	2.89	3.04
H ₂	22.51	22.51	21.01	20.25	20.51	20.59	20.40	20.55	20.60
O balance	70.55	69.64	71.42	71.33	72.04	72.07	72.21	72.12	71.9
H balance	130.88	131.94	132.12	132.2	131.52	131.36	131.58	131.76	132.52

GAS COMPOSITION OVER CARBON II AS A FUNCTION OF TIME

	<u>Inlet</u>	<u>Exit</u>					
CO	41.7	34.45	32.42	31.52	33.33	34.23	35.58
CH ₄	19.98	22.83	22.93	23.27	22.39	23.71	22.83
CO ₂	13.53	16.54	18.95	19.09	18.08	17.31	16.80
H ₂ O	.47	2.17	2.76	2.20	2.06	2.07	2.06
H ₂	~24.5	*	*	*	*	*	*

* Calculated from difference

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