AN INVESTIGATION OF THE BOSCH PROCESS

by

Michael Patrick Manning

B.S., University of Notre Dame du Lac (1967)

Submitted in Partial Fulfillment
of the Requirements for the
Degree of Doctor of Science

at the

Massachusetts Institute of Technology

January 1976

Signature of Author: Signature redacted
Department of Chemical Engineering

Certified by: Signature redacted
Thesis Supervisor

Accepted by: Signature redacted
Chairman,
Departmental Committee on Graduate Theses

Thesis
Chowning
[illegible]
[illegible]

AN INVESTIGATION OF THE BOSCH PROCESS

by

Michael Patrick Manning

Submitted to the Department of Chemical Engineering in Partial
Fulfillment of the Requirements for the Degree of Doctor of Science

ABSTRACT

The Bosch process for reduction of metabolic carbon dioxide with hydrogen has been proposed as the basis for a life support system for long-range space flights. Operating recycle reactors to accomplish the process have been built, but little is known concerning the kinetic rates of the constituent reactions in the process. A thermogravimetric reactor was devised to operate with various feed gas mixtures. Chromatographic analysis of the inlet and outlet gas concentrations and gravimetric measurements of the amount of carbon deposited on a steel wool catalyst allowed evaluation of the reactions involved in the process. The rate of carbon deposition from H_2-CO gas mixtures on fresh, reduced steel wool catalyst was correlated by a least-squares technique. The process of carbon deposition appears to increase the catalyst surface area causing an increase in the observed rate of the carbon deposition reaction(s) and the reverse water-gas shift reaction. As the catalyst surface area was not measured during the course of reaction, rate equations for other component reactions could not be determined. The relative rates of several reactions in the process are discussed. Carbon did not deposit from CO-CO_2 mixtures where the CO/CO_2 ratio was in the range required for formation of iron oxide. This is consistent with the hypothesis of other authors that carbon deposition will not occur on an oxide surface. Process equilibrium and material balance calculations for several alternative flowsheets have been performed and are discussed.

Thesis Supervisor: Dr. R.C. Reid, Professor of Chemical Engineering

ACKNOWLEDGMENTS

This project was supported by a research grant from the National Aeronautics and Space Administration. The assistance of Dr. Philip D. Quattrone, NASA Technical Officer, is gratefully acknowledged. The cooperation of Mr. Robert DiGiaccomo of the Chemistry Department in fabricating and repairing parts of the quartz reactor was most helpful and timely. Paul Bletzer, Reed Fulton, Arthur Clifford, and Charles Foshey provided guidance in the fabrication of many other pieces of the experimental apparatus. Stan Mitchell provided parts, assistance, advice, and a kind word when they were needed most. Ken Hellyar contributed more than one half the effort required to take the multitude of experimental readings on which this thesis is based. His assistance and friendship were invaluable. Alice Maxwell typed the thesis and provided incentive for this "lollygagging MIT student."

Dr. Maurice R. Everett of the Atomic Energy Establishment, Winfrith, and Mr. T.J. Gibbons of the American Steel Wool Company very courteously replied to my correspondence and forwarded additional information when requested. My parents and Dr. J.T. Banchero were responsible for my initial interest in a graduate degree. Their original impressions were reinforced by three years with the United States Navy which provided no technical development but an invaluable education. A particular word of thanks is due the MIT Chemical Engineering graduate students especially Bill Siflett, Fred Tompkins, Jerry Mayer, Sanjay Amin, Bill Porteous, and the "veterans" from the Fuels Lab, who helped to keep my education in context. However, my accomplishments in this endeavor are due mainly to the patient guidance and enthusiastic inspiration of Dr. Robert C. Reid and the moral support of my wife, Susan.

Department of Chemical Engineering
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139
January 29, 1976

Professor Irving Kaplan
Secretary of the Faculty
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Dear Professor Kaplan:

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

Respectfully submitted,
Signature redacted
Michael P. Manning

Table of Contents

Table of Contents (continued)

Page

Table of Contents (continued)

Figures

Figures (continued)

Figures (continued)

Tables

1. SUMMARY

The Bosch process, a potential process for the reduction of metabolic carbon dioxide to water, utilizes a catalytic recycle reactor as shown in Fig. 1 to achieve the overall reaction

$$2H_2 + CO_2 \rightarrow C + 2H_2O \tag{A}$$

Subsequent electrolysis completes the overall process

$$\begin{array}{rcl} 2H_2 + CO_2 & \rightarrow & C + 2H_2O \\ 2H_2O & \rightarrow & 2H_2 + O_2 \\ \hline CO_2 & \rightarrow & C + O_2 \end{array}$$

upon which oxygen recovery for astronaut life support systems is based. While reaction (A) represents the overall stoichiometry of the process accomplished in a Bosch recycle reactor, reaction (A) is neither a mechanism step nor a constituent reaction of the overall process. Indeed, the recycle stream has been determined to contain both carbon monoxide and methane, neither of which are components in reaction (A). This investigation was undertaken to determine the component reactions which occur in the Bosch process.

1.1 Previous Investigations

Since solid carbon is one of the products of the Bosch process and since the gas recycle stream of Bosch process reactors has been observed to contain hydrogen, carbon monoxide, carbon dioxide, methane, and water, thermodynamic calculation of the yields achievable in a Bosch reactor has been performed by considering the equilibrium of β-graphite with a gas phase containing these five components. The solution of this computational problem has been discussed by Tevebaugh and Cairns (1964), who presented their results graphically on triangular C-H-O diagrams such as that shown in Fig. 3. The two solid lines in Fig. 3 represent the carbon deposition boundaries at atmospheric pressure and at 811 and 922 K. Any gas phase mixture with a C-H-O composition represented by a point in the region marked carbon-forming will deposit carbon in proceeding to its final equilibrium state.

Under conditions similar to those existing in a Bosch reactor, authors have previously reported observing several reactions. Kusner (1962) investigated the reverse water-gas shift, reaction (B), in a single-pass reactor.

$$H_2 + CO_2 \rightarrow CO + H_2O \qquad \text{(B)}$$

The observed reaction rate was found to be rapid and limited by mass transfer of the reactants from the bulk gas phase to the catalyst surface at 922 K. Under almost identical feed and flow conditions, Barkley _et_ _al_. (1952) found the observed reaction rate at 811 K was controlled by the kinetic reaction rate at the catalyst surface. Neither carbon nor methane were formed.

Walker _et_ _al_. (1959) studied the deposition of carbon from H_2/CO mixtures on an iron powder catalyst in the temperature range 723 - 973 K. Feed mixtures were rich in CO, and the CO/H_2 ratio was varied from 4.2 to 124. At low concentration, hydrogen increased the rate of carbon deposition significantly. However, the carbon source could have been either reaction (C) or reaction (D).

$$2CO \rightarrow C + CO_2 \qquad \text{(C)}$$

$$CO + H_2 \rightarrow C + H_2O \qquad \text{(D)}$$

Examination of the reaction products, after catalytic activity had ceased, revealed that the iron had been converted to cementite (iron carbide, Fe_3C). Hence, Walker et al. suggested that iron, but not iron carbide, is a catalyst for carbon deposition from H_2/CO mixtures. Similar observations had been made by Chatterjee and Das (1954) and Das and Chatterjee (1952, 1955).

Ruston et al. (1966, 1969) examined the metallurgical processes occurring on polycrystalline iron and steel surfaces exposed to various partial pressures of carbon monoxide at 823 K. Four forms of solid phase products were observed: cementite, fibrous carbon, lamellar carbon, and small crystallites. Cementite crystals at the surface decomposed to disrupt the iron surface and to produce lamellar carbon. During this surface disruption, the small crystallites are freed from the metal matrix and form the catalytic growth centers for the fibrous carbon. Although Ruston reported that the small crystallites were identified by x-ray diffraction as Fe_7C_3, this conclusion has been disputed by Renshaw et al. (1970) and Ratliff (1968), who indicated that other carbides could yield similar results.

Carbon deposition from an argon stream containing traces of CO and H_2 was reported by Everett (1967) and Everett and Kinsey (1965) to be first order in carbon monoxide partial pressure. The same data have been shown in this investigation to be consistent with a rate expression which is half order in both carbon monoxide and hydrogen partial pressures. The results of this thesis also indicate that the rate of carbon deposition is approximately half order in both component partial pressures. A more important proposal, advanced by Everett and Kinsey, was that two conditions must be met for carbon deposition to occur on an iron catalyst. The first condition was that the C-H_2-CO-CH_4-CO_2-H_2O equilibria must favor carbon formation (i.e., the gas mixture C-H-O composition should be in the carbon-forming region of the triangular diagram). The second condition was that the ratio of H_2/H_2O in the gas phase must be such that the reaction

$$4H_2 + Fe_3O_4 \rightarrow 4H_2O + 3Fe \text{ (below 850 K)}$$

or

$$H_2 + FeO \rightarrow H_2O + Fe \text{ (above 850 K)}$$

would proceed as written and that the stable state of the iron catalyst would be reduced iron. Thus, Everett and Kinsey proposed that carbon formation could be prevented by adjusting the ratio of H_2/H_2O in the gas phase so as to maintain a surface oxide layer on the catalyst. This hypothesis was tested by Warzee _et_ _al_. (1967), who demonstrated that various steel alloys would not act as catalysts for carbon deposition when exposed to gas mixtures forming surface oxide films of the alloying elements.

1.2 Iron Carbides and Carbon Fibers

The role of iron carbides in the carbon deposition process is not well understood. However, the bulk of available evidence indicates that they are a reaction product rather than a catalyst. Three iron carbides have been reported. Cementite, Fe_3C, is the only carbide which appears in the accepted iron-carbon phase diagrams which have been reviewed critically by Hansen (1958), Elliott (1965), and Shunk (1969). Walker _et_ _al_. (1959) and Podgurski _et_ _al_. (1950) have reported that this carbide is observed as a reaction product when the activity of an initially-reduced iron catalyst has ceased. Moreover, Podgurski _et_ _al_. (1950) demonstrated that iron carbide would not chemisorb carbon monoxide and thus concluded that it could not function as a catalyst for carbon deposition. Walker _et_ _al_. (1959) and Browning _et_ _al_. (1950) have demonstrated that cementite is rapidly reduced by hydrogen at temperatures above 573 K to produce methane. Hence, this carbide may be an intermediate in methane formation. The equilibrium constant for the reduction of iron carbide by hydrogen was measured by Browning et al. (1950).

Hägg carbide, originally reported by Hägg in 1932 to be Fe_2C, was later shown to be Fe_5C_2 by Jack (1946), Duggin and Hofer (1966) and Jack and Wild (1966). Two variations of Hägg carbide were identified by the magnetic measurements of Hofer, Cohn and Peebles (1949). Both variations decomposed to give cementite and carbon at temperatures above 773 K.

A third carbide, originally termed FeC, has been reported by Eckstrom and Adcock (1950) and later confirmed by Louw et al. (1957) and Kohn and Eckart (1962). All three occurrences of this carbide were noted in pressurized (>20 atm) reactors. Herbstein and Snyman (1964) determined on the basis of x-ray diffraction measurements that the carbide was actually Fe_7C_3.

Examination of the carbon product from Bosch recycle reactors has revealed that much of the carbon appears as fibers. Similar fibers have been observed in carbon deposits on such metals as iron, cobalt, nickel, and chromium exposed to a variety of gaseous carbon forming materials including carbon monoxide, acetone, methane, butane, benzene, and acetylene. The first direct observation of carbon fiber growth was accomplished by Baker and Harris (1972) through development of controlled atmosphere electron microscopy. This technique allowed direct observation of the growth of carbon fibers from nickel crystallites under controlled partial pressures of acetylene. Movie or videotape filming in conjunction with this technique enabled review and analysis of the time sequence of events to determine single fiber growth rates. Based on the observed sequence of events, Baker et al. (1972) proposed the fiber growth mechanisms shown in Fig. 19.

In (a) a crystallite has been liberated from the support - for iron this could be by the mechanism proposed by Ruston et al. (1969). Gas phase components such as methane, acetylene, carbon monoxide are then free to react and deposit carbon on the crystallite. Carbon from the decomposed gases can be taken into solution in the metal. A concentration gradient of carbon results and carbon diffuses through the crystallite to be deposited predominantly in the protected regions to produce the situation shown in (b) and (c). The precipitation of carbon at the rear of the particle builds up a deposit of carbon which forces the particle away from the support as shown in (d). If the diffusion of carbon through the particle is slow enough to limit the rate of the above process, then eventually the surface of the entire crystallite will be covered with carbon and catalytic activity will cease as shown in (e). The shape of the catalytic crystallite and differing diffusion paths lead to the hollow core shown in (d) and (e).

Subsequently, Baker and Waite (1975) reported that carbon filaments also formed on other metals, such as chromium, or in the presence of silicon by a variation of this growth sequence as shown in Fig. 20. In this sequence electron diffraction data indicated phase separation of the alloy constituents occurred at 690 K. As previous work had indicated that iron would produce filaments only above 925 K, the initial decomposition at 690 K was attributed to the catalytic effects of platinum as shown in (b). Carbon deposited on the platinum surface was free to migrate across the surface and to diffuse through the bulk platinum and iron as shown in (c). The resultant observed behavior was the "extrusion" of a carbon filament from a crystallite fixed on the surface as shown in (d). Although these carbon fiber growth sequences were observed in an acetylene atmosphere, the similarity of the final products leads one to conclude that a similar growth mechanism is responsible for producing the observed carbon fibers found in Bosch product carbon.

1.3 Experimental Approach

The experimental apparatus is shown in Fig. 21. Chemically pure or prepurified grade bottled gases were fed from cylinders through individual pressure regulators to a mass flow regulator. The gas flow rate from the mass flow regulator was measured with calibrated capillary flowmeters. The mixed gas stream was subsequently dried over a bed of indicating silica gel or saturated with water in a packed tower. Partial pressures of water up to 0.035 atm were obtained using these methods.

The thermogravimetric reactor consisted of a 2300-W electrical heater with electronic temperature controller, a quartz preheater and reactor, and an analytical balance. Temperature control was regulated by a proportional controller actuated by a chromel-alumel thermocouple located in a thermocouple well in the quartz reactor support tube as shown in Fig. 24. The quartz reactor was a three-part apparatus connected by a ground glass joint as shown in Figs. 24 and 25. Feed gas from the preparation section passed through the 7-mm-OD, 6-m-long quartz preheater to the base of the catalyst support tube, up the support tube, over the catalyst, and out either the exhaust or sample tubes.

The third piece of the reactor was the catalyst carrier section shown in Fig. 25. The catalyst carrier consisting of the outer part of a quartz 19/38 standard taper ground joint and a quartz suspension rod was supported in the reactor by the inner part of the ground joint which had been affixed to the vertical support tube. Thus, when the catalyst carrier rested on its support, all the gas passing up the support tube passed over 250 mg of steel wool catalyst mounted between quartz wool plugs. The quartz suspension rod passed from the top of the catalyst carrier up through the weighing port to an analytical balance; so that when the suspension rod was lifted, the weight of the carrier, catalyst, and deposited carbon product could be determined to within ± 1 mg.

The inlet stream, outlet stream, and a preanalyzed calibration gas mixture were analyzed with a gas chromatograph. A sample valve system controlled the pressure and temperature of the fixed gas volume injected for analysis. A mixed H_2/He carrier gas allowed direct analysis of hydrogen by the method of Purcell and Ettre (1965). All chromatograph peak areas were recorded with an electronic digital integrator.

1.4 Results and Discussion

From the studies of Walker _et al_. (1959) it was expected that the CO mixtures would deposit carbon rapidly. Figure 29 shows the amount of carbon deposited on 250 mg of fresh steel wool catalyst as a function of time for a typical run. The amount of carbon deposited during the early portion of the run is approximately a linear function of time. Over long periods the rate of deposition increases as more carbon is deposited. During the same period the reactor exit gas analysis indicated up to 0.37 mole % water and up to 0.41 mole % carbon dioxide. No determination could be made as to whether the carbon deposition process was a combination of reactions (C) and (D) in parallel or reactions (B) and (D) in series*

$$H_2O + CO \rightarrow CO_2 + H_2 \qquad (B)$$

$$2CO \rightarrow CO_2 + C \qquad (C)$$

---

*Note that reactions shown are not independent, i.e., (C) = (D) + (B).

$$CO + H_2 \rightarrow H_2O + C \qquad (D)$$

To determine whether the initial catalyst condition influenced the carbon deposition rate, 250 mg of fresh steel wool catalyst were oxidized in the reactor using a flowing stream of carbon dioxide at 823 K for one hour. After a 30-min helium purge, a 25% carbon monoxide - 75% hydrogen mixture was passed over the catalyst. The subsequent carbon deposition was an order of magnitude faster than that for the same mixture over an untreated catalyst. Scanning electron photomicrographs of a catalyst surface, after CO_2 oxidation and prior to exposure to the CO/H_2 mixture, indicated that oxidation of the catalyst surface resulted in a roughened porous surface. Hence, it is possible that the oxidized surface increased the carbon deposition rate either by providing higher specific area or by providing a surface which readily forms the crystallites described by Ruston (1966, 1969).

In all other experiments, a stream of dry hydrogen was passed through the reactor and over the fresh steel wool catalyst to prevent catalyst oxidation as the reactor was heated. The results of seven experiments in which a 50% H_2 - 50% CO mixture was passed over the reduced catalyst are shown in Fig. 34. Similar results from nine other experiments for mixtures containing 25, 10, and 5% CO in hydrogen are shown in Fig. 35.

For each set of experimental data shown in Figs. 34 and 35, the rate of carbon deposition was determined graphically from the slope of the initial linear portion of the curves. The resulting values of carbon deposition rate were correlated with hydrogen and carbon monoxide partial pressures using a least-squares technique. The best resulting correlation was:

$$\text{rate (gmole/cm}^2\text{-sec)} = 4.3 \times 10^{-8} \, (P_{CO} P_{H_2})^{0.42 \pm 0.10}$$

(based on initial iron surface area)

where the component partial pressures are in atmospheres. The approximately half order dependence on both carbon monoxide and hydrogen partial pressures is consistent with the reanalyzed data of Everett (1967). One additional experiment at 773 K with a 25% CO - 75% H_2 mixture permitted calculation of an approximate activation energy of 70 kJ/mole.

The reaction of methane and hydrogen mixtures on a Bosch catalyst was investigated by passing several hydrogen-methane mixtures over 250 mg of steel wool catalyst with approximately 400 mg of deposited carbon at 823 K. As shown in Fig. 36, the net amount of carbon on the catalyst decreased sharply with an inlet stream of pure hydrogen. The reactor exhaust contained between 0.17 and 0.27 mole % methane indicating that carbon was being removed from the catalyst and converted to methane. However, when the methane concentration in the inlet gas was increased to 60 or 75%, the amount of carbon remained constant. During this same period, the inlet and outlet gases were identical in composition, within the limits of analytical accuracy. Thus, with more than 60% methane in the gas phase, all carbon-forming or consuming reactions stopped. Changing the inlet gas composition to 25 mole % methane and 75 mole % hydrogen caused the amount of deposited carbon to decrease again.

At 823 K the equilibrium constant for reaction (E) is 0.966.

$$C + 2H_2 \rightarrow CH_4 \tag{E}$$

while the equilibrium constant for reaction (J) is 2.48

$$Fe_3C + 2H_2 \rightarrow 3Fe + CH_4 \tag{J}$$

according to Browning _et al_. (1950). The equilibrium concentrations of methane for these two reactions would then be 38 and 53%, respectively.

To determine whether methane would form from free carbon at an appreciable rate in the absence of iron, 426 mg of activated charcoal (finer than 200 mesh with a BET area of $\sim$850 m^2/g) were charged to the reactor. The reactor was heated to 823 K in a flowing stream of hydrogen. No methane was detectable in the reactor exhaust gas nor was any change in the catalyst weight observed. Thus, reaction (J) is the probable source of methane. However, since the amount of carbon removed by pure hydrogen (>75 mg carbon) exceeds that which could form a stoichiometric carbide, Fe_3C, with all the iron present (17 mg carbon), formation of methane from a carbide would require simultaneous formation of the carbide from the iron and carbon present.

From this information several conclusions can be drawn:

- For gas mixtures on the methane-rich side of the equilibrium concentration, no carbon formation from the decomposition of methane is observed experimentally.

- For gas mixtures on the hydrogen-rich side of equilibrium concentration, hydrogen reacts (probably with iron carbide) to form methane.

The results shown in Fig. 37 were obtained by passing various CO-CO_2 mixtures over 250 mg of steel wool catalyst and approximately 700 mg of deposited carbon at 823 K. An inlet gas composition of 50 mole % each of carbon monoxide and carbon dioxide caused no observable change in total weight of carbon deposited. Also, no change in gas composition through the reactor was observed. However, when a gas mixture containing 55 or 60 mole % carbon monoxide was fed to the reactor, no consistent weight gain or loss was observed, although both losses and gains were noted. One difficulty leading to these uncertain observations is that weight gain can be caused either by carbon deposition or by oxidation of the catalyst by reaction (L):

$$\frac{3}{4}Fe + CO_2 \rightarrow CO + \frac{1}{4}Fe_3O_4 \qquad (L)$$

The equilibrium constant for reaction (L) at 823 K is 1.11 corresponding to an equilibrium mole fraction of CO of 53%. When a gas stream containing 66 mole % carbon monoxide was fed to the reactor, a large, rapid weight gain occurred clearly indicating carbon deposition. The equilibrium constant for reaction (C) at 823 K is 48.8 corresponding to an equilibrium

$$2CO \rightarrow CO_2 + C \qquad (C)$$

mole fraction of CO of 13%.

From these data the following conclusions can be drawn:

- For gas mixtures on the CO_2-rich side of the equilibrium concentration, no reaction other than catalyst oxidation occurs. No carbon is removed or deposited.

- For gas mixtures on the CO-rich side of the equilibrium concentration, carbon deposition occurs.

- For gas composition very close to equilibrium, for reaction (L), no distinction could be made between carbon deposition and catalyst oxidation using the experimental apparatus.

- Although carbon deposition by reaction (C) is possible under all the experimental conditions shown in Fig. 37, no carbon deposition occurs when the catalyst is expected to be oxidized by reaction (L).

From the results of Kusner (1962), it was expected that the reverse water-gas shift reaction would proceed slowly over a low surface area iron catalyst such as steel wool. Indeed, when a gas stream containing 50% hydrogen and 50% carbon dioxide was passed over a fresh steel wool catalyst at 823 K, the product water and carbon monoxide were barely detectable

(0.02%) in the reactor outlet stream. However, with the same amount of iron catalyst after deposition of ∿500 mg of carbon, reactor outlet concentrations of 5 to 7% each carbon monoxide and water were obtained using the same feed mixture. No carbon was deposited from this gas mixture. As the same weight of iron catalyst is present in both experiments, it is obvious that the formation of deposited carbon on the catalyst has a large effect on its activity with respect to the reverse water-gas shift reaction.

This increase in activity resulting from carbon deposition can result from an increase in active iron surface area or from the carbon fiber surface if it is catalytic. To determine which of these hypotheses was true, approximately 425 mg of activated charcoal (finer than 200 mesh, with a BET area of ∿850 m^2/g) was charged to the reactor, and the reactor was heated to 823 K in a flowing stream of 75% hydrogen and 25% carbon monoxide and only small amounts (<0.07 mole %) of carbon dioxide and water were found in the exhaust gas. The inlet gas was then changed to 50% hydrogen and 50% carbon dioxide, and less than 0.33 mole % carbon monoxide and water were observed in the exhaust gas. As the reaction rate of each of the reactions

$$CO + H_2 \rightarrow C + H_2O \qquad (D)$$

$$CO_2 + H_2 \rightarrow CO + H_2O \qquad (B)$$

is slower by at least an order of magnitude than the same reaction over a similar Bosch catalyst with approximately one fifth the carbon surface area, one can conclude that the carbon surface area is not influencing the observed rate of reaction. Hence, the iron must be responsible for the observed reaction rate increase. This conclusion, along with the experimentally observed increase in the carbon deposition rate and reverse water-gas shift rate as carbon is deposited, leads to the conclusion that the catalytic iron surface area increases by some mechanism in the process of carbon deposition. This observation can also be substantiated by estimation of the amount of iron surface area present. That is, if one calculates the surface area of iron distributed in the carbon fibers as shown by transmission electron microscopy, the iron surface area per unit weight of iron increased at least two orders of magnitude during carbon deposition.

Since equipment was not available to make direct measurements of iron surface area in this investigation, the change in catalytic surface area leads to the conclusion that the data obtained may be used qualitatively to determine the effects of gas composition and temperature on reaction rates but cannot be used to determine quantitatively the individual catalytic reaction rates. One exception, however, is that reaction rate data may be obtained from the initial portions of the experimental runs. That is, the initial rate of carbon deposition can be determined as a function of temperature and gas composition where the initial surface area is fixed.

1.5 Application of Results

To apply results of this investigation, several alternatives to the conventional Bosch process flowsheet, shown in Figs. 41-44, have been evaluated. The thermodynamic analysis of Tevebaugh and Cairns (1964) was extended to determine the gas phase concentrations of H_2, CO, CH_4, CO_2, and H_2O that would be in equilibrium with iron and iron oxide or in equilibrium with carbon at various temperatures and pressures. The equations describing these equilibria were determined and solved numerically. A typical sample of the results for 1 atm and 800 K is shown on a triangular diagram in Fig. 16. The curve abc is the carbon deposition boundary determined by Tevebaugh and Cairns (1964). The curve dbe corresponds to the gas phase C-H-O composition of mixtures of H_2, CO, CH_4, CO_2, and H_2O that would be in equilibrium with solid phases of iron and iron oxide, Fe_3O_4. In the region above this line, iron would be present only in the reduced metallic state; below this line, iron would exist as an oxide.

The results shown in Fig. 16 are typical of the results up to ∿930 K. At these temperatures, the lines abc and dbe intersect. The intersection of these two lines (representing the solid carbon-gas phase equilibrium and the iron-iron oxide-gas phase equilibrium) indicates the one point at which carbon, iron, and iron oxide may coexist at equilibrium with a gas phase containing H_2, CO, CH_4, CO_2, and H_2O. As temperature is increased, however, the curve abc moves toward the carbon apex while curve dbe moves toward the base of the triangular diagram. At ∿930 K the two lines no longer intersect. If the Bosch reactor effluent is assumed to be a mixture in equilibrium with both the carbon product and the iron catalyst, the point corresponding to the composition of the Bosch reactor effluent will be at the intersection of the equilibrium curve (bde or abc) and an operating line (O/H ratio equal to 0.5). The equilibrium line will correspond to curve bde at low temperatures where carbon, iron, and iron oxide may coexist at equilibrium, but will correspond to curve abc at higher temperature where only carbon and iron may coexist at equilibrium in the reactor. The alternative Bosch process flowsheets were evaluated on the basis that conversion obtainable in a Bosch reactor at equilibrium would correspond to a point on curve bde or abc appropriate to the temperature and pressure of operation.

To overcome the difficulties in starting a reactor which operates as shown in Fig. 1, an alternative scheme as shown in Fig. 42 could be used. In this process, a feed mixture containing two moles of hydrogen for each mole of carbon dioxide is fed to a reverse water-gas shift reactor at 922 K. Using a pelleted iron powder catalyst with high specific surface area, Kusner (1962) has shown that the shift reaction rate at 922 K over an active catalyst is limited by mass transfer of reactants from the gas phase to the catalyst surface. The product stream from the shift reactor is then fed to a recuperative heat exchanger where water is condensed and separated. If equilibrium is reached in the shift reactor, 0.562 moles of water would be obtained per mole of CO_2 fed. The remaining gas stream containing 18 mole % carbon dioxide, 59 mole % hydrogen, and 23 mole % carbon monoxide (on a dry basis) is then fed to a recycle reactor at 823 K to produce both carbon and water.

This operating scheme has several advantages. First, 28% of the water formed in the overall process can be recovered after one pass through the shift reactor. Secondly, a rapid start of the recycle reactor should be achievable by using the H_2-CO-rich stream from the shift reactor and a catalyst activation procedure such as surface oxidation by carbon dioxide. Additionally, the flowsheet shown in Fig. 42 can be simplified by using only the second heat exchanger for both reactors; that is, the product stream from the shift reactor could be introduced directly into the recycle loop after the recycle reactor and before the heat exchanger as shown in Fig. 43. Finally, even more favorable yields of water and carbon monoxide are obtainable by increasing the shift reactor temperature or by increasing the H_2/CO_2 ratio of the feed mixture. The latter, however, would lead to accumulation of hydrogen in the second recycle reactor requiring an occasional reactor purge and, thus, a more complicated operation. To increase the H_2/CO_2 feed ratio above two without purging, a hydrogen separator, such as a palladium-silver semipermeable membrane, could be added as illustrated in Fig. 44.

The experimental results also indicate that methane is formed from the reaction of hydrogen with the carbide present when carbon is deposited on the steel wool catalyst. Thus, in any recycle loop, such as those shown in Figs. 41-44, or when methane is not removed, an accumulation of methane in the recycle loop must be expected. Based on the data obtained using binary mixtures and the results of Browning _et_ _al_. (1950), the concentration of methane in the recycle stream would be expected to increase at least until reaching a concentration corresponding to equilibrium for reaction (E).

To evaluate the advantages of the various flowsheets presented in Figs. 1 and 41-44, the mass balances expected at equilibrium conversion (the most favorable operating conditions achievable) were calculated for each flowsheet. In all cases, it was assumed that, in a reverse water-gas shift reactor, equilibrium conversion was obtainable without carbon deposition and without methane formation. Thus, the outlet composition of the reverse water-gas shift reactor depended only on the reactor temperature and H_2/CO_2 feed ratio. The inlet H_2/CO_2 ratio was assumed to be two in all cases where a hydrogen separator and hydrogen recycle were not employed. The outlet composition of the Bosch reactor was assumed to be the equilibrium mixture expected at the appropriate $C-Fe-Fe_3O_4$(or FeO)$-H_2-CO-CH_4-CO_2-H_2O$ or $C-H_2-CO-CH_4-CO_2-H_2O$ equilibrium. The water separation system was also assumed to be 100% efficient. In each case, the number of moles of reactants recycled in a Bosch recycle loop is calculated as a function of the adjustable processing parameters: the reverse water-gas shift reactor temperature, the Bosch reactor temperature, and the H_2/CO_2 ratio of the feed to the water-gas shift reactor. The results of this calculation are presented graphically in Fig. 45.

In Fig. 45 the two solid lines represent the number of moles, r, of gas which must be recycled in the Bosch reactor loop per mole of inlet CO_2. The upper solid line, A-A', represents the amount of recycle required if a Bosch reactor is operated without a reverse water-gas shift prereactor as shown in Fig. 1; the lower line represents the amount of recycle required with the addition of a prereactor operating at the same temperature. If the temperature of the water-gas shift reactor is increased above the temperature of the Bosch reactor, the minimum recycle required decreases slightly as indicated in Fig. 45 by the dotted lines corresponding to an H_2/CO_2 feed ratio, n, of 2 as indicated in the flow diagrams of Figs. 42 and 43. Finally, if an H_2/CO_2 feed ratio above 2 is employed with hydrogen recycle as shown in Fig. 44, the required recycle decreases as shown by the dotted lines for H_2/CO_2 feed ratios of 10 and 20.

The recycle required for the flowsheets shown in Figs. 1 and 41 decreases rapidly with increasing temperature up to approximately 900 K. As shown in Fig. 45, the addition of the reverse water-gas shift prereactor decreases the required recycle by 21% at 800 K and 14% at 900 K. Increasing the reverse water-gas shift reactor temperature to 1100 K results in an additional 11% decrease at 800 K and an additional 8% decrease at 900 K. The largest single factor decreasing the required amount of recycle, however, is the Bosch reactor temperature.

The use of increased H_2/CO_2 ratios for the reverse water-gas shift reactor is also shown to decrease the number of moles of material that must be recycled through the Bosch reactor as shown in Fig. 45. This decrease is accomplished, however, by the addition of a hydrogen recycle loop. For all reactor temperatures above 800 K, the number of moles of hydrogen that must be recycled exceeds the decrease in the number of moles that must be recycled through the Bosch reactor. For some reactor operating conditions below 800 K, the total number of moles to be recycled, n+r-2, decreases for values of n larger than 2 and then increases as n becomes large. This means that a reactor cycle such as shown in Fig. 45 can be optimized for the minimum value of (n+r-2) if the Bosch reactor will operate at temperatures below 800 K and if operations at such low temperature are favored from other weight, volume, or power considerations.

Finally, there is a minimum value of r for the flowsheets shown in Figs. 41-43. The minimum occurs at reactor temperatures of 915 K for these process flowsheets at atmospheric pressure. The composition of the gaseous effluent from the Bosch reactor, which is determined by the -Fe-Fe_3O_4(or FeO)-H_2-CO-CH_4-CO_2-H_2O equilibrium below this temperature, becomes determined by the C-H_2-CO-CH_4-CO_2-H_2O equilibrium at higher temperatures.

In conclusion, each of the reactor flow schemes shown in Figs. 1 and 41-44 has advantages and disadvantages. The final selection and optimization of the proposed schemes will require an analysis of the aggregate weight, volume, and power requirements of the various flowsheets.

2. INTRODUCTION

2.1 Rationale

For long-range space missions which involve astronauts, a reliable life support system is necessary. Integration of portions of this system to achieve less weight, smaller volume, lower power, or to simplify operations is a desirable goal. One key step in the life support system is the reduction of metabolic carbon dioxide to oxygen. To accomplish this step, a number of schemes have been proposed; at present there remain three primary candidates: the Bosch, Sabatier, and Solid-Electrolyte processes. The latter two will not be discussed here.

In the Bosch process, carbon dioxide is converted to solid carbon and water by reaction with hydrogen in one reactor as shown in Fig. 1:

$$CO_2 + 2H_2 \rightleftarrows C(s) + 2H_2O \tag{A}$$

Reaction (A) should, however, be visualized only as an equation representing the overall stoichiometry of the process. In a typical Bosch system, fresh CO_2 and H_2 are mixed with recycle gas and passed through a reactor usually containing an iron catalyst at 800-950 K. In addition to carbon and water, other products form: primarily CO and CH_4. Solid carbon deposits in the catalyst mass, water is condensed in an external heat exchanger, and all other gases are recycled and mixed with fresh feed. An overall "black box" analysis of the system would then appear as written in (A) and shown in Fig. 1.

The product water would be electrolyzed to reform oxygen, and the hydrogen would be recycled to the Bosch reactor inlet. Thus, the net effect of the two reactors is to reduce CO_2 to carbon and oxygen.

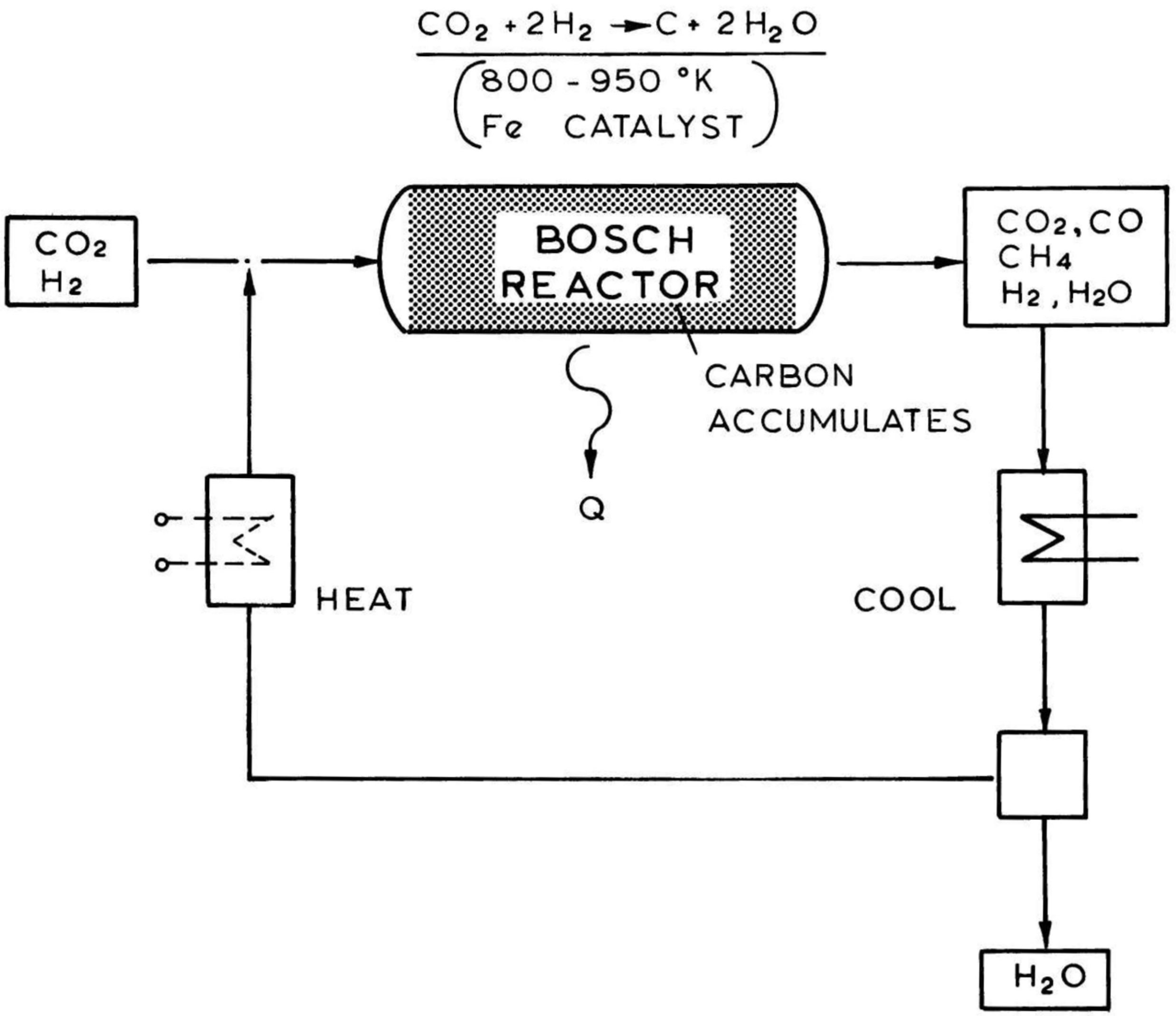


FIGURE 1, THE BOSCH REACTOR

$$\begin{array}{l}
CO_2 + 2H_2 \rightarrow C + 2H_2O \\
2H_2O \rightarrow 2H_2 + O_2 \\
\hline
CO_2 \rightarrow C + O_2
\end{array}$$

To understand the Bosch process so as to optimize operating conditions, it is desirable to examine in detail the individual reactions which may occur. The situation turns out to be quite complex. Not only must the reactions involving CO_2, H_2, CO, H_2O, CH_4, and solid carbon be considered, but under some conditions, the stable phase of the iron catalyst could, in actuality, be an iron oxide or carbide. Thus reactions involving the gas phase and catalyst must not be ignored.

It is the goal of this study to determine the individual reactions which are important in this processing scheme and the variables which affect the rates of these reactions. In addition, it is desirable to formulate recommendations as to the optimum method by which the Bosch process should be carried out in a manned spacecraft.

2.2 Previous Work

2.2.1 Water-Forming Reactions

To start a typical Bosch system, the reactor is charged with an iron catalyst, brought up to temperature (800-950 K), and fed with a 1:2 mixture of CO_2 and H_2. Too often, nothing much happens. Little water appears in the product condenser and the unreacted gases must be recycled many times through the reactor before a "start" is achieved, i.e., before much water begins to condense and carbon to form.

We might then examine first what reactions are to be expected between CO_2 and H_2 on an iron catalyst. It appears that the only reaction of any consequence that occurs is the reverse water-gas shift.

$$CO_2 + H_2 \rightleftarrows CO + H_2O \qquad (B)$$

Under conditions very similar to those used in the Bosch process, Kusner (1962) studied the iron catalyzed reaction of CO_2 and H_2 at 922 K with H_2/CO_2 feed ratios ranging from 0.5 to 3.0. A single-pass, fixed-bed reactor was employed and both inlet and outlet gas compositions were measured. Several different iron catalysts were tried and all were found active. Iron or iron oxide powders were ground, pelleted with a starch binder, dried, and fired in air to burn off the starch and to partially sinter the pellets. After a subsequent reduction in H_2 at 1092 K, the pellets were cooled in hydrogen, crushed, and sieved. The final average particle size used was about 3 mm, the density 3.97 g/cc, the porosity 61%, and the BET area about 1 m^2/g. A final annealing in H_2 completed the pretreatment. The amount of catalyst used ranged from 100 to 600 g. As the reactor was a vertical Vycor tube, 90-cm long by 5.9-cm diameter, the packed height (porosity = 0.46) varied from about 2.6 to 15.6 cm. Various flow rates were studied to cover a particle Reynolds number domain between 1.7 and 16. The flow was, therefore, laminar. Conversions were as high as 60% in some runs; expressed differently, the fractional approach to equilibrium was as high as 96%. A convenient way to represent the reaction path is shown on Fig. 2 from the thesis of Kusner (1962), on which the ordinate represents the fraction carbon as CO while the abscissa shows the fraction hydrogen present as water. A CO_2-H_2 feed lies in the lower left-hand corner since neither CO nor H_2O is present. Depending upon the ratio of CO_2 to H_2 fed to the reactor, as reaction proceeds, the operating point

$$CO_2 + H_2 \rightleftharpoons CO + H_2O$$

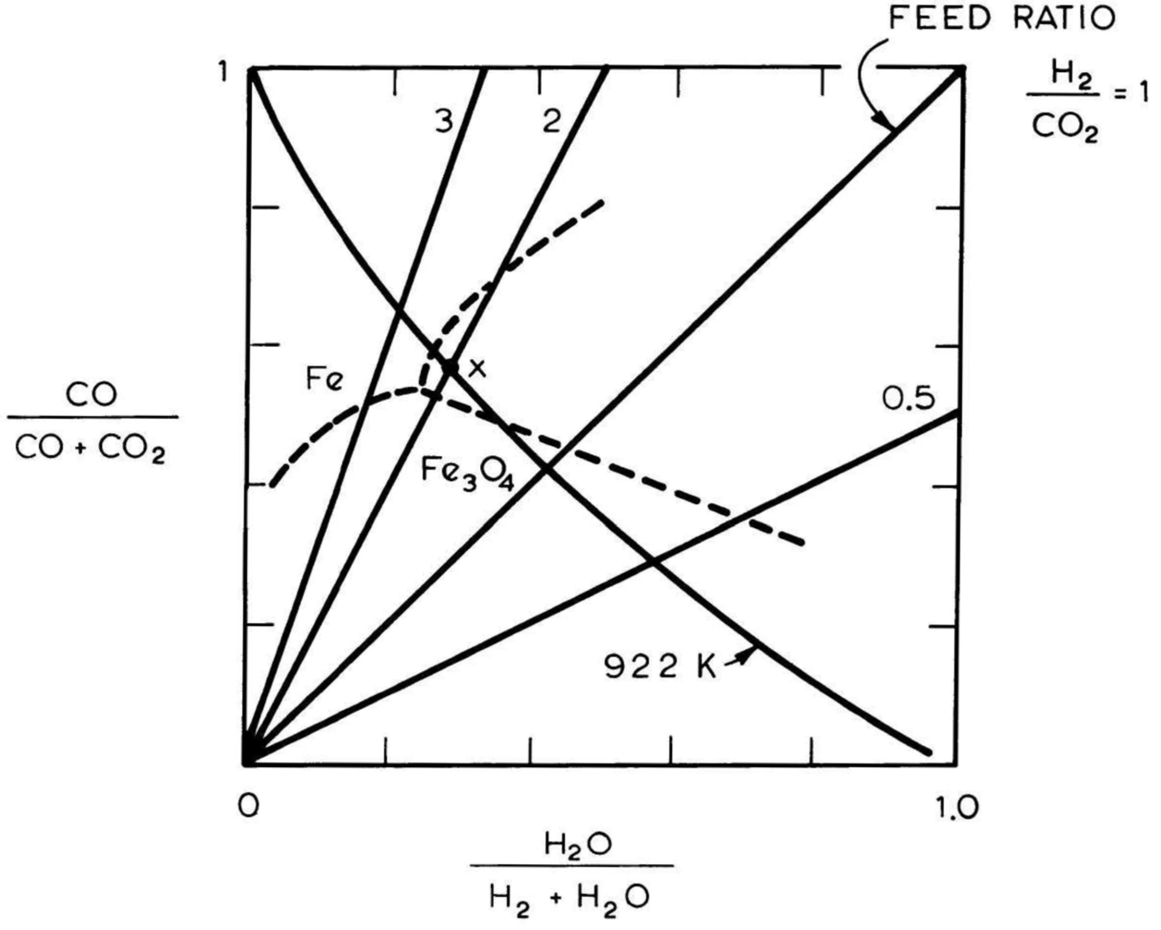


FIGURE 2, REACTION DIAGRAM FOR THE REVERSE WATER GAS SHIFT REACTION (KUSNER 1962) moves along a straight line away from the corner. Also shown is the isotherm which represents equilibrium conditions at 922 K and one atmosphere. For example, proceeding along the line representing an H_2/CO_2 feed ratio of 2, at point x where the line intersects the 922 K equilibrium curve, the ordinate and abscissa show the equilibrium conversions for reaction (B).

Finally, as indicated, for an iron catalyst, the equilibrium solid phase may be the α-phase of iron or some iron oxide depending on the temperature and oxidizing or reducing nature of the gas mixture. The dotted lines shown in Fig. 2 are algebraic representations of various equilibrium criteria. For example, the dotted line separating the regions labelled Fe and FeO is the locus of points which simultaneously satisfy the equations

$$\frac{P_{H2}}{P_{H_2O}} = K_4$$

and

$$\frac{P_{CO}}{P_{CO_2}} = K_5$$

where K_4 and K_5 are the equilibrium constants for the reactions

$$Fe + H_2O \rightarrow FeO + H_2$$

and

$$Fe + CO_2 \rightarrow FeO + CO$$

respectively. If the above two reactions are both at equilibrium at one temperature and pressure and if the reverse water-gas shift reaction is also at equilibrium with the gas phase containing only H_2, CO, CO_2, and H_2O, then the phase rule indicates that the equilibrium state is completely fixed and that the gas phase composition is not variable. The point representing the fixed gas composition defined by specifying the temperature, pressure, and equilibrium constants for the three reactions is located at the intersection of the dotted line and the equilibrium isotherm.

Although the equilibrium solid phase for many of Kusner's experiments should have been an iron oxide, Kusner reported that catalyst weight gain was negligible and that chemical analysis showed only 0.02 - 0.07% oxygen combined with iron. While it may be possible that the catalyst was covered by a surface oxide layer undetectable by weight gain or by chemical analysis, no definite conclusion is possible. As is obvious from Fig. 2, no solid carbon or carbide phase is considered, nor was any ever detected. Also, no methane was found in any experiment except those with a H_2/CO_2 ratio of three and, even here, only traces were noted.

With a variety of iron catalysts, Kusner attained high conversions and water yields with but a single pass. This result is of interest as it has been observed in Bosch process systems that there is usually a significant induction period before any appreciable reaction occurs. Many have suspected an inactive iron catalyst and special techniques for activation have been employed. Yet, it is proposed here that the metal catalyst surface area available for reaction is of greater significance. Most Bosch process tests have been made with reactors packed with steel wool. Steel wool fibers vary in diameter, but typical available areas are in the range of 0.01 to 0.04 m^2/g. This is far less specific area than that of the catalyst used by Kusner. It is, therefore, not surprising that little reaction is noted in a single pass or even in many cycles.

Also Kusner definitely established the reverse water-gas shift reaction is rapid over reduced iron at 922 K. In his reactor, the rate controlling step was not chemical but one which involved the mass transfer of either or both the CO_2 and H_2 to the iron surface. Although this point will be discussed later, it is noted here to emphasize that to initiate the Bosch process with a CO_2-H_2 feed, a large area of iron catalyst must be available and the flow dynamics must enhance mass transfer. The following conclusions can be reliably drawn from Kusner's thesis:

(1) High area iron catalysts are sufficiently active at 922 K to lead to an overall rate equation which is mass transfer limited.

(2) Neither carbon nor appreciable methane form in a single pass from feeds with H_2/CO_2 feed ratios ranging from 0.5 to 3.0.

The reverse water-gas shift reaction has also been investigated in a single pass fixed bed reactor by Barkley et al. (1952) with feed gas H_2/CO_2 ratios of between 0.25 and 4.0 at flow rates between 0.0235 and 0.224 m^3/hr (STP). The catalyst was a commercial promoted iron oxide shift catalyst in the form of cylindrical pellets 3 mm in diameter and 1.75-mm long. The pellets were packed in a 19-mm Vycor tube in depths ranging from 1.0 to 6.4 cm. The Reynolds number based on particle size thus ranged approximately from 3 to 30. Conversion of the inlet carbon dioxide varied from 5 to 60%, or the fractional approach to equilibrium varied from 10 to 100% depending on the experimental flow conditions. The authors reported no observed mass transfer limitations and a kinetic rate equation at 811 K of:

$$\text{rate (g } CO_2 \text{ converted/hr-g catalyst)} = \frac{0.595\left(P_{H_2}P_{CO_2} - \frac{P_{CO}P_{H_2}}{0.267}\right)}{1 + 4.46\ P_{CO_2} + 41.65\ P_{CO}}$$

where the component partial pressures are in atmospheres. The accuracy of the final rate expression and rate constants may, however, be questionable in that the authors also reported a temperature drop of 50 K in the first

2.5 cm of bed depth and ±25 K sinusoidal fluctuation in bed temperature with time.

As in Kusner's studies, no carbon deposition or methane formation was noted. Since the flow conditions, as reflected by the particle Reynolds numbers, are only slightly different in the experiments of Kusner and Barkley et al., one would expect the mass transfer coefficient for the two series of experiments to be similar. Yet, in contrast to Kusner's finding that mass transfer limited the overall reaction rate at 922 K, Barkley et al. found a kinetically-controlled reaction rate at 811 K. It would appear that the activation energy of the reverse water-gas shift reaction may be high enough to cause a transition from a kinetically-controlled reaction regime at 811 K to a bulk mass transfer-controlled regime at 922 K.

2.2.2 Carbon-Forming Reactions

2.2.2.1 Equilibrium Considerations. The fact that no carbon formed during the experiments of Kusner and Barkley et al. might first appear unusual. To illustrate, consider what reactions might be expected to produce carbon. The two normally suggested are:*

$$2CO \rightleftarrows C + CO_2 \tag{C}$$

$$CO + H_2 \rightleftarrows C + H_2O \tag{D}$$

For either reaction (C) or (D) to occur, the thermodynamic driving force must be such as to cause the reactions to proceed from left to right. That is, as reaction (B) proceeds, CO is produced. If the CO concentration becomes sufficiently high, reaction (C) may commence. It turns out, however,

---

*Note that reactions (C) and (D) are not independent if (B) is also considered. That is, (B) + (C) = (D).

that even if reaction (B) proceeds to equilibrium under the conditions studied by those authors (no methane formation) where the CO concentration would be the highest possible, there is still an insufficient concentration of CO to cause reaction (C) to proceed from left to right. In fact, if carbon were present, CO_2 and carbon would be consumed to form even more CO. The same conclusion is also reached if reaction (D) is considered. Never do the CO and H_2 concentrations become sufficiently large to lead to carbon formation.

Without carbon, methane might not also be expected since many believe the principal formation reaction to be:

$$C + 2H_2 \rightleftarrows CH_4 \tag{E}$$

Thus, it is tentatively concluded that carbon can be deposited only if the CO-H_2-CO_2 concentrations allow reactions (C) and (D) to proceed to the right. Another way to show this conclusion is to refer to Fig. 3 (Tevebaugh and Cairns, 1964). A C-H-O triangular diagram is plotted with isotherms at 811 and 922 K. These isotherms represent the equilibrium C-H-O compositions for systems in which free solid carbon is present and the gas phase contains CH_4, CO, CO_2, H_2, and H_2O. Any gas mixture with an overall composition lying in the area marked carbon forming can deposit carbon and, at equilibrium, would be on the appropriate isotherm found by the intersection of this isotherm with the extension of a straight line drawn through the original C-H-O composition and the C-apex. Any mixture composition lying in the no carbon region cannot deposit solid carbon while reacting. Note that a mixture of 2 moles hydrogen and 1 mole CO_2 lies well within the no carbon region for reactions at 922 K. Compositions richer in hydrogen will not deposit carbon

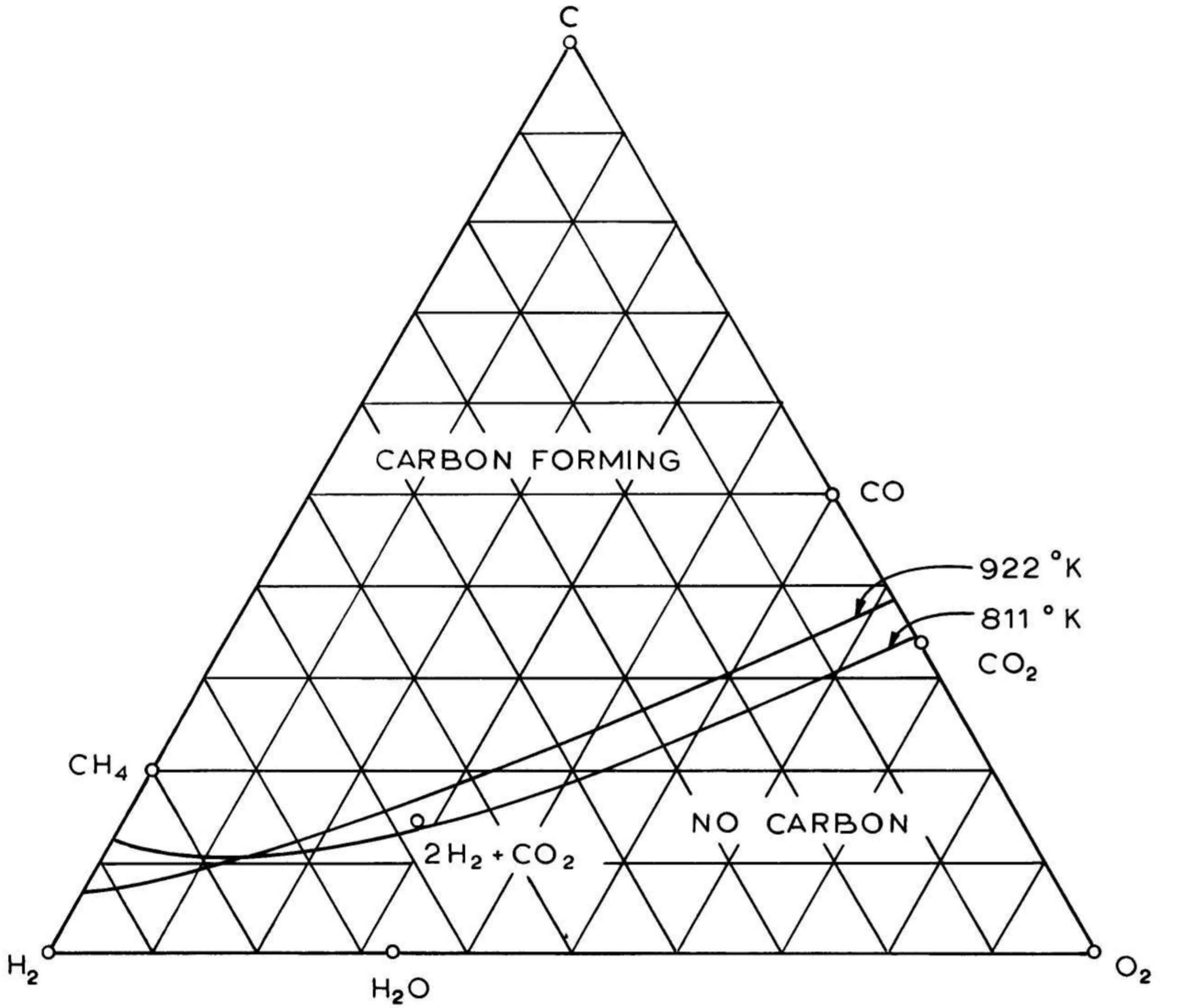


FIGURE 3, C-H-O TRIANGULAR DIAGRAM AT 1 ATM (TEVEBAUGH AND CAIRNS, 1964) even at much lower temperatures. These conclusions agree completely with Kusner's findings.

It has been proposed above that the reverse water-gas shift reaction (B) must be driven to the right by the removal of water to increase the CO concentration sufficiently to initiate the deposition of carbon. It is also suggested here that reactions (C) and (D) are those primarily responsible in forming carbon. Previous work involving carbon deposition from CO-H_2 mixtures will now be briefly examined in the light of these proposals.

2.2.2.2 Carbon Deposition from CO-H_2 Mixtures. Probably the most complete studies were by Walker, Rakszawski and Imperial (1959). They used a reduced iron powder catalyst placed in a boat set in the bottom of a 25-mm-ID Vycor tube. The feed gases were CO-H_2. By monitoring both the feed gas rate and the product gas rate (after removal of CO_2 and water), they could infer the rate of carbon deposition though they could not distinguish whether the carbon came from reaction (C) or (D). Most runs were with a CO-rich gas (CO/H_2 ratios were normally between 4.2 and 124). Temperatures ranged from 723 to 973 K. Flow rates were varied and a number of reduced iron powders used. Baker analyzed reagent-grade iron powder, 10 μm average diameter, reduced in hydrogen at 673 K for 24 hr, gave the most active catalyst; it had a BET area of about 1 m^2/g. The mass of carbon formed is shown as a function of time in Fig. 4. The curve is sigmoidal in shape with a weak induction period and an asymptote at long times.

Carbon deposition was rapid even for the 0.8% H_2 feed. Carbon deposition rates maximized at a temperature between 825 and 900 K depending on CO/H_2 ratio; but at all temperatures, they were surprisingly constant over several hours before decreasing rapidly. In most runs, about 8 to 10% of the inlet CO deposited as carbon.

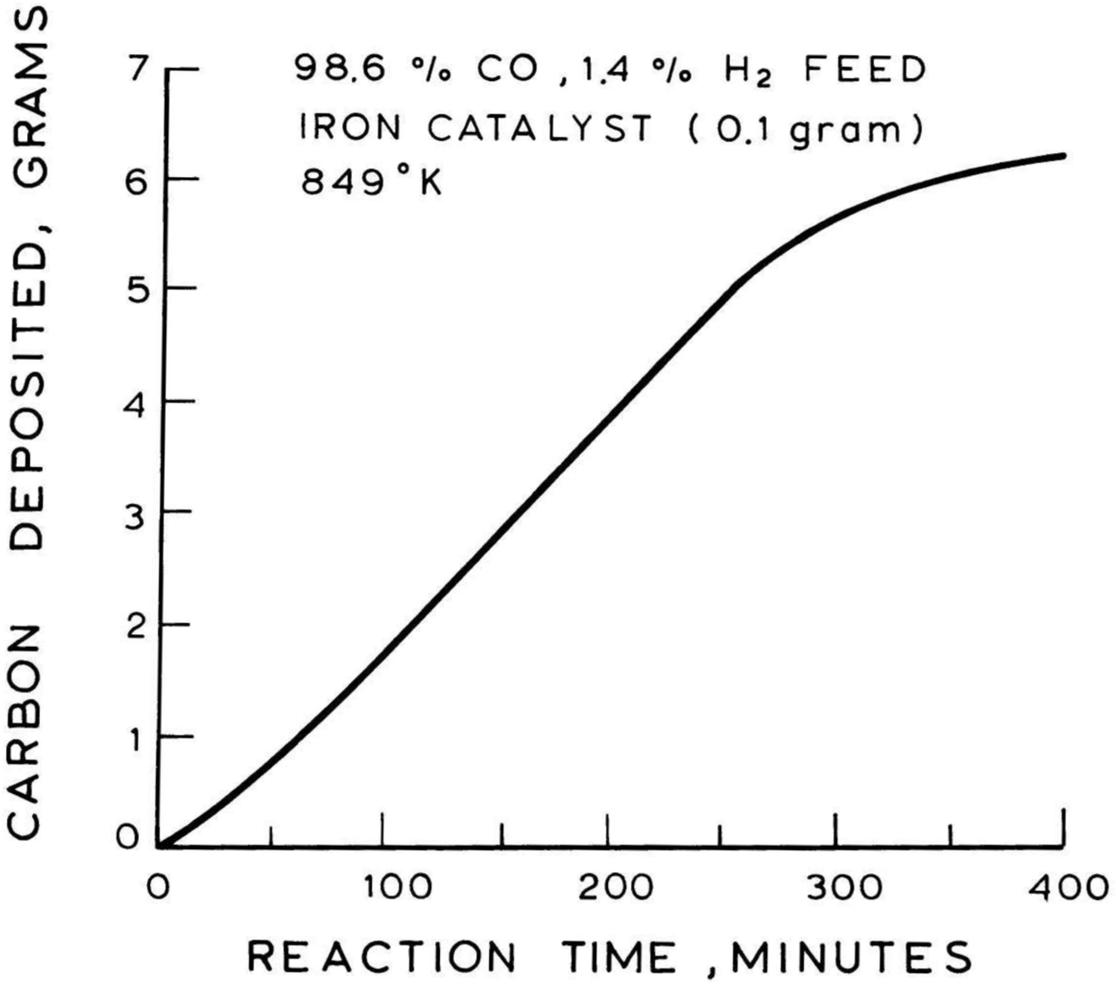


FIGURE 4. TYPICAL CARBON DEPOSITION PLOT (WALKER et al., 1959)

Another interesting result was the fact that at temperatures greater than about 850 K, the rate of formation of carbon was quite sensitive to the hydrogen concentration. At a constant total flow rate, maximum reaction rates were found for inlet H_2 mole fractions of around 9%. The experimental data for a run at 875 K are shown in Fig. 5. This effect of hydrogen is very strong as can be seen in the high rates of carbon formation from CO-H_2 mixtures relative to the rate of carbon deposition from pure CO (dotted line in Fig. 5). It is probable that mass transfer was, in reality, controlling (see Appendix 8.1.1 for additional discussion) the observed reaction at high reaction rates.

In all cases, the iron catalyst disintegrated and formed filaments with lengths over 10 μm and with diameters between 100 and 500 nm. Many were twisted. Crystals were often found at what appeared to be the ends of the filaments. BET areas ranged up to and over 100 m^2/g and atomic C/Fe ratios were sometimes well in excess of 100. C/H atomic ratios in the filaments varied from 10-30 and increased with temperature.

Electron micrographs of carbon filaments are shown later, but it should be noted here that filaments have been found in many previous studies. For example, Berry _et al_. (1956), Podgurski _et al_. (1950), and Tesner _et al_. (1970) reported similar filaments in the study of the thermal decomposition of CO, acetylene, and other hydrocarbons on iron, iron oxides, and nichrome wire. Also, Robertson (1970) and Tamar _et al_. (1969) noted their appearance in the carbon product of methane pyrolysis on iron, cobalt, and nickel.

2.2.2.3 <u>Carbon Deposition from Carbon Monoxide</u>. Probably the most extensive metallurgical study of the decomposition of pure CO on iron was published by Ruston _et al_. (1969). They carefully examined the processes

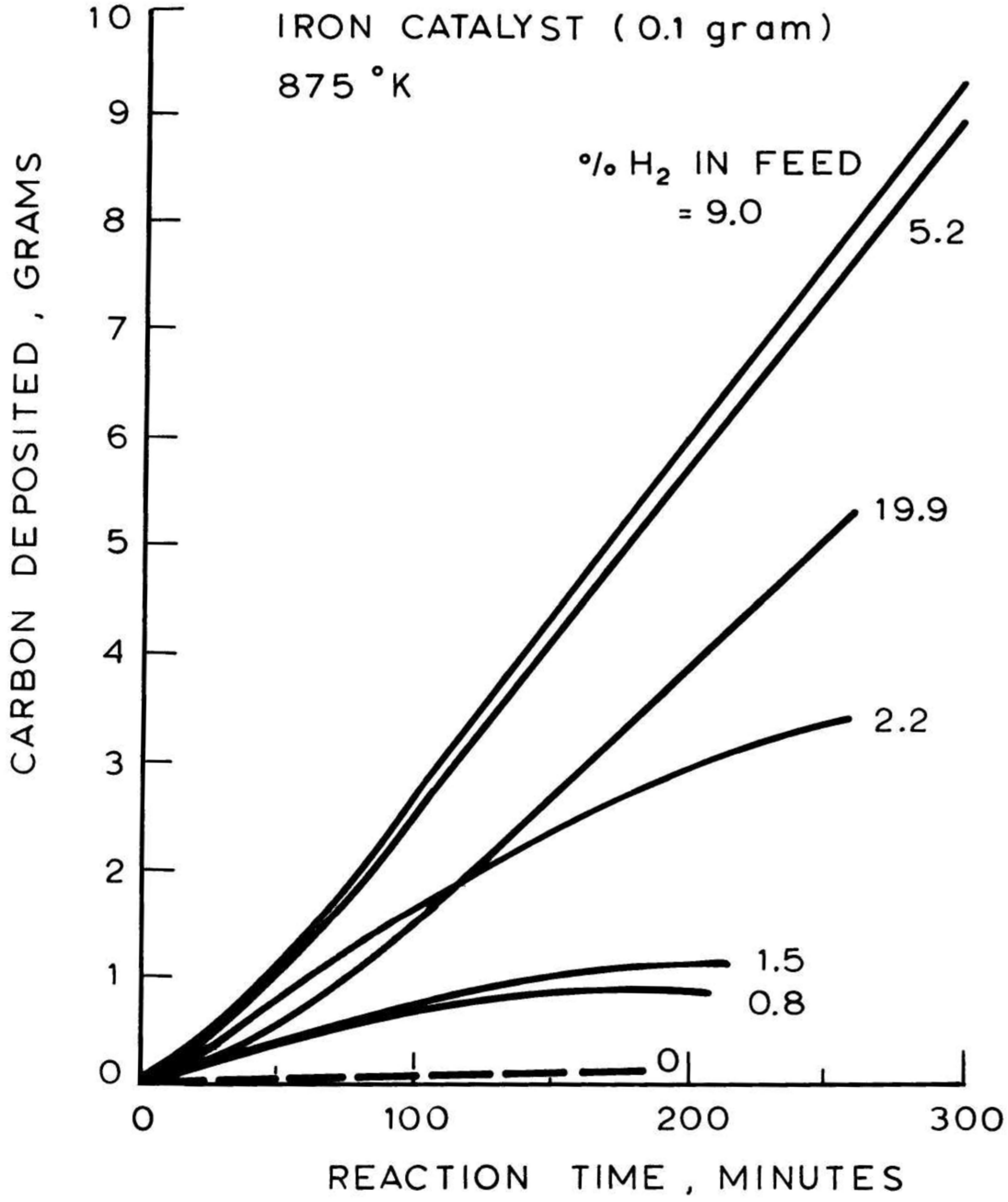


FIGURE 5. EFFECT OF HYDROGEN ON CARBON DEPOSITION FROM CO - H_2 MIXTURES (WALKER et al., 1959)

occurring within the metal catalyst and proposed the following mechanism: CO first adsorbs on the reduced iron surfaces. Depending upon the temperature and CO concentration, various carbides can form; some CO decomposes to carbon and oxygen atoms; the oxygen atoms react with adsorbed CO to form product CO_2. The carbon atom is relatively mobile and diffuses into the α-iron along an intergranular path. Within the metal, the carbon reacts to form Fe_3C which is stable under compressive stress. The subsurface Fe_3C crystal grows until it erupts from under the surface. In the absence of compressive stress on the surface, the Fe_3C decomposes to iron and carbon. This causes disruption of the surface grains and pitting is observed.

Another simultaneous carbide crystal formation was also detected. These crystallites formed within the single crystal grains of the α-iron at the surface and were most noticeable when the metal had been exposed to low CO pressures for prolonged periods. They appeared to grow epitaxially and uniformly over a single crystal grain, but their size and shape varied depending on the crystal grain face. Ruston _et_ _al_. identified these crystallites as Fe_7C_3 from x-ray diffraction data. However, this identification is questioned by other authors.

Furthermore, Ruston _et_ _al_. proposed these Fe_7C_3 crystallites as the catalytic species producing the filaments of carbon observed. They stated that the small crystallites became disengaged from the iron substrate by carbide decomposition and then were catalytically active to promote further CO decomposition. They also noted that this process did not continue indefinitely as the Fe_7C_3 crystallite disintegrated, leaving behind iron-rich fragments as the carbon filament grew. The crystallite is no longer active when the carbon-iron filament drops to less than about 3 wt % Fe (C/Fe = 150).

Ruston's findings are particularly valuable for their insight into the overall processes occurring on the surface of polycrystalline iron. However, several objections have been raised to his conclusion that the small crystallites grown on single crystal iron surfaces are Fe_7C_3. Ruston formed this conclusion primarily on the basis of x-ray diffraction data, and yet both Renshaw et al. (1970) and Ratliff (1968) contend that the reported x-ray diffraction data can also be interpreted as either Fe_3C or Fe_2C.

Westerman, in a thesis at Georgia Institute of Technology in 1967, studied the kinetics of carbon formation on iron from pure carbon monoxide. His work was extensive and requires careful consideration. Several types of experiments were performed; the most important employed is an electrobalance-furnace apparatus to permit continuous, accurate weighing of catalyst samples in a flowing stream of CO at temperatures up to 1323 K. The electrobalance used was of the pan type; the catalyst sample weight was continuously recorded. The catalyst itself was a 64.5-cm length of 20-mil iron wire formed into a coil approximately 1.2-cm long and 1.8 cm in diameter. The nominal surface area was 10 cm^2. The wire coil was placed on a weighing pan 2 cm in diameter centered in the furnace tube. The furnace tube, 3.8 cm in diameter, was resistance heated and controlled in temperature to within ±2 K of the set point.

Purified CO gas was metered through the furnace tube at approximately 30 standard cc/min while the catalyst weight was recorded for experimental runs lasting 20 hr. Reacted catalyst samples were also etched and observed using standard metallurgical procedures to determine the effects of exposure to the reacting gases.

The results of the gravimetric data are shown in Figs. 6 through 9. In Fig. 6, the gain in weight (on 10 cm^2 of original surface area) of

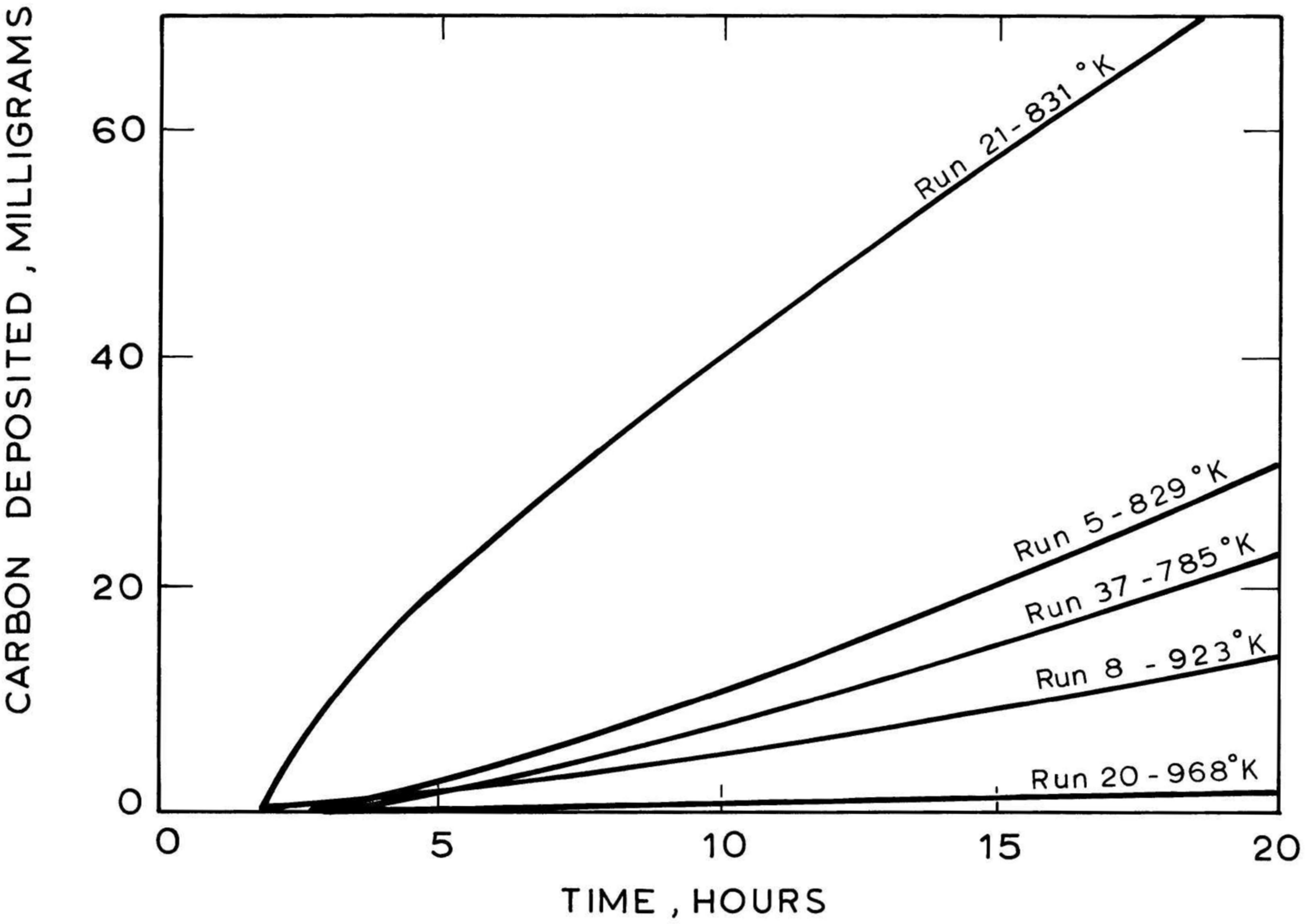


FIGURE 6, TYPICAL CARBON DEPOSITION PLOT (WESTERMAN, 1967)

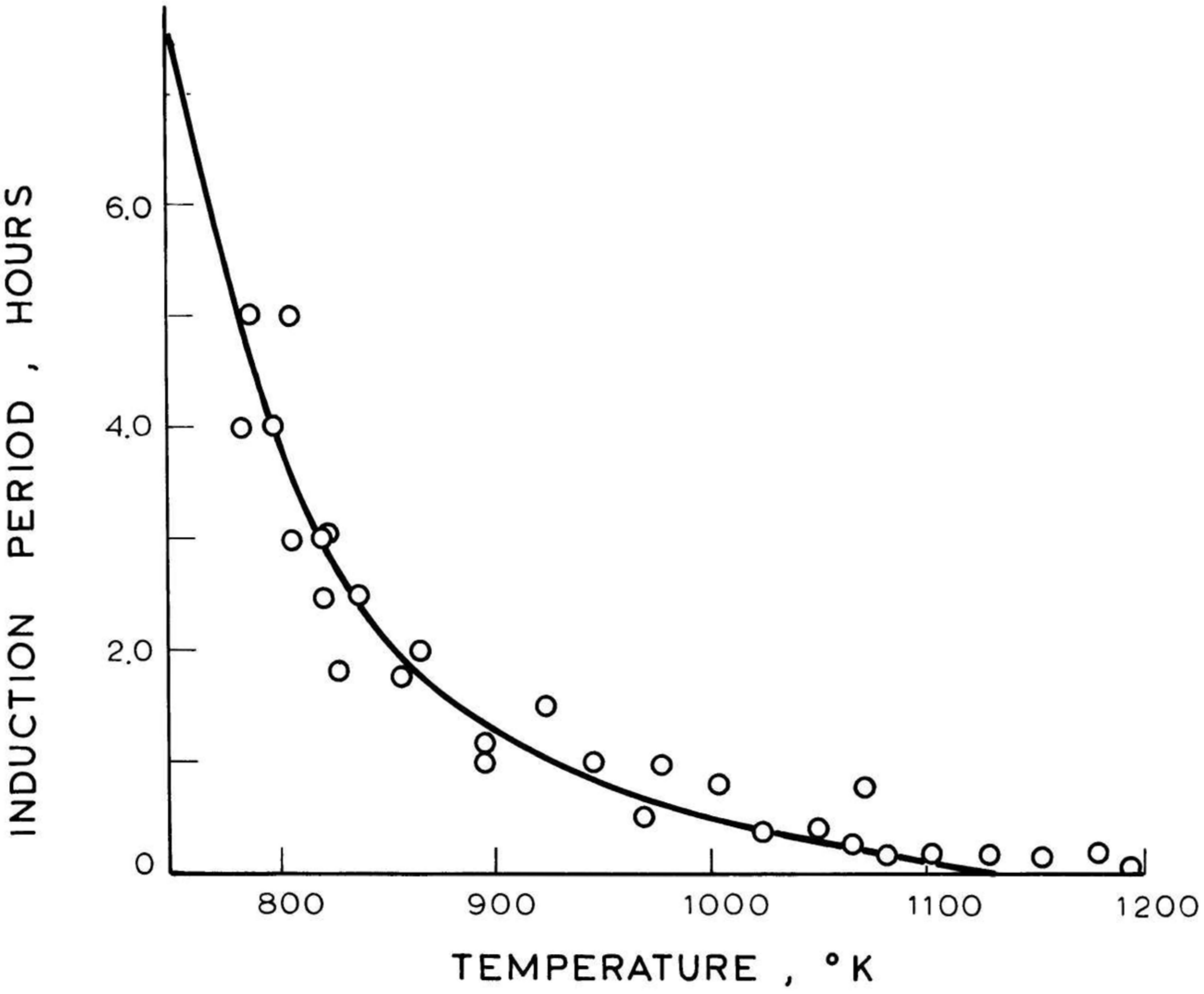


FIGURE 7, INDUCTION PERIOD FOR CARBON DEPOSITION
(WESTERMAN , 1907)

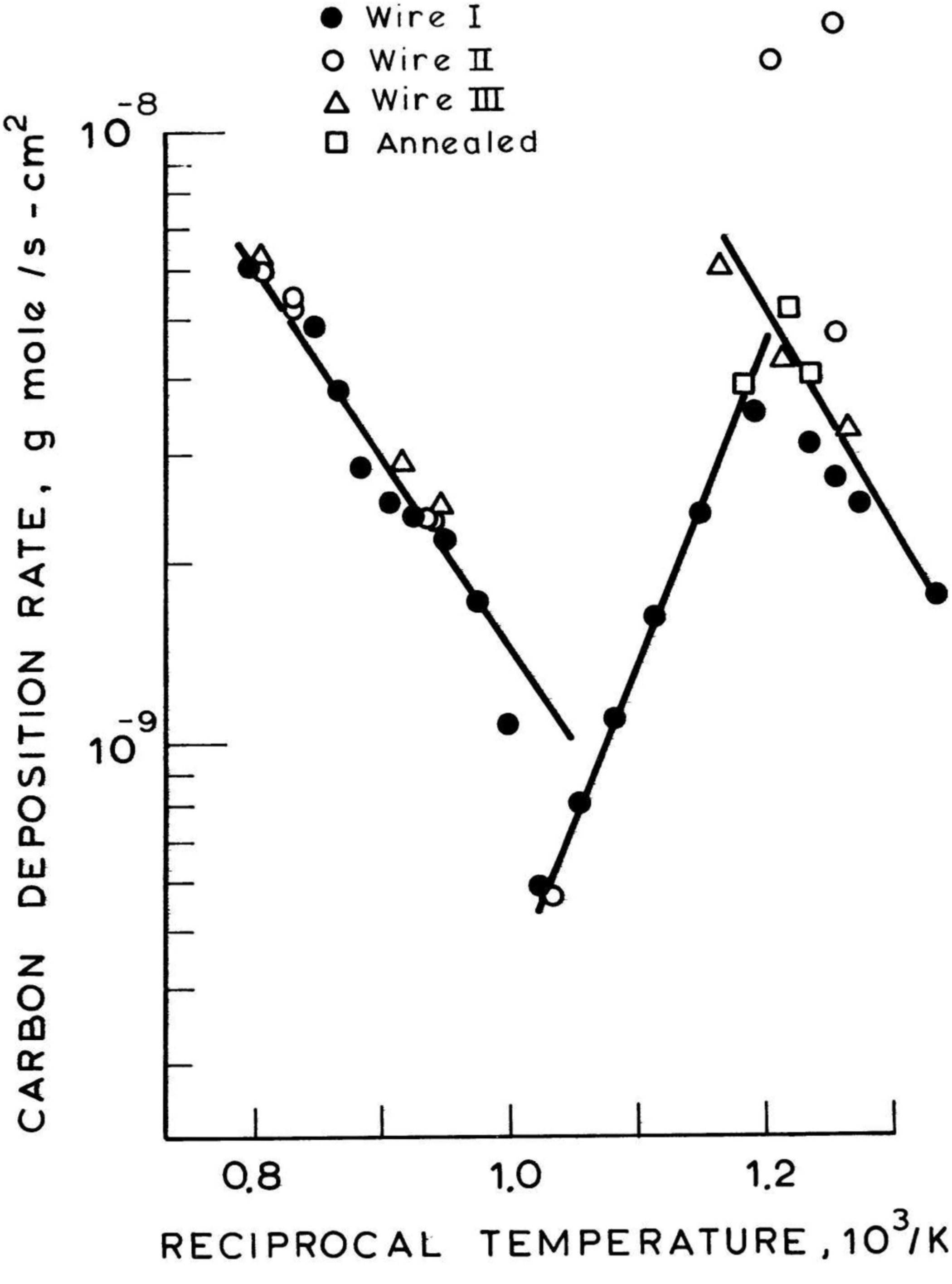


FIGURE 8, CARBON DEPOSITION RATE THREE HOURS AFTER INDUCTION PERIOD (WESTERMAN 1967)

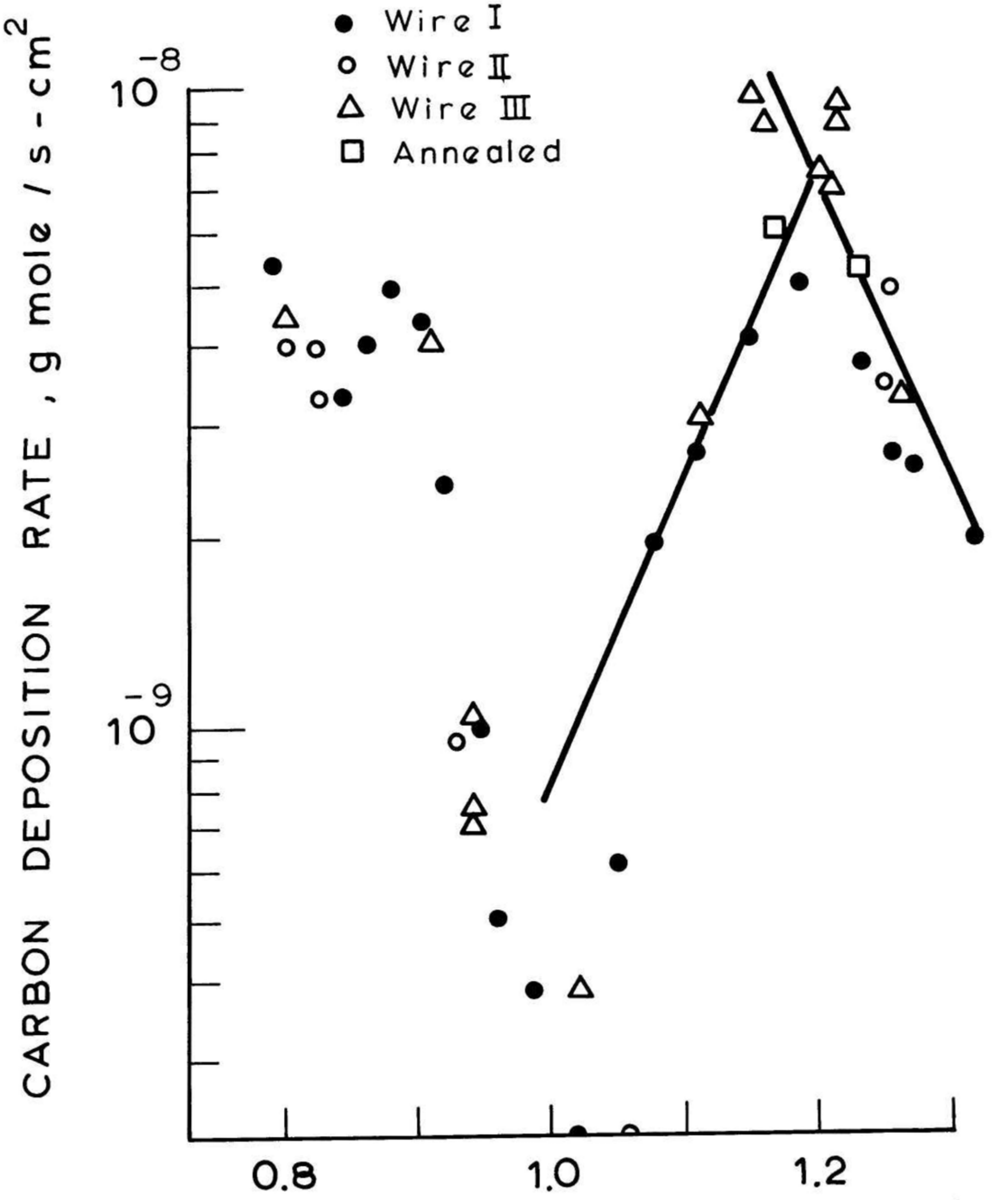


FIGURE 9, CARBON DEPOSITION RATE AFTER 16 HOURS (WESTERMAN, 1967) the catalyst during a run is shown for several different temperatures. The weight gain curves obtained are not unlike those of Walker et al. (1959) except for Run 21 which will be discussed later. Again, an induction period is apparent and this period seems to be a function of temperature. Westerman termed this period an "incubation period" in that he regarded it as a period during which the primary process occurring within the metal was the formation of cementite (Fe_3C) nuclei. Figure 7 shows a plot of Westerman's induction period versus temperature. This induction period was determined as the amount of time passed from introduction of the CO until some weight gain became perceptible. Westerman also reported that when the data were plotted as the logarithm of the induction period versus reciprocal absolute temperature, a linear plot was obtained. The apparent activation energy for this process was calculated to be 79.8 kJ/mole. Thus, Westerman asserted that since the activation energy corresponded approximately to the reported activation energy for the diffusion of carbon in α-iron (Wert, 1950) and since no other perceptible processes were occurring, the observed incubation period was the result of the activated formation of growth nuclei for the cementite crystal phase.

The significance of Westerman's induction period is not clear. The point is vaguely defined. However, if the point at which a weight gain becomes perceptible is taken as 0.2×10^{-4} mg/cm^2, a number typical for Westerman's data, then the incubation period corresponds to approximately 20 monolayers of carbon on the iron surface. If the process is autocatalytic, as most of Westerman's data show, then the induction period simply corresponds to the length of time required for the process to increase to an experimentally observable rate. Hence, the conclusion that the same process was not occurring during the induction period is incorrect.

Figures 8 and 9 show carbon deposition rates as a function of reciprocal absolute temperature. The carbon deposition rate is expressed as the sample weight gain per unit original surface area per unit time and was calculated from the slopes of experimental curves such as those in Fig. 6. In Fig. 8, the slope was taken at a time three hours after the induction period; while in Fig. 9, the slope was determined 16 hr after the start of the run. No reason was given for choosing these two times. The rates shown in Fig. 8 are slightly lower than those of Fig. 9, but there is good general agreement in the features of the two plots between 700 and 1000 K. The most readily apparent feature of these two plots is the rate maximum at approximately 830 K.

Westerman discusses the mechanism for two temperature regions - above and below 996 K. This is a logical dividing point as iron undergoes a phase transition from body-center cubic ferrite to face-centered cubic austenite at this temperature. In the region below 996 K, the mechanistic steps are postulated to be:

(1) Adsorption of CO on iron

(2) Boudouard reaction ($2CO \rightarrow C + CO_2$)

(3) Formation of cementite ($3Fe + C \rightarrow Fe_3C$)

(4) Decomposition of cementite to iron and carbon at the surface

(5) Repeat

Steps (1) and (2) were postulated to be fast and the observed temperature dependence of the rate was attributed to steps (3) and (4). In the region below 830 K, i.e., on the ascending portion of the rate curve, step (4) was reported to be fast and step (3) to be the rate limiting step. This was supported by several pieces of experimental evidence. First, the activation energy of the carbon deposition rate at temperatures below 830 K was shown to be about 84 kJ/mole. This activation energy is the same as the activation energy for the diffusion of carbon in α-iron which was shown by Wert (1949) and Zener (1949) to be the limiting step for the precipitation of cementite from solid solutions of carbon in α-iron. Second, since the decomposition of surface cementite is fast in this same temperature region, no large amounts of cementite should be formed at the surface. This was demonstrated by metallurgical etchings of surface cross sections.

Above 830 K, the rate of step (3) becomes faster than the rate of step (4), and step (4) becomes the rate limiting step. This was shown by a series of metallurgical etchings which show larger and larger amounts of surface and interior cementite formation as reaction temperature increases.

Westerman also noted that the initial iron catalytic activity was dependent on its specific history. Wires with very small grain size or those which had been cold-worked were found to be more active initially. Three separate lots of electrolytic iron were used in the experiments. However, the second lot used (wire II) had been cold-worked. Its atypical high initial rates can be seen in Fig. 6, where Run 21 was made using a sample of wire II. In Fig. 8 also, the atypical reactivity of samples of wire II can be noted below 996 K. Figure 9 shows that the high activity decreases with time in that after 16 hr, the samples of wire II show normal activity. It was found experimentally that annealing at high temperature and subsequent recrystallization resulted in more reproducible data. This can be seen in Figs. 8 and 9 where the points labeled "annealed" are samples of wire II annealed at 1225 K for 1 hr and then lowered to 700 K before reaction.

Ratliff (1968) in a subsequent Ph.D. thesis at Georgia Tech studied the first stages of reaction between pure carbon monoxide and single-crystal thin iron films in the temperature range 520-870 K. The single-crystal films were grown epitaxially on a crystal face of a sodium chloride substrate by vapor deposition. The thin film was subsequently annealed in vacuum and exposed to CO in pressures ranging from 0.67 to 133 N/m^2 for various lengths of time. Most runs were one hour long. Changes occurring at the iron surface were observed by electron microscopy. These observations showed the growth of a new phase which was determined by x-ray diffraction to be cementite, Fe_3C. The overall process observed was thus:

$$2CO \rightarrow C + CO_2 \tag{C}$$

$$C + 3Fe \rightarrow Fe_3C \tag{F}$$

Data were taken to determine the cross-sectional area and population density of the Fe_3C crystals as a function of time and CO pressure. These data indicated that the production of cementite was controlled by the diffusion of carbon in α-iron and followed an analytical model for the precipitation of Fe_3C from a supersaturated solution of carbon in α-iron similar to that described by Wert (1949) and Zener (1949). The rate of cementite formation (and hence CO disproportionation) was reported to be independent of CO gas phase pressure for pressures above 67 N/m^2. The overall activation energy for the process was determined to be 89.5 kJ/mole, a value which is in good agreement with the activation energy for the diffusion of carbon in α-iron as reported by Wert (1950). However, as in Westerman's thesis, the zero order rate dependence above 67 N/m^2 is not conclusively demonstrated. Ratliff based his assertion of a zero order rate dependence on a comparison of five experimental runs. All of the runs were at 623 K under CO pressures of 0.67, 13.3, 33.2, 67.0, and 133 N/m^2. The measured total surface cross-sectional area of the product cementite particles was shown to increase as the CO pressure varied from 0.67 to 67 N/m^2, but was approximately identical at 67 and 133 N/m^2. An extrapolation from this limited data to higher pressures may not be warranted.

Concerning the identification of iron surface phases by x-ray diffraction techniques, Ratliff states, "Not every pattern was completely solvable. However, the presence or absence of Fe_3O_4 and graphite was readily determinable in all instances due to their particularly characteristic patterns. Identification of the carbide was more complex. For cementite, there have been more than 100 interplanar spacings or d-spacings reported between the values of 0.989 and 6.943 A. Similar conditions exist for the Hägg carbide. Epsilon carbide and Fe_7C_3 have been reported to have thirteen and seventeen different reflections respectively between d-values of 1.04 and 4.40 A. Within the latter range, the d-spacings for either epsilon carbide or Fe_7C_3 correspond within the limit of error to reported spacings for either cementite or Hägg carbide. The problem is compounded by the fact that there is a degree of uncertainty with all the reported values..." "Magnetite, Fe_3O_4, was found to form on exposure of the films to the atmosphere." This explanation accounts for the large number of conflicting claims as to the nature of the "true" catalyst in CO disproportionation.

Indeed, the work of Nelson (1937) had shown that a clean iron surface upon exposure to air at room temperature rapidly formed a surface layer that when analyzed by electron diffraction appeared to be Fe_3O_4. Renshaw, Roscoe, and Walker (1970) had reported that α-Fe_2O_3 was the catalytically active species in disproportionation on iron catalysts based on extensive electron diffraction studies. In their discussion of results, however, they also admit that the species identified could have also have been "$Fe_{3-Z}O_4$ where $\frac{1}{3} > Z > 0$," and they also noted that the oxide layer was in all probability extremely thin (∿20 Å). Thus, it would appear that reports of iron oxide catalytic species based on electron diffraction evidence alone are very questionable.

2.2.2.4 Previous Experiments with the Bosch Process. Several aspects of the Bosch process have been explored by Stricoff (1972) and Wilson (1971) using small horizontal Vycor tube reactors with various types of iron catalysts ranging from single, solid rods of electrolytic-pure iron, coils of pure iron wire, to steel wool plugs. In most cases, the iron was degreased and reduced in hydrogen at temperatures between 850 and 1000 K before use. The reactors were single-pass with an analysis by gas chromatograph of the inlet and all outlet gases except water. The latter was determined indirectly by passing the gas through calcium carbide to convert the water to calcium hydroxide and acetylene.

$$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2 \qquad (G)$$

Acetylene concentrations were then used to back-calculate water yields. The analytical technique for the determination of water is questionable when carbon dioxide is present in the exit gases since when water reacts with calcium carbide, one of the reaction products is calcium hydroxide. The calcium hydroxide product is then free to react with CO_2 in the gas stream as follows:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \qquad (H)$$

Analytically, this would lead to artificially high values of water concentration and low values of CO_2 concentration. The analysis of hydrogen which was accomplished by difference was an additional source of error.

A number of different gas feeds and reaction temperatures were employed. As expected, with pure CO_2-H_2 feed gases over an iron catalyst, the only products found were CO and water. With pure CO-H_2 feed gases, there always was a rapid reaction with carbon and water as principal products; only traces of methane were ever found in the exit gas. In runs with carbon deposition, the product carbon fibers were examined in an electron microscope and the iron content of the carbon deposit measured. Electron micrographs of the fibers are shown in Figs. 10 and 11. These photographs were made at about 189,000X and 243,000X. The fibers exceed 1000 nm in length and are between 100 and 500 nm wide. An electron dense crystallite is clearly evident on most filaments. Many filaments also showed dark granular, electron-dense regions which probably represented the disintegration products of the heads during the growth process. Various authors refer to these carbon fibers as filaments. This suggests a cylindrical shape. Some, however, examined under high magnification (see Fig. 10 at 189,000X) appear to be in the shape of ribbons with a thickness of approximately 10 nm.

Wilson (1971) showed that the carbon ribbons are themselves catalytic as long as there is a reasonable concentration of iron. This was demonstrated by scraping the first carbon deposit from the iron rod after completion of a run. This carbon was used as the catalyst for a subsequent test. Several such dilutions were made in sequence, and it was found that as long as the iron concentration in the carbon was over 1-2%, the carbon remained an active catalyst. Photomicrographs of the dilute iron-carbon ribbons did, however, show that as the iron concentration decreased, fewer heads could be seen and these were smaller. Simultaneously, as noted above, there developed a granular structure along the ribbons which can logically be attributed to a non-

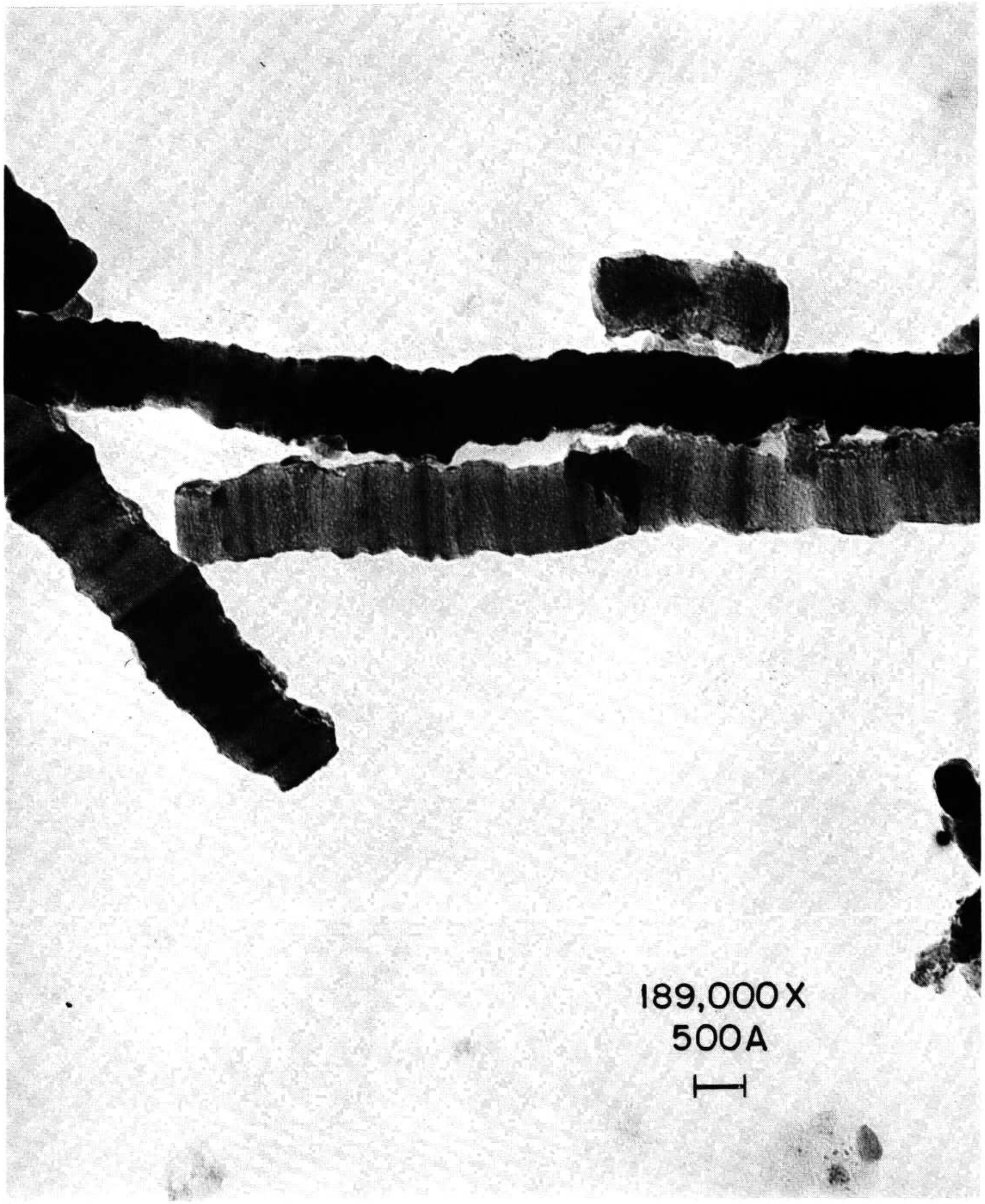


FIGURE 10

ELECTRON MICROGRAPH OF BOSCH CARBON

FIGURE 11

ELECTRON MICROGRAPH OF BOSCH CARBON

active dispersion of iron or iron carbide. The carbon had BET areas in excess of 60 m^2/g.

2.2.2.5 High Temperature Gas-Cooled Reactor (HTGR) Studies. The appearance of carbon filaments has been reported in a number of other investigations. However, the appearance of these carbon fibers as a corrosion product initiated considerable research in the Dragon Project, a program to develop a High Temperature Gas-Cooled Reactor (HTGR). The HTGR is a nuclear reactor with a graphite core. Heat released by nuclear reactions in the graphite core at 1073 K is transferred by a flowing helium stream to the tubes of a stream generator operating between 773 and 823 K. If any water from the steam generator leaks into the primary helium heat transfer media, the water reacts with the graphite core by

$$H_2O(g) + C(s) \rightarrow CO(g) + H_2(g) \tag{D}$$

However, in the steam generator, at lower temperatures than the core, the reverse reaction is free to occur on the catalytic steel heat exchanger tubes. As the observed carbon product does contain iron removed from the high pressure heat exchanger tubes, this phenomenon poses a serious corrosion problem sometimes referred to as "metal dusting." The investigations of Ruston et al. (1966, 1969) studied the solid phase effects of this corrosion. The only difference between HTGR corrosion studies and the previously mentioned Bosch investigations is the extremely dilute gas phase concentrations involved. In that HTGR corrosion and the Bosch process involve the reaction of the same gaseous reactants over nearly identical catalysts in the same temperature region, the two processes are expected to have many common features.

One study of HTGR corrosion by Karcher and Glaude (1971) reported attempts to develop an inhibitor to prevent carbon deposition on iron and steel surfaces.

A steel sample was hung in a heated combustion tube at 823 K from an electrobalance. Argon gas containing various amounts of CO, H_2, and possible inhibitors was passed through the combustion tube and carbon deposition monitored by weighing the steel sample. Several compounds were found to inhibit carbon deposition; for example SO_2 and silanes reacted irreversibly with the iron surface and covered it with an inert phase. SO_2 was visually determined to form FeS on the iron surface, while the silanes reacted to deposit a silicon film on the surface as determined by electron microprobe analysis. This mechanism was termed irreversible inhibition.

A second mechanism was proposed for inhibition by traces of CO_2, NH_3, or H_2O. This mechanism was termed reversible inhibition as the inhibitor did not react irreversibly with the catalyst. CO_2 and NH_3 were found to be weak inhibitors while water was found to be a strong inhibitor. The data reported are shown in Fig. 12. The first plot shows the ratio of carbon deposition rates with and without water versus the partial pressure of water in the gas stream. Replotting the data against the ratio of H_2 to H_2O partial pressures gives the second plot. As can be seen, the data for two concentrations of H_2 and CO are reduced to one curve when plotted on these coordinates; thus, it is the ratio P_{H_2}/P_{H_2O} which is important in determining the carbon deposition rate. Also apparent is that at a ratio of P_{H_2}/P_{H_2O} of about 20, the rate of carbon formation is zero (i.e., an equilibrium is achieved). The cause of this apparent "equilibrium" was not delineated. Karcher and Glaude speculated that the phenomenon observed was due to the competitive adsorption of the inhibitor on the catalyst sites with the reaction partners CO and H_2.

Everett (1967) and Everett and Kinsey (1965) studied the deposition of carbon on various steel surfaces from a helium stream containing carbon

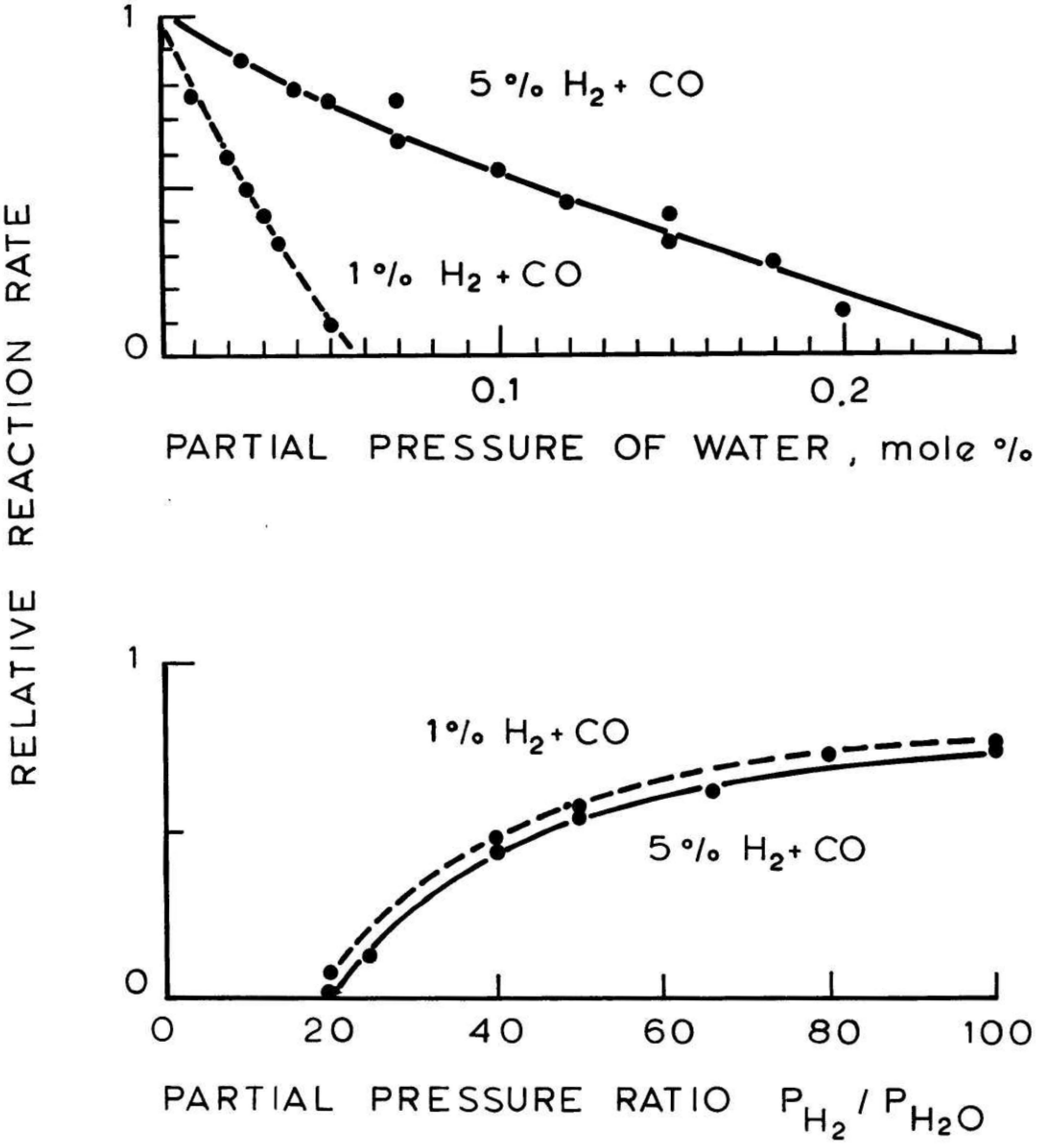


FIGURE 12, EFFECT OF WATER ON CARBON DEPOSITION AT 823 K (KARCHER AND GLAUDE, 1971) monoxide and hydrogen (less than 1 mole % each). A pump recirculated the gas stream continuously around a loop which contained an electrolytic moisture meter, a gas chromatograph, and an infrared gas analyzer to determine gas composition. A molecular sieve bed was used to adsorb product carbon dioxide and water from a portion of the total gas stream. The reactor was a long silica tube mounted in a tubular furnace. Catalysts including coiled iron wire and steel discs were tested.

Everett reported that, if helium containing 1% each of carbon monoxide and hydrogen was passed at a slow flow rate for a length of time over a set of identical isothermal iron specimens, the rate of carbon deposition was a maximum on the specimens at the entrance to the furnace and the rate decreased on successive specimens in the direction of flow. This observation was reported to be indicative of a reaction which is inhibited by its products. That is, if the carbon formation reaction has water or carbon dioxide as a product and if the water or the carbon dioxide inhibits the carbon formation reaction, one would expect the rate of reaction to be fastest at the entrance to the reactor where the concentration of products is lowest and to be slowest at the reactor exit where the concentration of products is highest. Similar experimental observations were made by Wilson (1971) for his experiments with an iron catalyst. In this experiment, an iron rod was mounted coaxially within a tubular flow reactor. After exposure to a flowing stream of hydrogen and carbon monoxide, the catalyst was removed from the reactor. A large quantity of carbon was found on the rod end nearest the reactor inlet, and no carbon was found on the rod end nearest the reactor outlet. The results of both authors are in agreement with the reports by other authors that water and carbon dioxide inhibit the carbon deposition reaction(s).

Everett performed two other series of experiments. The first series was to determine the effects of the hydrogen to carbon monoxide ratio, carbon monoxide concentration, and temperature on the rate of carbon deposition over a preactivated iron catalyst. The second series determined the rate of development of catalytic activity as a function of temperature, gas composition, steel composition, the nature of the steel surface, and time.

Typical results from the first set of experiments are shown in Fig. 13. This figure shows the rate of production of carbon calculated from the rate of appearance of carbon dioxide and water in the circulating gas stream as a function of temperature. The catalyst in these experiments was a length of coiled iron wire with 1000 cm^2 initial surface area which had been pretreated by several hundred hours exposure at room temperature to a gas mixture containing 0.5 atm each carbon monoxide and hydrogen. From these data, Everett concluded that the rate of production of carbon was approximately first order in carbon monoxide concentration at temperatures below 773 K (500 °C). The activation energy of the carbon deposition reaction is 41.8 kJ/mole from the data of Fig. 13 below 773 K. At temperatures above 773 K, equilibrium limitations caused the observed decrease in formation rates. Based on the data in Fig. 13, Everett reported that the carbon deposition rate from a helium stream containing equal amounts of hydrogen and carbon monoxide at 773 K could be expressed as

$$r = 6 \times 10^{-3} \times P_{CO} \qquad (1)$$

where:

r = carbon deposition rate, mg carbon hr^{-1} μatm^{-1} CO cm^{-2} of catalyst

P_{CO} = partial pressure of CO, μatm

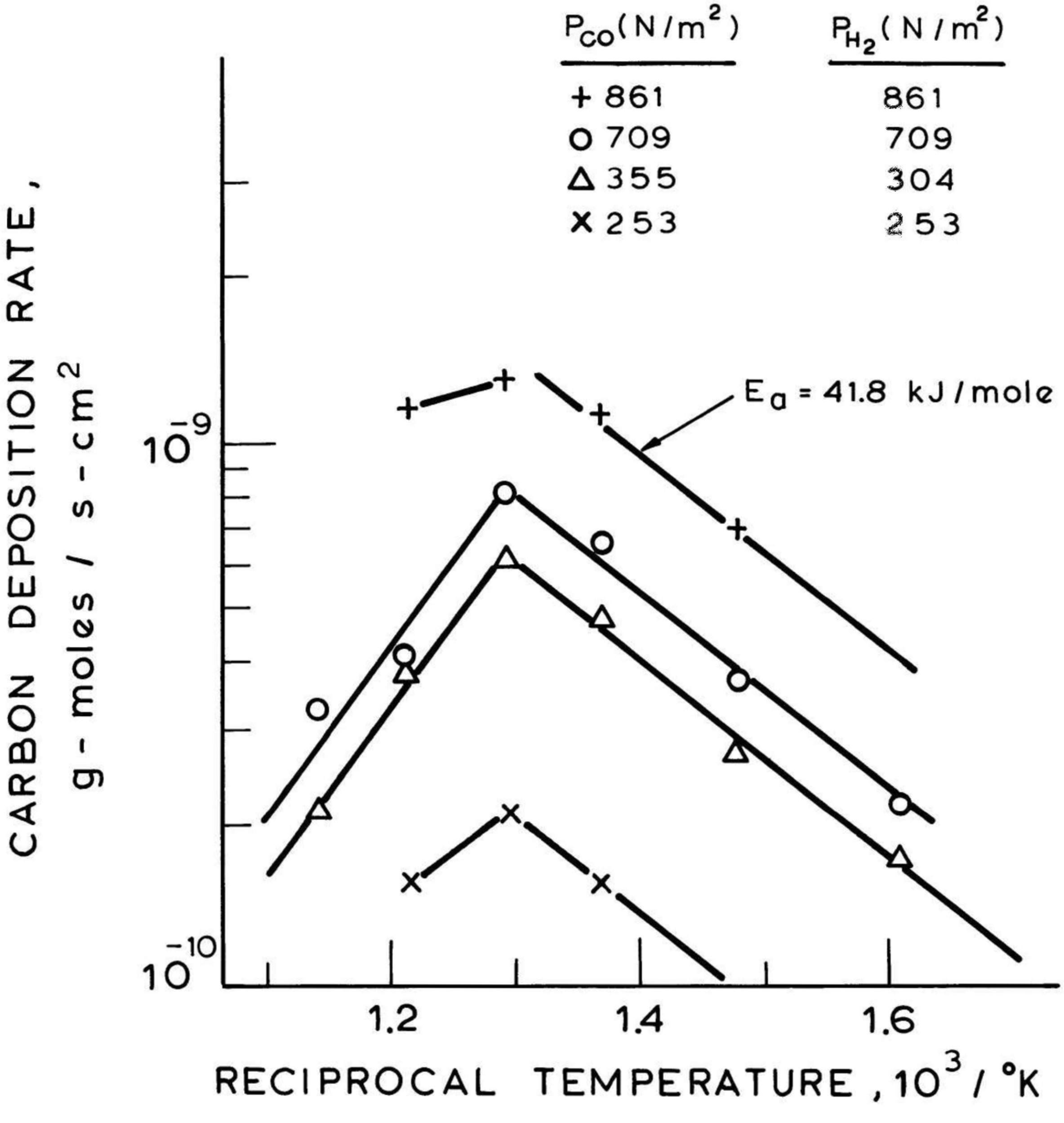


FIGURE 13, RATE OF CARBON DEPOSITION (EVERETT, 1967)

While the above expression adequately represents the four experimental data points at 773 K shown in Fig. 13, it applies only when the partial pressure of hydrogen and carbon monoxide are approximately equal. Specifically, it does not apply to the data of five other experiments reported by Everett with large ratios of carbon monoxide to hydrogen. However, in Fig. 14 the data presented by Everett at 773 K are replotted to show rate of carbon deposition as a function of the product of carbon monoxide and hydrogen partial pressures. The data points are the rate of carbon deposition calculated from the rates of formation of water and carbon dioxide given for all nine experiments reported by Everett. Also shown is the best line of slope 0.5 fitted by a one-constant least squares technique and drawn through the data. As can be shown from Fig. 14, the nine data points can also be represented adequately by the equation (based on initial iron area)

$$\text{rate (gmole/sec-cm}^2) = 1.39 \times 10^{-9} P_{CO}^{0.5} P_{H_2}^{0.5} \qquad (2)$$

where the component partial pressures have the units kN/m^2. This equation reduces approximately to Eq. (1) presented by Everett when the partial pressures of hydrogen and carbon monoxide are equal. If the 41.8 kJ/mole activation energy is included, the equation becomes

$$\text{rate} = 9.49 \times 10^{-7} \exp(-\frac{5050}{T}) P_{CO}^{0.5} P_{H_2}^{0.5}$$

However, in a second experiment, Everett showed that the catalytic activity of a steel sample was not constant, but rather increased with time. This was demonstrated using a single pass reactor containing 10 steel discs with a total initial surface area of 50 cm^2 and an inlet gas helium stream containing 1% each carbon monoxide and hydrogen at a total flow rate of one

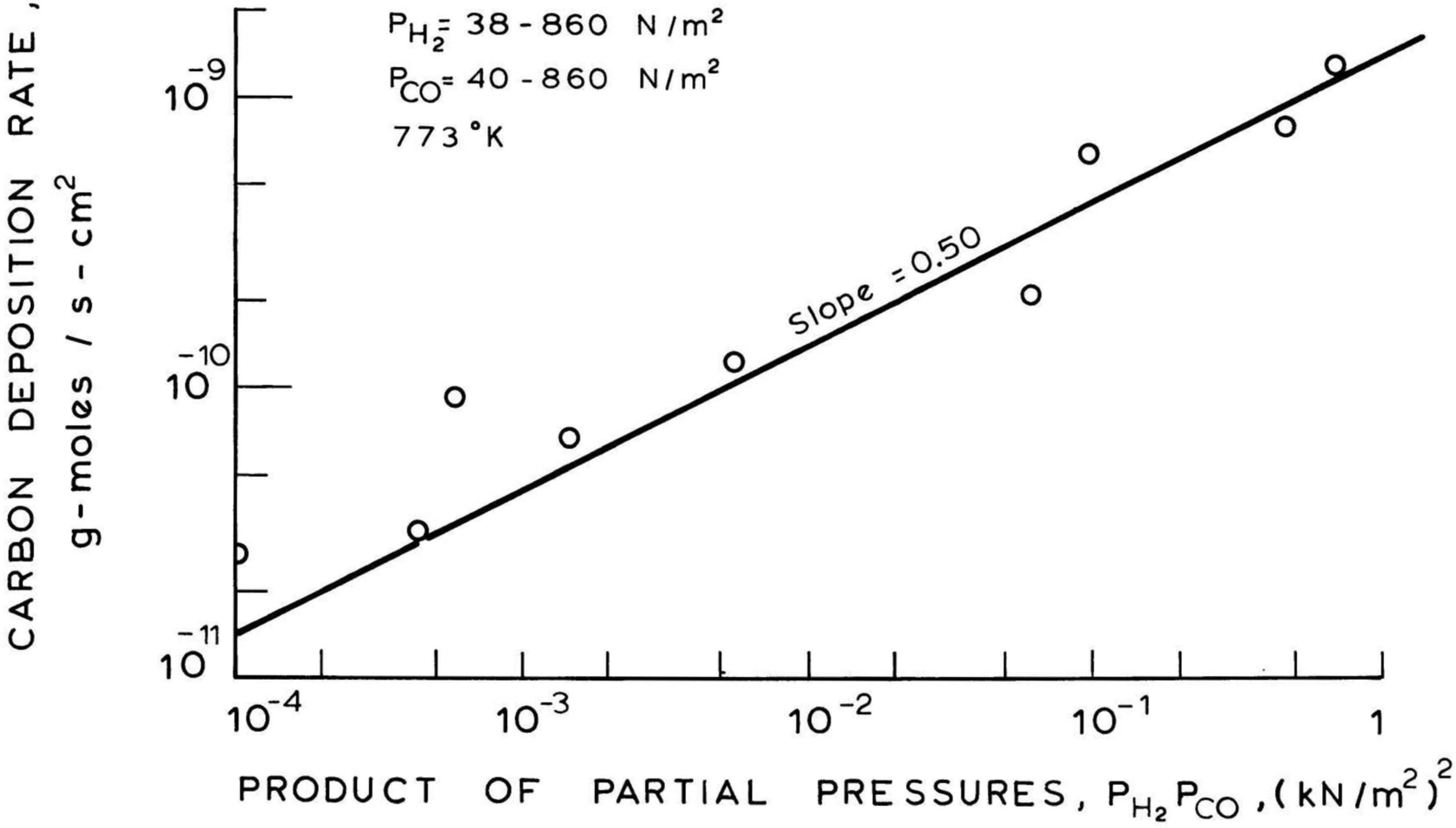


FIGURE 14, EFFECT OF H_2 AND CO ON CARBON DEPOSITION RATE liter/min. Results from this experiment are shown in Fig. 15 as the carbon deposition rate as a function of time. The weight percent iron contained in the carbon product is also shown as a function of time. As can be seen from this figure, the carbon product initially contained 25 wt % iron and the iron content of the product dropped until reaching a value of about 4.0 wt %. Also an "induction period" of approximately 70 hr was noted prior to achieving a linear increase in rate with time. Indeed, Everett reported that based on experiments with a wide variety of samples and carbon monoxide concentrations, the induction period was approximately equivalent to one atm-hr of exposure to carbon monoxide at 773 K. Some variation in this rule of thumb was noted for oxidized surfaces which were reported to require longer induction periods. Everett also reported that preoxidized samples, after the induction period, were significantly more active initially than were unoxidized samples. Similar increases in initial activity were reported for cold worked or stressed areas such as sawed faces and mechanically polished surfaces. In all cases, however, the initially high activity was only temporary and the samples after longer exposure periods behaved similarly to control samples. These results are very similar to those reported by Westerman (1967).

Finally, Everett noted that the carbon product was catalytically active. This was shown by removing the catalyst once a day and removing the product carbon with a stiff Nylon brush. As can be seen in Fig. 15, this produced a 75% decrease in the slope of the rate vs time curve. Everett concluded from this observation that most of the catalytic activity came from the metal surface itself rather than from the product carbon.

As mentioned previously, Everett and Kinsey (1965) attributed the decrease in carbon formation rates above 773 K to equilibrium limitations. More specifically, Everett and Kinsey advanced the hypothesis that carbon

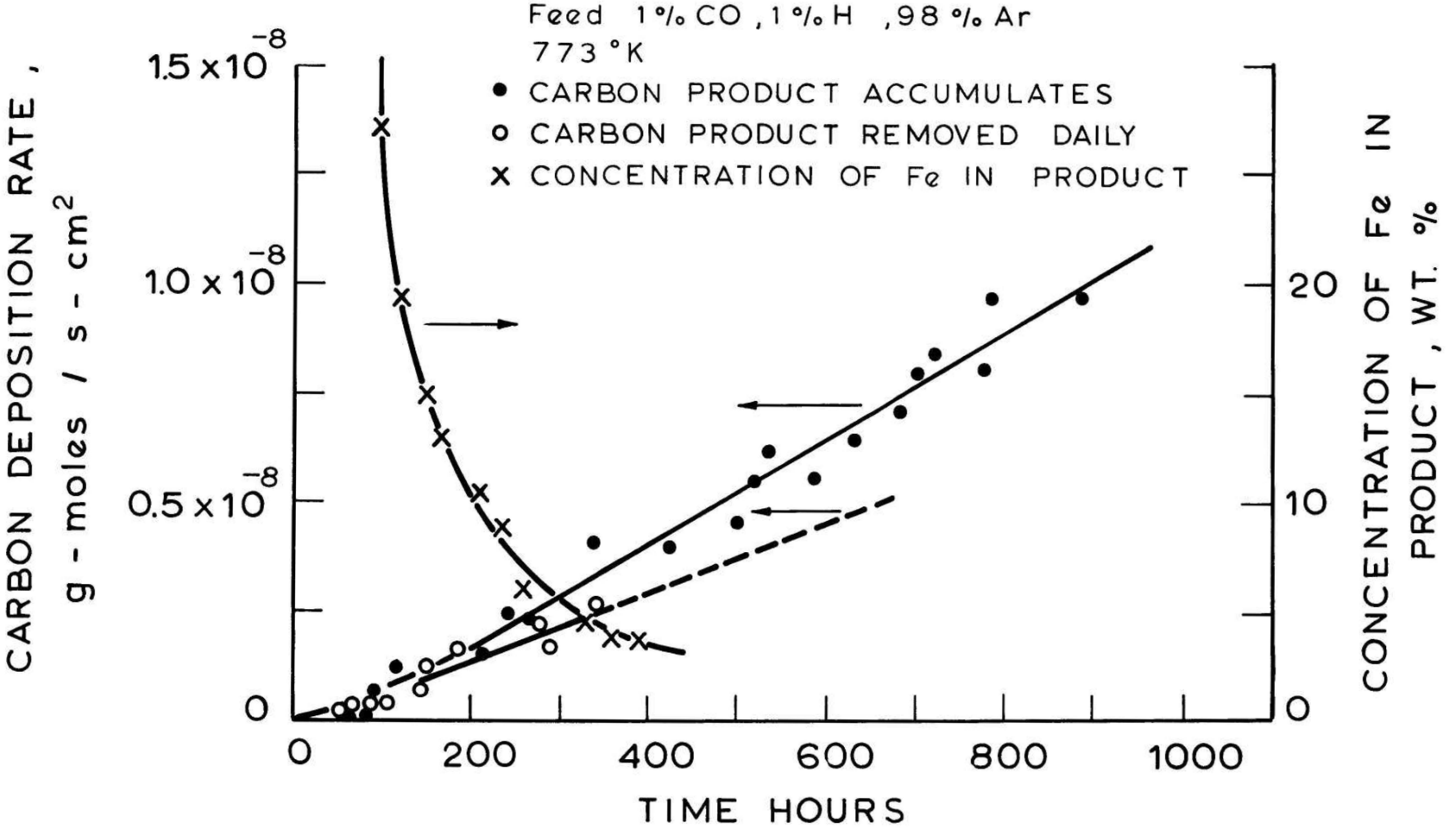


FIGURE 15, RATE OF CARBON DEPOSITION ON MILD STEEL (EVERETT, 1967) *deposition would occur only on a metallic iron surface and not on an oxidized surface*. As the gas phase systems they considered contained mainly H_2, H_2O, and CO, they regarded the H_2/H_2O ratio as the primary criterion for possible carbon deposition (i.e., the H_2/H_2O ratio had to be such that the reactions

$$H_2 + FeO \rightarrow H_2O + Fe$$

or

$$H_2 + \frac{1}{4}Fe_3O_4 \rightarrow H_2O + \frac{3}{4}Fe \qquad (I)$$

would proceed from left to right and the stable metal phase would be reduced iron). The second criteria was that the $C\text{-}H_2\text{-}H_2O\text{-}CO\text{-}CO_2$ equilibria were favorable for carbon deposition.

The hypothesis of Everett and Kinsey (1965) was tested by Warzee *et al*. (1967) who investigated the inhibition of carbon deposition on various iron alloys by surface oxide layers formed from the alloying elements. The effects of surface pretreatment was also examined by comparing identical specimens which had been either electropolished in an aceto-perchloric acid bath or cold-worked by milling. The alloy samples were first exposed to four gas mixtures containing H_2, CO, H_2O, CO_2, and argon diluent as shown in Table 1.

Table 1. Experimental Gas Mixtures Employed by Warzee *et al*. (1967)

	Compositions in vol %				
Mixture	CO	CO_2	H_2	H_2O	Ar
1	0.05	0.005	0.05	0.005	balance
2	5	0.5	5	0.5	balance
3	0.05	0.0005	0.05	0.0005	balance
4	5	0.05	5	0.05	balance
test	20	-	20	0.0005	60
Ar-CO	50	-	-	-	50

The gas compositions are such that the ratios

$$\frac{P_{H_2}}{P_{H_2O}} = \frac{P_{CO}}{P_{CO_2}} = 10 \text{ for mixtures 1 and 2}$$

and

$$\frac{P_{H_2}}{P_{H_2O}} = \frac{P_{CO}}{P_{CO_2}} = 100 \text{ for mixtures 3 and 4}$$

These mixtures were selected for specific reasons. First, according to the hypothesis of Everett and Kinsey (1965) no carbon deposition is possible at 823 K from exposure of any sample to gas mixture 1. Also, all gas mixtures had compositions such that at 823 K the alloying elements Cr, Mn, Si, and Al would be oxidized to Cr_2O_3, MnO, SiO_2, and Al_2O_3, respectively; yet, under these conditions the iron would not be expected to be oxidized. Alloy samples were exposed to one of the gas mixtures at 823 K for a period of 120 hr, and then to a test mixture containing 20% CO, 20% H_2, 5 ppm H_2O (by volume), and 60% argon for 24 hr. The results of the initial exposure to gas mixtures 1, 2, 3, and 4 and the final exposure to the test mixture varied considerably for the alloys tested and depended also on the surface preparation. Basically, however, a complete surface oxide coating consisting of oxides of the alloying elements (mainly a spinel oxide, $MnO \cdot Cr_2O_3$) which could not be reduced under the test conditions was found to protect the subsurface iron alloy from both surface and grain boundary carbon deposition. Only ferritic chromium steel in the annealed state (electropolished surface) with 13% chromium was found to develop protective oxide coatings under all the experimental conditions employed. In a subsequent test it was shown that pretreatment of the ten alloy specimens with a hydrogen stream containing 5 ppm H_2O and 2 ppm O_2 (by volume) at 1073 K gave a protective oxide layer on all steel specimens which resisted carbon formation when exposed to gas mixture 4 for 120 hr at 823 K.

2.2.3 Methane-Forming Reactions

Several mechanisms for the formation of methane are possible. Compared to the direct hydrogenation of graphite, the hydrogenation of carbon obtained from decomposition of iron carbides has been reported to be much faster. Browning, DeWitt, and Emmett (1950) reported that a small amount of free carbon present while measuring the equilibrium of reaction (J)

$$CH_4 + 3Fe(\alpha) \rightleftarrows Fe_3C(\beta) + 2H_2 \qquad (J)$$

in the range 575 to 625 K did not affect the value of the equilibrium constant measured and concluded that the formation or reduction of free carbon was slow compared to the formation or reduction of the carbide.

Walker *et al.* (1959) reported that methane was formed when an "inactive" iron catalyst was treated with hydrogen at 873 K. The catalyst had become inactive in producing carbon from carbon monoxide-hydrogen mixtures and was determined by x-ray diffraction to contain only graphite and iron carbide. Treatment with a flowing stream of hydrogen at 873 K served to regenerate the catalyst. During the regeneration process, however, volumetric gas data from wet-test meters indicated that 0.50 g of free carbon had been converted to methane. This was subsequently found to be in agreement with gravimetric data. The production of methane from 0.50 g of carbon from a bed containing 0.10 g iron indicated that some methane was formed from free carbon rather than from the carbide. After reactivation the iron catalyst was found to contain only α-iron by x-ray diffraction.

Podgurski *et al.* (1950) reported that samples of iron containing carbidic carbon could be reduced with hydrogen (to produce methane) at 573 K in 16 hr. They commented that under similar conditions the removal of free carbon at a reasonable rate would require temperatures in the range of 773 K.

Karcher and Glaude (1972) reported that the direct formation of methane from nuclear graphites in hydrogen atmospheres with no catalyst depended on the square of the hydrogen partial pressure. In examining the rate of disappearance of the carbon between 873 and 1423 K, they also reported that the apparent activation energy of the process below 973 to be about 210-250 kJ/mole. In addition, they reported that the reaction was so slow at 873 K that a weight loss and gas chromatographic technique could not be used to determine the activation energy or formation rate accurately.

In summary, previous investigations have found that methane is not formed at observable rates by direct hydrogenation of carbon at temperatures below 823 K. At these same temperatures, methane can be formed by reduction of iron carbide with hydrogen. Moreover, in experiments where hydrogen was passed over carbon containing an iron catalyst, methane was formed at temperatures below 823 K. However, as the amount of methane formed exceeded the maximum amount that could be formed by reduction of carbide alone, it is probable that carbon is being converted to a carbide and then converted to methane.

2.2.4 C-H-O-Fe Equilibria

2.2.4.1 Phase Rule Considerations. As indicated earlier, the equilibrium between a gas phase containing $CO-H_2-CO_2-H_2O-CH_4$ and a solid carbon phase has been discussed by Tevebaugh and Cairns (1964). Using the phase rule, they showed that by specifying the temperature, pressure, equilibrium constants from three independent reactions, and the O/H ratio of the gas phase, the final equilibrium state of the system was fixed. Algebraic equations relating the mass balances and equilibrium constraints were derived and solved numerically. Results were presented in both tabular and graphical form such as those of Fig. 3. It should be noted, however, that the results of Tevebaugh and Cairns are applicable to the Bosch process only if the iron catalyst does not react with any other components so as to affect the mass or equilibrium constraints and if the system can react to form the equilibrium mixture.

In the event that other solid phases such as iron oxides or carbides are present and react with the gaseous components, the computed equilibrium gas phase concentrations are different from those found by Tevebaugh and Cairns. For example, consider an equilibrium system containing five components in the gas phase (CO_2, H_2, CO, H_2O, CH_4) and two components, iron (α-Fe) and iron oxide (Fe_3O_4), as solid phases. Assume that carbon formation is not possible. An application of the phase rule shows that the number of variables, V, required to completely specify the system consisting of seven components, C, and three phases, P, is

$$V = C - P + 2 = 7 - 3 + 2 = 6$$

Thus, the following set of variables is a sufficient set to specify the equilibrium:

(1) pressure
(2) temperature
(3) C/H ratio in the gas phase
(4)-(6) equilibrium constants from the following set of independent reactions:

$$H_2O + \frac{3}{4}\,Fe \rightleftarrows H_2 + \frac{1}{4}\,Fe_3O_4$$

$$CO_2 + \frac{3}{4}\,Fe \rightleftarrows CO + \frac{1}{4}\,Fe_3O_4$$

$$CH_4 + H_2O \rightleftarrows 3H_2 + CO$$

This set of conditions can be transformed into five simultaneous, non-linear algebraic equations with five unknown variables, the gas phase component concentrations, by an approach similar to that of Tevebaugh and Cairns. The equations may be solved numerically to produce the graphical result shown in Fig. 16. In this figure, a triangular diagram of the C-H-O gas phase system is shown for a temperature of 800 K and total pressure of 1 atm. The curve abc on the diagram represents the carbon deposition boundary calculated by Tevebaugh and Cairns. The curve dbe represents the iron-iron oxide boundary calculated by the above approach. Thus, an equilibrium gas mixture with C-H-O composition represented by a point in the region above the curve dbe would be in equilibrium with one solid phase, iron. Conversely, a gas mixture represented by a point in the region below the curve would be in equilibrium with iron oxide. For points on the curve, the gas phase will be in equilibrium with both solid phases.

In addition, consider an equilibrium system at fixed temperature, again containing the same five components in the gas phase but in equilibrium with the three solid phases: iron, iron oxide and carbon (β-graphite). Another application of the phase rule shows that the number of variables required to completely specify the equilibrium state of the system is again

$$V = C - P + 2 = 8 - 4 + 2 = 6$$

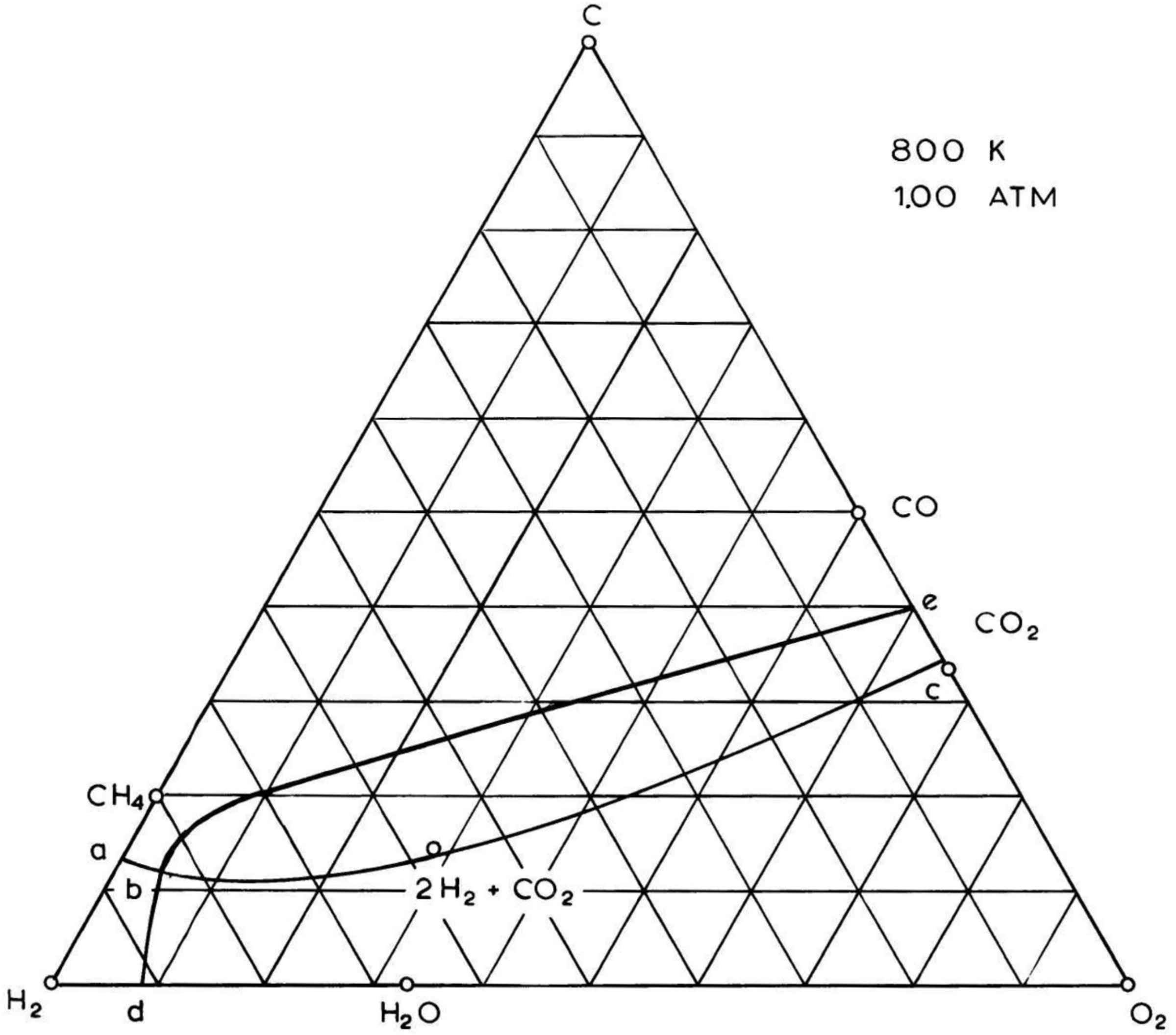


FIGURE 16, C-H-O TRIANGULAR DIAGRAM WITH SOLID PHASE EQUILIBRIA

The total number of variables to be specified has not increased because the effect of addition of a new component is countered by the requirement that an additional phase be present at equilibrium. In this case, the following set of variables is selected as sufficient to specify the equilibrium:

(1) pressure

(2) temperature

(3) - (6) equilibrium constants from the following independent reactions:

$$H_2O + \frac{3}{4} Fe \rightleftarrows H_2 + \frac{1}{4} Fe_3O_4$$

$$CO_2 + \frac{3}{3} Fe \rightleftarrows CO + \frac{1}{4} Fe_3O_4$$

$$C + 2H_2 \rightleftarrows CH_4$$

$$C + CO_2 \rightleftarrows 2CO$$

Thus, after specifying the temperature, pressure, and equilibrium constants, the equilibrium state of the system is specified and the O/H ratio of the gas phase is fixed. The equilibrium gas mixture in this circumstance will have the C-H-O composition represented by the intersection of curves abc and dbe. Only at this intersection, point b, will the three solid phases of iron, iron oxide, and carbon coexist with a gas phase containing H_2-CO-CH_4-CO_2-H_2O.

The preceding equilibrium considerations indicate the complexity involved if formation of Fe_3O_4 is possible at 800 K. Similar results are obtained above 860 K where the stable iron oxide is FeO. Similar computations could be performed for the iron carbides if equilibrium data were available. The major implication of the analysis is, however, that the computed equilibrium gas phase compositions are affected by the phase rule assumption that the solid phases present and reactions possible are known.

2.2.4.2 Iron Carbides. Iron carbides ranging in Fe/C ratio from 3 to 1 have been reported by several authors. Among the authors there is little general agreement on the stoichiometry and properties of any carbide except cementite, Fe_3C (also known as θ-iron carbide). Hansen (1958), Elliott (1965), and Shunk (1969) have critically reviewed the available reported data from which the accepted iron-carbon phase diagram has been derived. These authors present two-phase diagrams for the iron-carbon system representing the differing data obtained from experiments with the stable iron-graphite equilibrium and the metastable iron-iron carbide equilibrium. Shunk states that crystalline structure of Fe_3C has been confirmed by several investigators, but that higher carbides have not been uniquely identified as to structure and composition.

In 1932, Hägg had reported the existence of a new carbide, Fe_2C (also known as Hägg carbide or χ-carbide). The detection and stoichiometry of this carbide were determined by x-ray diffraction. Jack (1946) announced the discovery of a new iron percarbide, $Fe_{20}C_9$, which resulted from the tempering of martensite at temperatures between 473 and 773 K. The carbon content of the carbide was reported to be 30.5-32.1 atomic percent carbon and identical to Hägg carbide. The stoichiometry $Fe_{20}C_9$ was based on x-ray diffraction measurements of the crystal cell parameters and the observed carbon content. The unstable carbide was not formed if tempering occurred above 773 K. Moreover, the carbide was also found to decompose rapidly to Fe_3C and carbon at 773 K. Duggin and Hofer (1966) and Jack and Wild (1966) concluded that the carbide was actually Fe_5C_2 (or $Fe_{20}C_8$). Hägg carbide was shown to be isomorphous with Mn_5C_2 by demonstrating that the unit cell dimensions of the solid solution carbides, (Fe, Mn)$_5$C$_2$, were linear functions of composition over the entire concentration range from Mn$_5$C$_2$ to Fe$_5$C$_2$. Hofer, Cohn, and Peebles (1949) had previously demonstrated by thermomagnetic measurements that two crystalline modifications of Hägg carbide existed. The first carbide, which they identified as "hexagonal close packed" Hägg carbide, was differentiated by its Curie point at 523 K and found to decompose to Hägg carbide at 573 K. Hägg carbide had a Curie point of 653 K and decomposed at 823 K.

A third iron carbide, FeC, was reported by Eckstrom and Adcock (1950). This carbide was first detected by x-ray diffraction of an iron catalyst from a pressurized (27 atm) hydrocarbon synthesis reactor. Chemical analysis of the catalyst indicated 77.4 wt % iron and 17.4 wt % carbon. The carbide decomposed rapidly at 873 K and had a Curie point of 523 K. Louw _et al_. (1957) reported finding a similar carbide in a Kellogg Synthol reactor operating at 20 atm. Kohn and Eckart (1962) also observed this carbide among the reaction products from a high temperature, high pressure ($\sim 5 \times 10^4$ atm) diamond synthesis reactor. Thus, the three reported observations of this carbide have common origins in pressurized reactors where either carbon or carbon forming materials were present. Further x-ray diffraction experiments by Herbstein and Snyman (1964) showed that the carbide was isomorphous with Cr$_7$C$_3$ and, hence, that the carbide was stoichiometrically Fe$_7$C$_3$.

McCartney _et al_. (1953) employed x-ray and electron diffraction to discriminate between surface and bulk carbide phases in iron catalysts from Fischer-Tropsch reactors. In all cases, no carbides were found in the surface layer of the catalysts. Both cementite and Hägg carbide were found in the interior of the catalyst samples. In no case were reflections similar to those of Eckstrom and Adcock found.

Podgurski et al. (1950) reported on the preparation, stability, and absorptive properties of cementite (Fe_3C), hexagonal Hägg carbide, and Hägg carbide. The composition and stability of the carbide formed depended on the compound used to carbide the catalyst sample. Specifically, for all samples carbided with carbon monoxide, 0.3% oxygen was invariably found in the carbide while no oxygen was found in samples carbided with hydrocarbon gases. Samples of Hägg carbide prepared by both procedures decomposed when heated to 673-723 K in vacuum. However, samples of cementite formed by the carbon monoxide carburization were indefinitely stable at 773 K in vacuum while cementite formed by hydrocarbon carburization decomposed under the same conditions. The additional stability of the former samples was attributed to the small amount of residual oxygen. Carbon monoxide would not adsorb on any of the carbides at temperatures above 373 K. Yet, at temperatures above 423 K, carburization of iron was so rapid that adsorption measurements could not be made on reduced iron. Thus, Podgurski et al. (1950) concluded that a carbide could not be an active catalyst in forming hydrocarbons or carbon since iron carbides could not adsorb the necessary reactants.

2.2.4.3 Reactions of Iron Carbides. Browning et al. (1950) measured the equilibria for the reactions:

$$CH_4 + 3Fe\ (\alpha) \rightleftarrows Fe_3C + 2H_2 \qquad (J)$$

$$CH_4 + 2Fe\ (\alpha) \rightleftarrows Fe_2C + 2H_2 \qquad (K)$$

Both these reactions are similar to reaction (E) except that the source of carbon for the methane is an iron carbide instead of β-graphite. The equilibrium constant for reactions (E), (J), and (K) is

$$K_p = \frac{P_{H_2}^2}{P_{CH_4}}$$

Browning et al. experimentally determined the partial pressures of hydrogen and methane in mixtures which had been equilibrated with an iron-iron carbide sample. The calculated equilibrium constants are shown in Fig. 17 along with a straight line fitted by a least-squares technique to the data. Open circles represent data obtained by approaching the equilibrium from the hydrogen-rich side of the equilibrium while closed circles represent equilibrium data approached from the methane-rich side. However, in the experiments approaching the equilibrium from the methane-rich side, the largest observed change in methane concentration was approximately 3%. Also shown in Fig. 17 is a line representing the equilibrium constant for reaction (E) calculated from the JANAF Thermochemical Tables (1971). The two dotted lines in Fig. 17 represent the equations presented by Browning et al. for the equilibrium constants for reactions (J) and (K). The equilibrium constant for reaction (K) was determined in the temperature range 568-623 K while those shown for reaction (J) were determined in the temperature range 593-741 K. The overlap in the temperature range for the correlations presented is not justifiable and violates the phase rule. Hence, a single line has been fitted to the data over the entire temperature range.

In the temperature range investigated by Browning et al. the equilibrium constants for reactions (J) and (K) differ from that of (E) by almost an order of magnitude. The difference, however, becomes smaller with increasing temperature. In fact, at 823 K, the difference has dropped to a factor of 2 and at 900 K, a factor of 1.37. As the Bosch process normally is accomplished in the temperature range 800-950 K, the effect of a carbide equilibrium

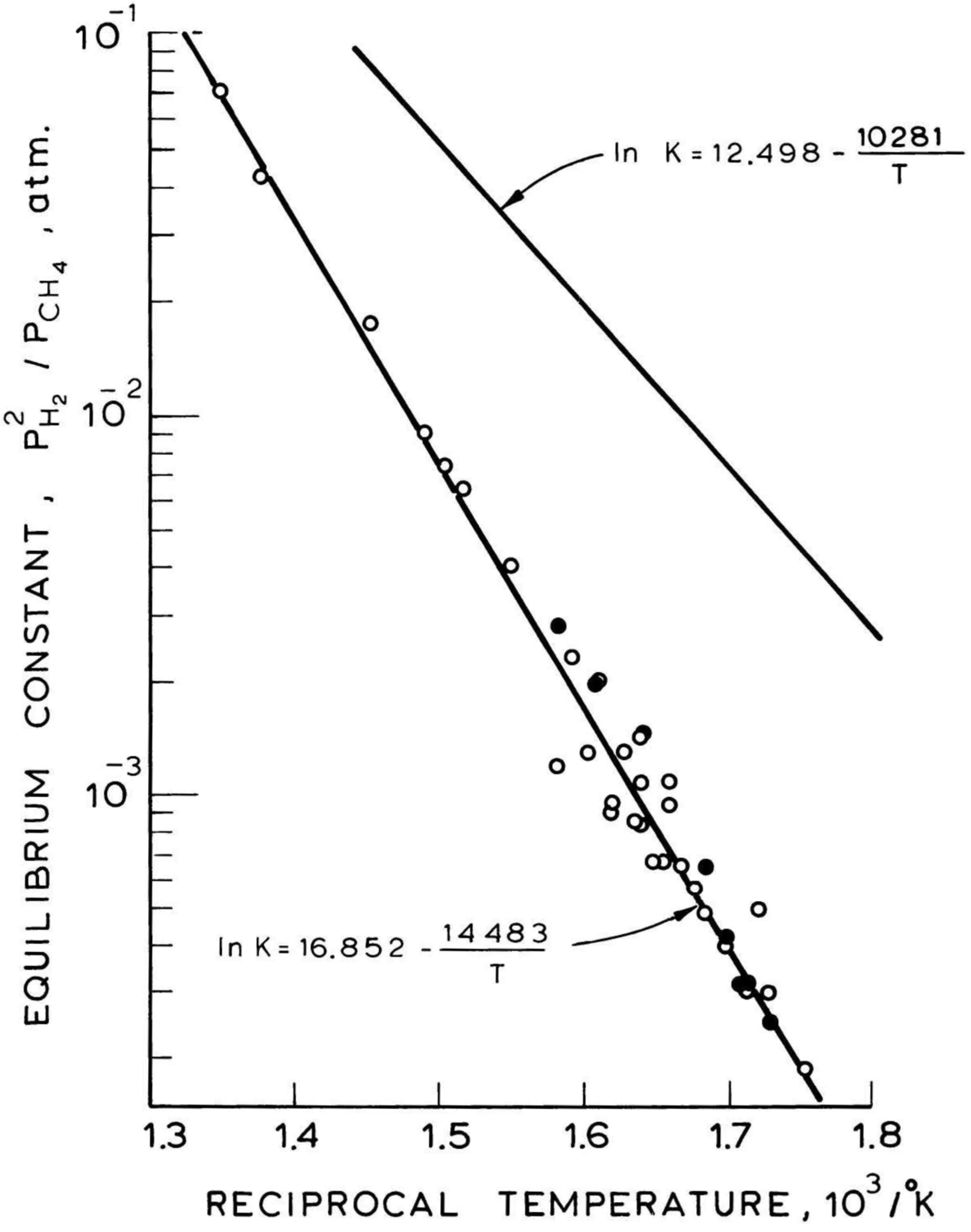


FIGURE 17 IRON CARBIDE FORMATION EQUILIBRIUM (DATA OF BROWNING et al., 1950)

phase should be small but detectable. Moreover, all authors agree that in this temperature range Hägg carbide, Fe_5C_2, and the Eckstrom and Adcock carbide, Fe_7C_3, are unstable and would decompose rapidly to form cementite and carbon.

2.2.5 Filament Growth Mechanisms

In many experiments involving the deposition of carbon on metal catalysts, an electron microscopic examination of the product carbon has revealed a "fibrous" or "filamentary" carbon. However, few explanations have been proposed to explain the growth mechanisms of these carbon fibers.

One mechanism to explain how iron could be removed from a catalyst surface and appear in a carbon product at a distance removed from the surface was advanced by Fleureau (1953), who proposed that a volatile iron carbonyl was formed by the reaction of carbon monoxide with the iron surface. The volatile iron carbonyl was then able to diffuse through the gas phase to the carbon surface where it decomposed. However, Fischer and Bahr (1928) had demonstrated that a volatile carbonyl was not responsible for the presence of iron in the carbon deposit by a rather simple experiment. Using an iron-copper catalyst heated to 773 K in the presence of CO, they formed a carbon product containing both iron and copper. As copper does not form a carbonyl, the formation of a carbonyl could not be responsible for the appearance of copper in the carbon product. Thus, some other mechanism is responsible for the transfer of the metal.

Davis, Slawson, and Rigby (1957) also suggested a mechanism to explain the growth of carbon fibers. Their concept to describe the growth of the fibers is as shown in Fig. 18. The first stage is the reduction of any iron oxides to iron and then to carbide by carbon monoxide. Subsequently, the

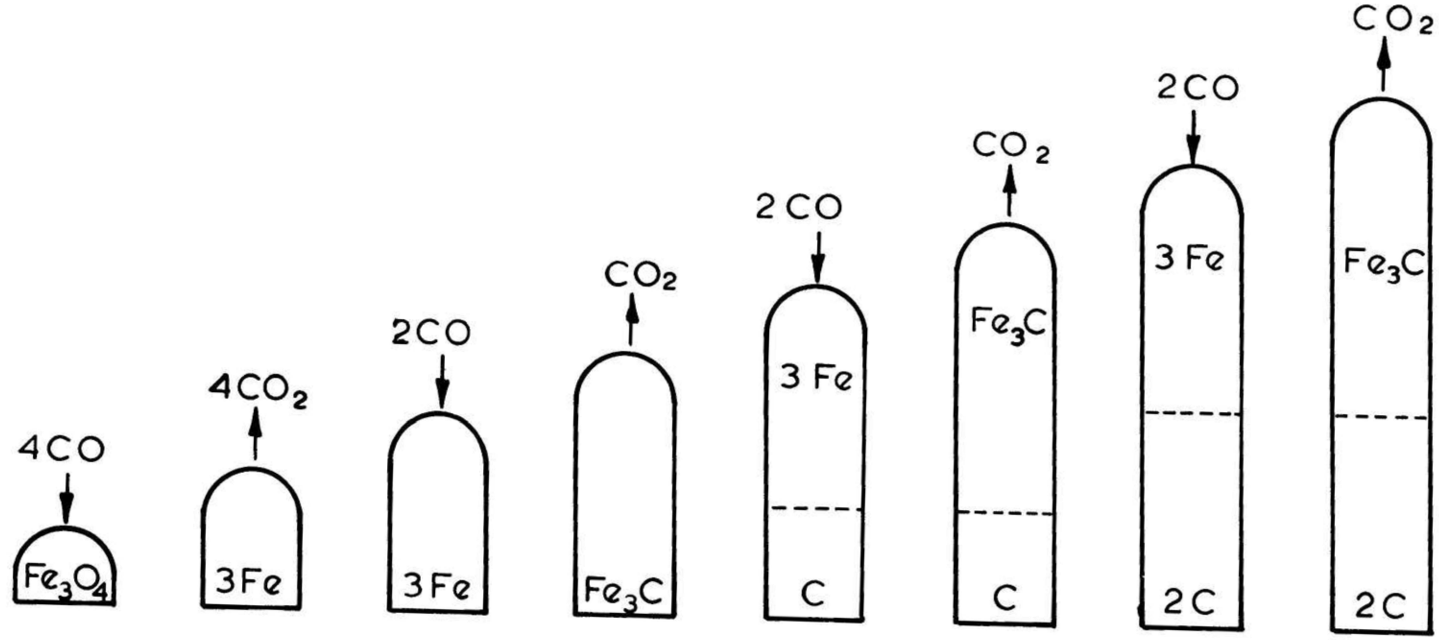


FIGURE 18, SUGGESTED FIBER GROWTH MECHANISM (DAVIS et al., 1965) decomposition of the iron carbide adds carbon to the growing "tail" while the iron "head" is again able to react with carbon monoxide. By this mechanism, the active iron "head" is moved away from its origin as the carbon fiber grows.

Boehm (1973) studied the nature of carbon fibers deposited from hydrogen-carbon monoxide streams on nickel carbonyl, iron carbonyl, Raney nickel, and powdered iron. By comparison of the resultant carbon, several conclusions were drawn. The first was that nickel and iron form different types of carbon fibers. The fibers formed on nickel are hollow, thin-skinned tubes, while those formed on iron are fine, dense fibers apparently containing bands and kernels of iron. Boehm concluded that the formation of carbon fibers on nickel and iron followed different mechanisms. The tubular shape of the carbon found from nickel carbonyl was explained by assuming that nickel in the form of globular particles and chains of fused particles analogous to carbon blacks had formed during pyrolysis of the carbonyl. Subsequent deposition of carbon on the nickel surface and leaching of the nickel during hydrochloric acid washing of the carbon served to leave only the outside carbon shell.

The carbon fibers formed from either iron carbonyl or reduced iron oxide appeared in a variety of shapes. Helically twisted filaments, tubes, and straight strands were all found. Indeed, some of the straight strands were noted to show low contrast indicating ribbon-like structures rather than a rod-like structure of circular or rectangular cross-section. Boehm also reported that extensive fibrous growth was only noted for carbon monoxide-hydrogen mixtures. In a pure carbon monoxide stream, only "empty skins" and "densely agglomerated material" were reported.

In 1972 Baker and Harris reported the development of a new instrumental technique, controlled atmosphere electron microscopy. In this technique a gas reaction cell is mounted on the viewing stage of an electron microscope. Provisions are made for heating the stage from ambient to 1500 K with a platinum ribbon resistance heater. Flow channels allow the introduction of gases at pressures up to 30 kN/m^2 (0.33 atm). The video display of the electron microscope is electronically recorded for later analysis. Using this technique, Baker _et al_. (1972) were able to observe directly the sequence of events occurring on a nickel surface during acetylene decomposition.

Baker _et al_. (1972) advanced an hypothesis which attempted to explain both the "hollow core" reported by many authors and the "kernel" of metal or carbide at the fiber tip. The proposed model is shown in Fig. 19. In (a) a crystallite has been liberated from the support - for iron this could be by the mechanism proposed by Ruston _et al_. (1969). Gas phase components such as methane, acetylene, carbon monoxide are then free to react and deposit carbon on the crystallite as shown in (b). Carbon can be taken into solution in the metal. A concentration gradient of carbon results and carbon diffuses through the crystallite to be deposited predominantly in the protected regions to produce the situation shown in (c). The precipitation of carbon at the rear of the particle builds up a deposit of carbon which forces the particle away from the support as shown in (d). If diffusion through the particle is slow enough to limit the rate of the above process, then eventually the surface of the entire crystallite will be covered with carbon and catalytic activity will cease as shown in (e). The shape of the catalytic crystallite and differing diffusion paths lead to the hollow cores shown in (d) and (e). Baker _et al_. (1972) alleged that the diffusion of

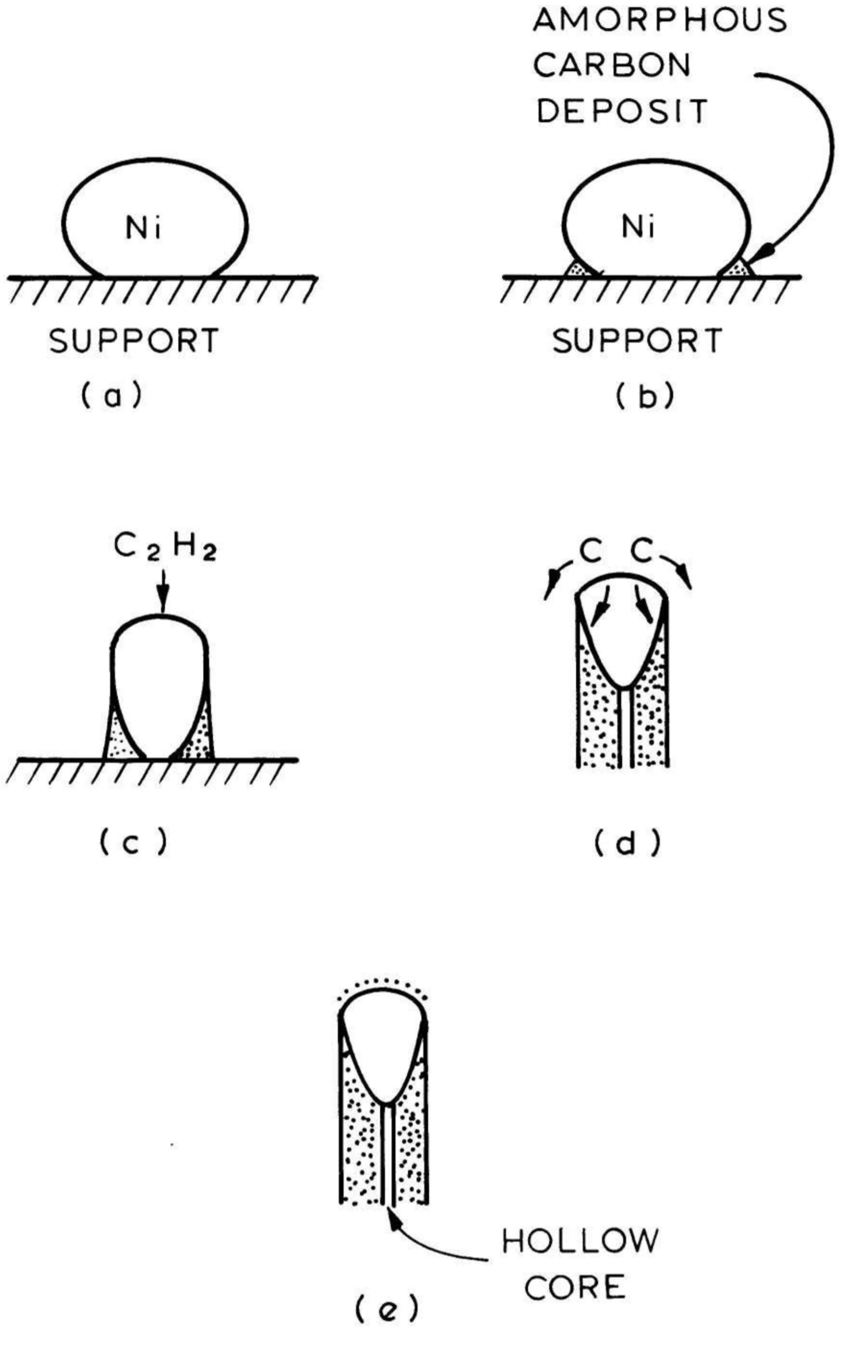


FIGURE 19, FIBER GROWTH MECHANISM (BAKER et al., 1972) carbon through the crystallite was caused by a thermal gradient. Their proposition was that the exothermic reaction occurring at the exposed surface caused a temperature gradient across the particle. In support of their hypothesis, they pointed out that the activation energy for the observed reaction was the same as the reported activation energy for the diffusion of carbon in nickel.

In Fig. 19 the metal crystallite is shown to have formed initially on the silica and graphite support material used to mount the specimen. While nucleation of 30-nm particles by heating microscopically-thin films on various supports is conceivable, the nucleation mechanism of such small particles from a planar surface of the same metal is not. Yet, Baker et al. report that identical behavior was observed when a nickel strip was substituted for the supported nickel-thin film. No detailed observations of the initial crystallite formation on the metal surface were given in that only an edge view was possible with the metal sample.

Evans et al. (1973) reported that impurities were responsible for the formation of filamentous carbon growth in methane gas samples. They studied the growths formed on electron microscope grids of nickel, iron, and stainless steel in atmospheres of methane and acetone. Several grades of methane including commercial, ultra pure, and research-grade were used. It was noted that filamentary carbon was never observed below 1173 K with exposure of ultra pure or research-grade methane to the grids. With commercial-grade methane or acetone, however, filamentous carbon was formed at all temperatures above 873 K. It was thus concluded that an impurity such as acetone must be responsible for the growths from "commercial"-grade methane in that pure methane alone did not cause fiber formation. This observation is in agreement with the mechanism of Baker et al. which implies that the carbon deposition process should be exothermic for filament growth to be observed.

Baker et al. (1973) demonstrated that the filament growth sequence observed in the decomposition of acetylene on nickel was also observed on iron, cobalt, and chromium. All four reacting systems had common features:

(1) The metal films supported on graphite all nucleated to form ∿10 nm crystallites at about 775 K.

(2) All filaments had a crystallite at their growing end.

(3) The filaments grew with random paths, forming loops, spirals, and networks.

(4) Crystallites that had ceased to grow all had a carbon deposit completely encasing the crystallite. By comparison, the crystallites at the end of a growing filament, if suddenly quenched, had no deposit at the face in the growth direction.

(5) Filaments contained an electron transparent channel through the center of the filament length.

(6) The outer walls of the filaments were more resistant to oxidation than was the central core.

(7) Filament growth rate increased with decreasing particle size.

(8) The activation energy for the filament growth rate was shown to be independent of particle size. The activation energy for filament growth was also found to be approximately equal to the activation energy for the diffusion of carbon in the four metals.

(9) When silicon was used as a support for the metal films, secondary filaments were observed to grow from fragments of the initial growth crystallite for cobalt and iron. Also, with a silicon support, chromium formed filaments by an "extrusion" process rather than the normal growth process outlined.

The extrusion variation of the filament growth process was subsequently discussed further by Baker and Waite (1975) who observed this carbon filament growth sequence on a platinum/46% iron catalyst. The growth sequence is shown in Fig. 20. In this sequence, irregular catalytic particles were nucleated by heating a thin film of the iron-platinum alloy on a graphite or silicon support in hydrogen to 920 K. The hydrogen was then removed and the crystallite/support cooled to ambient temperature. The hydrogen was then replaced with acetylene and the crystallites reheated. Baker and Waite reported that the irregularly shaped metal crystallites underwent a rapid change to a more spheroidal form as shown in (a) at 690 K. Electron diffraction data indicated phase separation of the alloy constituents was occurring at this temperature. As previous work had indicated that iron would produce filaments only above 925 K, the initial decomposition at 690 K was attributed to the catalytic effects of platinum as shown in (b). Carbon deposited on the platinum surface was free to migrate across the surface and to diffuse through the bulk platinum and iron as shown in (c). The resultant observed behavior was the "extrusion" of a carbon filament from a crystallite fixed on the surface as shown in (d). The filaments formed by this process were similar to those grown by the other process in that they contained an electron transparent core which was more easily oxidized than the outer shell. Coiled filaments were also produced by the process. The activation energy for filament growth in the range 690 to 990 K was 80 kJ/mole which was the same as the activation energy for carbon filament growth from iron crystallites.

The observations of Baker and his associates are the only direct *in situ* experimental observations available to date concerning the growth of carbon filaments. Although no observations were made with carbon monoxide

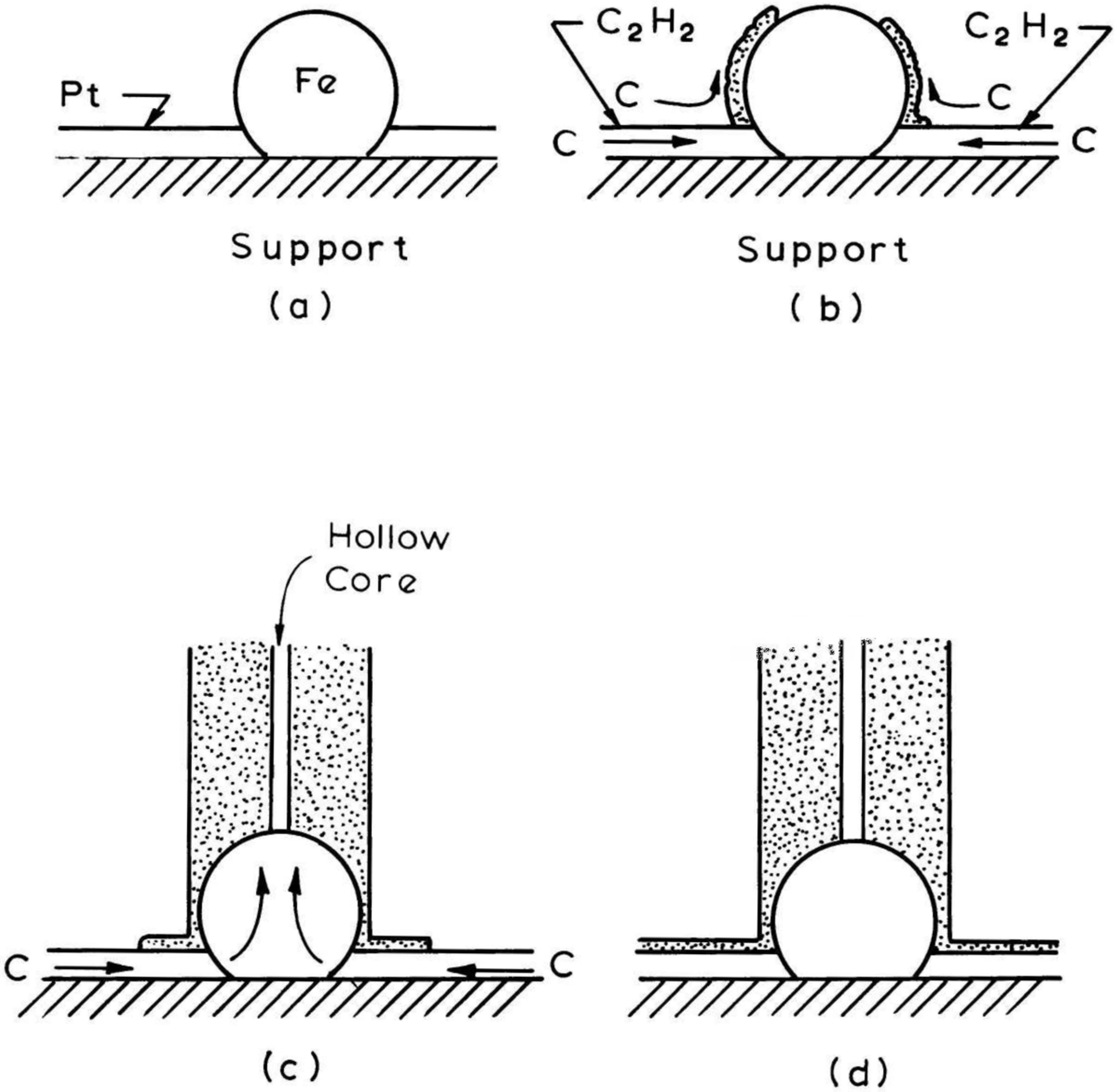


FIGURE 20, EXTRUSION MECHANISM OF FIBER GROWTH (BAKER AND WHITE , 1975) or carbon monoxide-hydrogen mixtures, the very similar nature of the carbon products would indicate that these growth mechanisms are identical. However, while the observations themselves are not subject to debate, the mechanism inferred by the authors to explain the observations is open to two questions. The first question concerns the formation of the initial crystallite, while the second concerns the manner of carbon and hydrogen transport from the catalytic surface to the growing carbon filament.

The question of how the crystallite forms on a metal surface cannot be answered from the observations of Baker et al. alone. As mentioned previously, a planar metal surface will not normally spontaneously form a number of very small crystallites of the same composition over the planar surface. Such a transition would undoubtedly involve a thermodynamically unfavorable increase in total energy due to the increase in additional surface area. However, if the planar surface and the nucleated crystallite are not of the same composition, this transition would not necessarily be unfavorable. This observation is consistent with other observations. Ruston, for example, observed crystallite formation in areas of surface cementite protrusions and in an undetermined stage of epitaxial development of Fe_7C_3 on single α-Fe grains. The precise mechanism and composition of the nucleated crystallite, however, have not yet been determined.

With respect to the transport of carbon and hydrogen, the mechanism of Baker et al. is not sufficiently developed. In most cases, the carbon transport is alleged to occur because of a "thermal gradient" arising from the exothermic reaction:

$$C_2H_2(g) \rightarrow 2C(s) + H_2(g)$$

This concept is not phenomenologically well-founded in that diffusional mass transfer is normally portrayed as occurring by virtue of a concentration gradient rather than a temperature gradient. If the solubility of one compound (carbon) in another (iron), however, changes with temperature, a temperature gradient in a saturated solution may induce a concentration gradient. In the case of α-iron, the carbon solubility increases with temperature up to the eutectic temperature of 996 K. Thus the leading edge of the crystallite, at a higher temperature than the trailing edge, would also have a higher carbon concentration at saturation. Hence, the direction of decreasing temperature would be the same as the direction of decreasing carbon composition. The opposite, however, is true above the eutectic temperature where carbon concentration in saturated α-iron decreases with increasing temperature. Baker et al. (1973) and Baker and Waite (1975) report the same observations with iron and iron-platinum catalysts both above and below the eutectic temperature. Hence, a mechanism involving a thermally induced concentration gradient in saturated α-iron will not fully explain the experimental observations.

The role of diffusion through the crystallite is also incompletely explained. Baker et al. (1972) indicated that the hollow center of the catalyst filaments was caused by a less-dense and unordered carbon deposit which resulted from the increased length of the carbon diffusion path. Yet Walker et al. (1959) have shown that the BET area and hydrogen concentration in the carbon filaments indicate that the central core is probably hollow and probably contains hydrogen chemisorbed at the basal plane edges of the graphitic carbon layers. No mention of hydrogen diffusion is included in the mechanism of Baker et al.

In addition, for crystallites as small as those observed, one might ask whether diffusion over the crystallite surface to the growing filament would not be much more significant than bulk diffusion through the crystallite. As surface diffusion coefficients are usually several orders of magnitude larger than bulk diffusion coefficients, this mode of transport may be the most important. However, no data on the surface diffusivity of carbon on iron are available at present.

3. APPARATUS AND PROCEDURE

3.1 Apparatus

A block diagram of the experimental apparatus is shown in Fig. 21. The apparatus can be divided into three basic sections: reactant gas preparation, thermogravimetric reactor, and gas analysis. In the reactant preparation section, gases are metered separately through mass flow regulators and capillary flowmeters. The separate gas streams are then mixed and dried in a dessicant tower. In the thermogravimetric reactor section, the gas stream flows through a preheater and reactor housed in a temperature controlled furnace. An analytical balance is used periodically to weigh the amount of carbon deposited on the catalyst. The reactor exhaust gas is sent to a vent fan and exhausted to the atmosphere. The gas analysis section consists of a gas chromatograph with ancillary equipment including a precision oven temperature controller, a gas sampling valve system, a recorder, a digital integrator, and a cylinder of mixed carrier gas. In addition to the apparatus already mentioned, a cinder block wall and a set of 6.5-mm-thick metal shelves isolate the reactor section from the other components for operator safety.

3.1.1 Reactant Gas Preparation

The reactant gas preparation consisted of a bank of bottled gas cylinders and a control panel upon which were mounted the necessary flow controllers, manometers, valves, dryer, etc. that were needed to meter, premix, and dry the required gas stream.

The reactant gases used were obtained from the Matheson Gas Company in standard size 1A cylinders and include:

hydrogen	(prepurified grade)

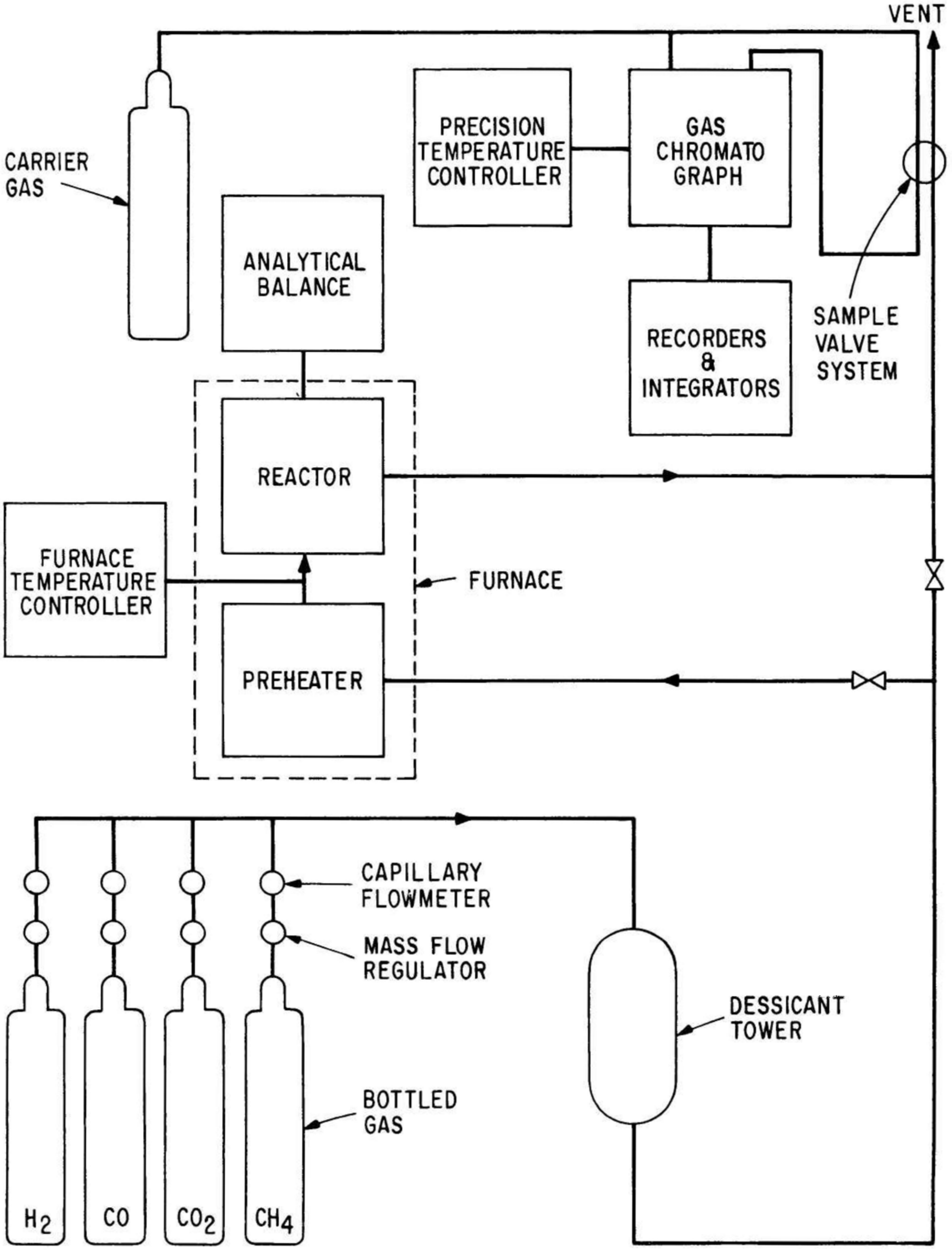


Figure 21, Experimental Apparatus Flowsheet

methane	(CP grade)
carbon monoxide	(CP grade)
carbon dioxide	(Bone Dry grade)
nitrogen	(prepurified grade)
helium	(prepurified grade)

All gas cylinders were equipped with approved two-stage regulators which fed gas at 4.5×10^5 N/m^2 (50 psig) to a toggle shutoff valve on the control panel.

After passing through the toggle shutoff valve, each gas flowed through a regulating and metering device as shown in Fig. 22. The mass flow regulator was a Brooks Model 8944 flow controller equipped with an inlet line filter and a direct reading digital handle. The inlet filter removed entrained particles larger than 2 μm. The digital handle provided an accurate and repeatable method of returning the valve stem to a predetermined position. The valve stems are available in six interchangeable tapers so that a wide range of flow rates could be obtained.

The exit of the flow controller was connected to a capillary flowmeter consisting of a glass capillary tube, U-tube manometer with shutoff valve, and a manometer trap. The glass capillary tubes were 91.5-cm long with capillary diameters between 1.0 and 1.4 mm. Fischer and Porter Co., Lab-Crest Division, supplied the capillary tubing and specifies the tolerance on capillary diameter as ±0.007 mm.

The pressure drop across the capillary was measured with U-tube manometers filled with Meriam Co. Hi Vac Manometer Fluid (density 1.04 g/cc). This manometer fluid was chosen because the low vapor pressure reduces potential contamination of the gas stream and yet enables accurate measurement of low pressure drops. All manometers were equipped with fluid traps

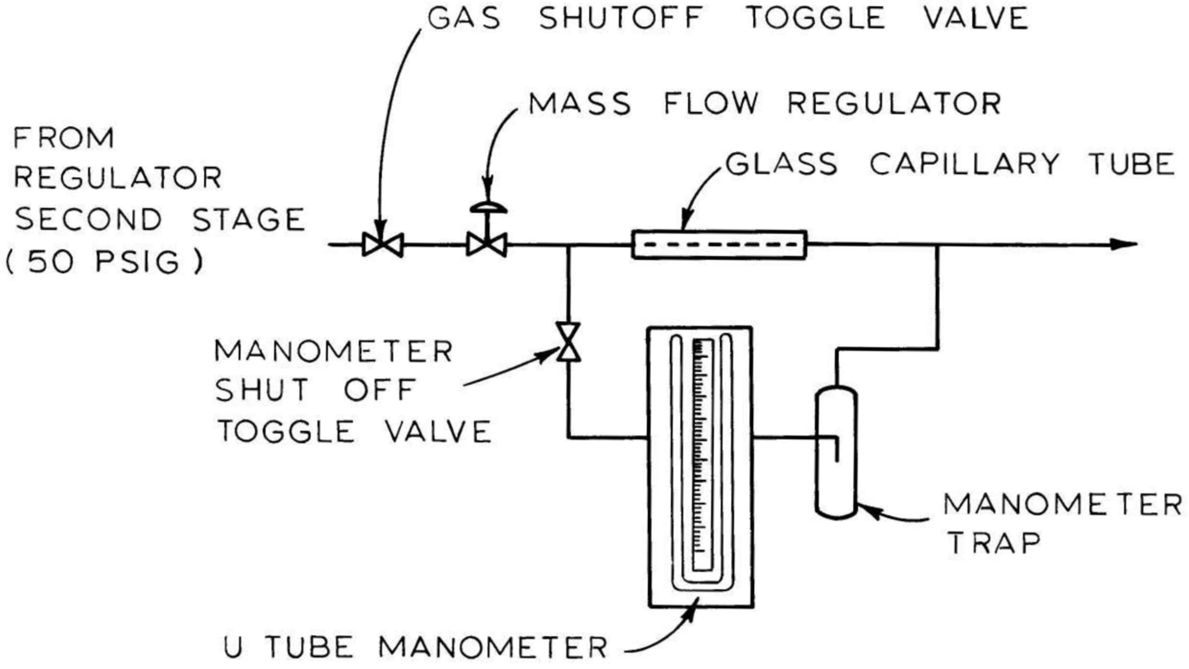


FIGURE 22. CAPILLARY FLOWMETER

on the low pressure side.

As long as the gas flow through the capillary tubes was laminar, the gas flow rate was directly proportional to pressure drop as given by Poiseuille's Law:

$$Q = \frac{\pi d^4 \Delta P}{128\ \mu L} \tag{3}$$

where:

Q = volumetric flow rate

d = capillary diameter

ΔP = pressure drop across capillary

μ = gas viscosity

L = capillary length

The equation is derived assuming isothermal laminar flow of fluid with constant viscosity. The capillary tubes used in this system were selected for each gas so that, for the experimental flow rates anticipated, gas flow in the capillary would remain laminar and essentially incompressible. Using the known dimensions of the capillary tube and properties of each of the gases, Eq. (3) gives the gas volumetric flow rate as a function of pressure drop. The flow rate predicted by this equation was checked experimentally for each of the gases by measuring flow rate as a function of manometer pressure drop using a wet-test meter and soap-film flowmeter. Thus, any variations in diameter and end effects were taken into consideration.

After the gases were separately metered using the capillary flowmeters, they passed into a single gas line and were introduced into a gas drying tower. The tower was a standard piece of laboratory glassware (Kimble Glass #19500) packed with indicating silica-gel dessicant. The gases were also mixed during flow through the packed bed of indicating dessicant. A pair of ball valves were then used to divert the mixed gas to either the reactor or the vent.

When water was desired as a component in the reactant gas feed stream, another gas stream was added. This separate gas stream passed through a capillary flowmeter and water saturator. This stream was mixed with the remainder of the gas stream downstream of the gas drying tower. Partial pressures of water up to 0.035 atm in the reactant gas stream could be obtained by varying the water saturation temperature and/or the relative volumetric flow rates of the gas streams.

3.1.2 Thermogravimetric Reactor

The thermogravimetric reactor section consisted of a furnace with an electronic temperature controller, a quartz preheater and reactor, and an analytical balance. The electric furnace was built in the M.I.T. shop facilities. The internal configuration of the furnace is shown in Fig. 23. The central component of the furnace was the cylindrical heating surface. This surface was composed of two THERMCRAFT Model RH 254 semi-cylindrical ceramic heating elements. The two units formed a heated cavity 75-mm in diameter and 30.5-cm deep. Wired in parallel to a 220-v electrical line, the heaters were capable of dissipating a total of 2300 W with a maximum temperature rating of 1450 K.

The electrical heaters are insulated primarily by Babcock and Wilcox Type K-30 insulating firebrick. A double layer furnace casing protected the firebrick insulation. The inner layer of the casing was 6.5-mm-thick asbestos board while the outer layer was fabricated from a 6.5-mm-thick sheet of TRANSITE, an asbestos-concrete composite. This material was sufficiently rigid and durable to support and protect the internal components of the furnace.

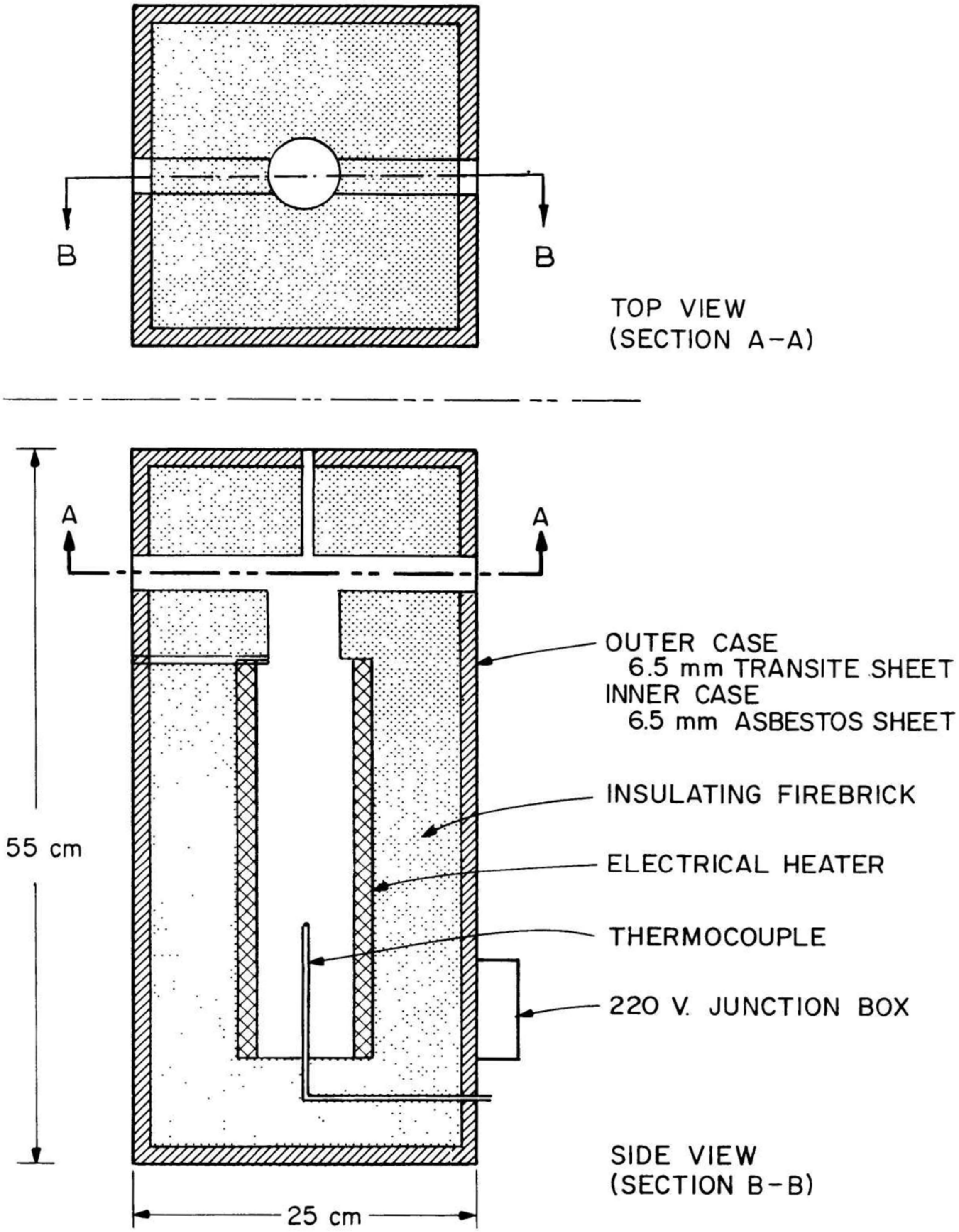


Figure 23, Reactor Furnace

The furnace temperature was controlled by a Thermolyne Dubuque III, Type 8700 controller. The controller sensor was a chromel-alumel thermocouple mounted on the furnace floor and protruded into a 110-mm-long thermocouple well in the quartz reactor. The controller varied the power fed to the electrical heater in proportion to the deviation from setpoint temperature. Thus, the controller acted as a proportional controller with a proportional band of ±10 K. The controller included a cold junction compensator for the sensing thermocouple and protective circuitry to shut off the furnace if the sensing thermocouple malfunctioned.

The quartz reactor was a three-part apparatus fabricated by a local glass blower. Two of the three pieces, connected at a ground-glass joint, form the body of the preheater and reactor support tube as shown in Fig. 24. Gas from the preparation section passed from the inlet, through the helical preheater coil, to the base of the reactor support tube, then up the support tube, over the catalyst, and out either the exhaust or sample tubes.

The preheater consisted of a 6-m length of 7-mm-OD quartz tubing closely wound into a helical coil on a 60-mm diameter. The base of the preheater terminated in the reactor support tube, a 28-mm-OD vertical quartz tube which served to support the catalyst bed. The top section of the catalyst support tube was a cross-shaped piece ending in a 7-mm-OD exhaust tube, a 7-mm-OD sampling tube, and a 6-mm-OD weighing port.

The third piece of the reactor was the catalyst carrier section shown in Fig. 25. The catalyst carrier consisted of the outer part of the quartz 19/38 standard taper ground joint and a quartz suspension rod. The catalyst carrier was supported in the reactor by the inner part of the ground joint which had been affixed to the vertical support tube. Thus, when the catalyst

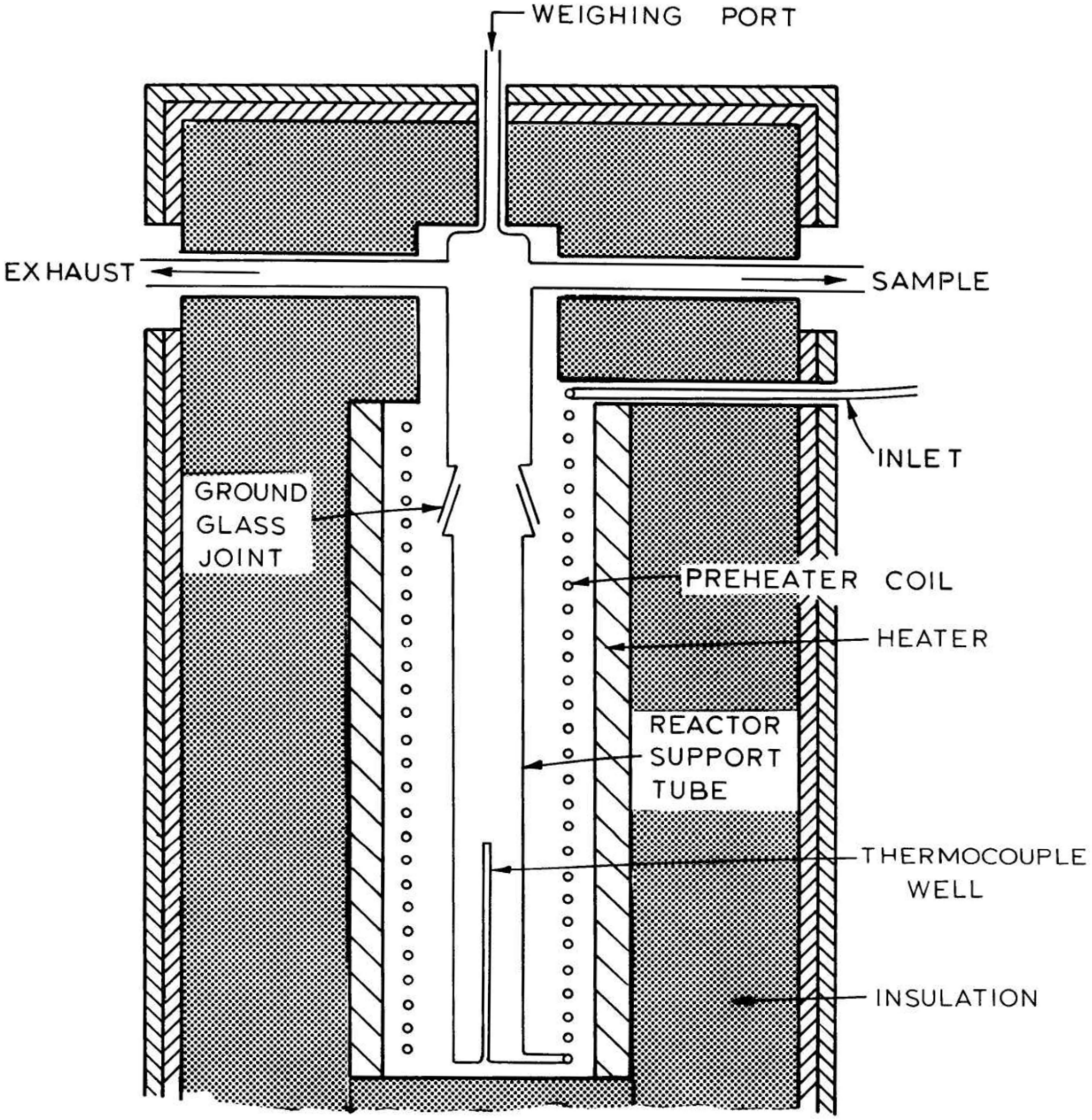


FIGURE 24, QUARTZ REACTOR IN FURNACE

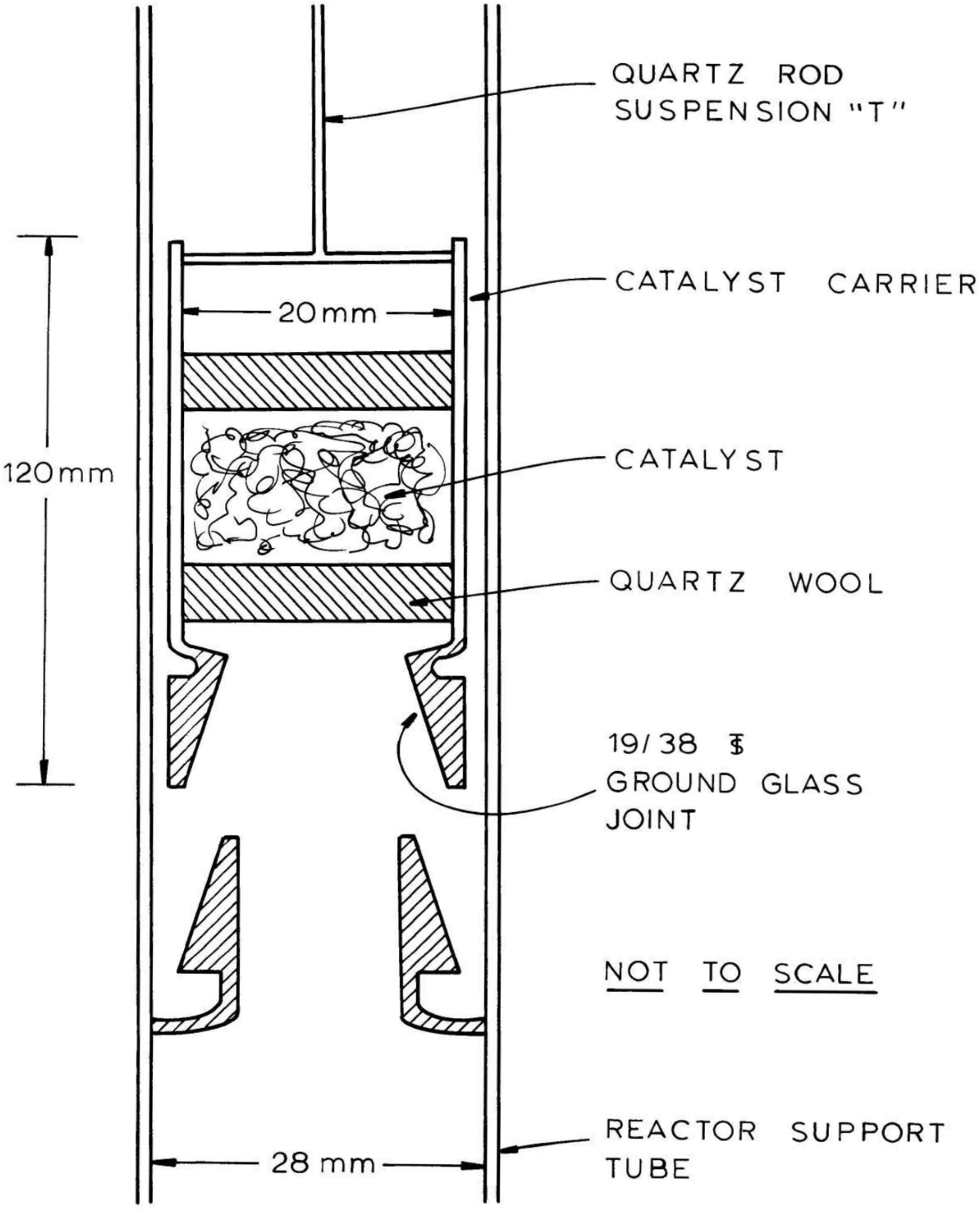


FIGURE 25, CATALYST CARRIER AND SUPPORT

carrier rested on its support, all the gas passing up the support tube passed over the catalyst.

The quartz suspension rod passed from the top of the catalyst carrier up through the weighing port to the outside of the furnace. Here it was connected to an analytical balance so that when the suspension rod was lifted, the catalyst carrier rose from its support and the weight of the carrier, catalyst, and deposited carbon product was measured.

The analytical balance was a Sartorius Model 2255 pan balance which was equipped to weigh samples below the balance case. A Nylon monofilament line and a set-screw collar connected the balance to the suspension rod of the catalyst carrier. The balance was capable of weighing samples of up to 160 g with an accuracy of ± 1 mg.

3.1.3 Gas Analysis

The main element of the gas analysis section was a Hewlett-Packard Model 700 gas chromatograph equipped with carrier gas flow controllers, sample injection ports, two analytical columns, and a thermal conductivity detector. Samples for analysis were fed to the chromatograph by a sampling device outlined in Fig. 26. This device was capable of sampling any of four possible sources and injecting the sample into either of the two analytical columns in the chromatograph.

As shown in Fig. 26, a four-way selector valve allowed the selection of a sampling stream from four sources: the reactor inlet gas stream, the reactor outlet gas stream, a preanalyzed standard gas calibration mixture, or ambient room air. Since all of these sources were at atmospheric pressure, a vacuum system was connected to the opposite side of the sampling valves through a toggle valve. Thus, by opening the toggle valve, a gas

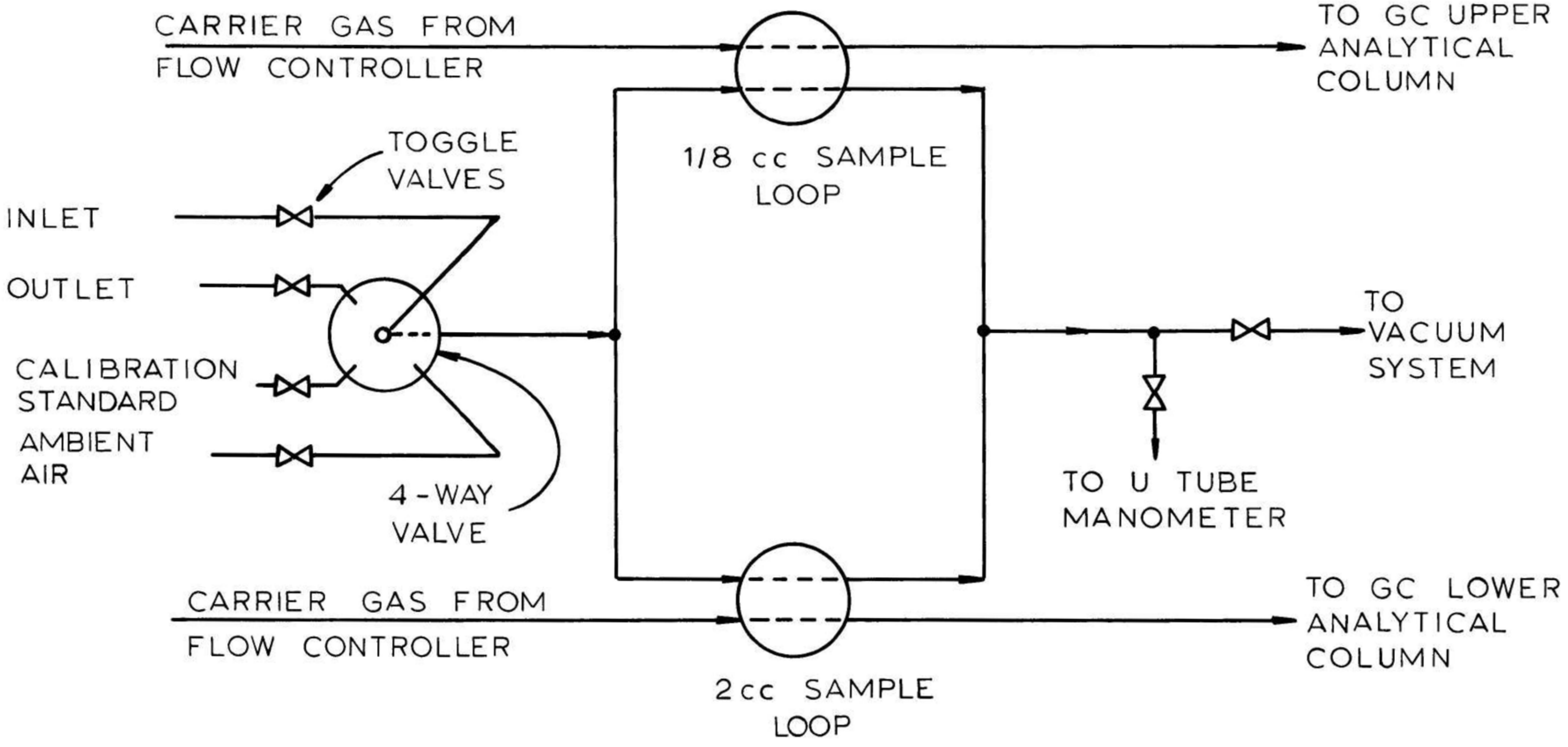


FIGURE 26, GAS SAMPLING VALVE SYSTEM

sample of the selected source was drawn through both of the sampling loops in the system. When the toggle valve was closed, sample gas continued to flow into the system until pressures were equalized. The pressure of the sample in the sample loop could be determined by a U-tube manometer installed in the system. Then, by operating one of the gas sampling valves, a 0.25-cc sample was injected into the carrier gas stream flowing to the upper analytical column of the chromatograph; or a 2-cc sample was injected into the carrier gas stream flowing to the lower column. A large metal heat sink with a temperature controller insured that the gas samples injected were at a known and reproducible temperature. Two different sized sample loops were employed so that in addition to the usually small sample required, a large sample could be injected to analyze for a very dilute component.

In the gas sampling apparatus, Whitey brand valves were used for the four-way selector valve and for the toggle valves. The sample valves and calibrated sample loops were Hewlett-Packard Model 19020. The selector valve and sample valves were mounted directly on a 9-mm x 75-mm x 210-mm aluminum plate which served as a heat sink. The plate temperature was controlled by a Hewlett-Packard Model 200 temperature controller which operated two 65-W cartridge heaters mounted in the aluminum stock. All valves and tubing of the gas sampling device were mounted in an insulated box so that operation at above ambient conditions was possible. Sampling lines between the reactor sampling port and the gas sampling valves and between the gas sampling valves and the chromatograph were heated to above 373 K to prevent condensation of water in the sampling lines.

Gas samples injected into the carrier gas stream were analyzed using two identical columns mounted in the chromatograph oven. The analytical columns were 3-mm-ID, 6.1-m-long teflon tubes packed with 50-80 mesh

Poropak Q. This packing was selected because it could separate all components of the anticipated gas reactant or product mixtures without retaining water for an excessively long time. The oven temperature of the chromatograph was also controlled by a Hewlett-Packard Model 220 temperature controller which had a sensitivity greater than ± 0.1 K.

The carrier gas was a mixture of 8.5% hydrogen in helium, which allowed a direct chromatographic analysis of hydrogen. However, the recording peak for hydrogen using this mixture is opposite in direction to the peaks of other components. A polarity switch was used to reverse the signal polarity after the hydrogen peak. Thus, all peaks appear positive. An Autolab Model 6300 digital integrator was used to measure the peak areas of all component peaks indicated on the recorder.

A typical chromatogram is shown in Figs. 27 and 28. Figure 27 shows a typical chromatogram of the calibration gas containing approximately 25 mole % each of hydrogen, carbon monoxide, methane, and carbon dioxide. As can be seen, the hydrogen peak is considerably smaller than the others because of the lower response of the thermal conductivity detector for hydrogen when using the mixed hydrogen-helium carrier gas. The digital electronic integrator allowed reliable measurement of this small graphical area. The hydrogen peak shown corresponds to an integrated area of approximately 5000 μV-sec while the sensitivity of the digital integrator is ± 1 μV-sec.

The water peak shown in Fig. 28 was obtained from a water-saturated sample of carbon dioxide. The peak shape shown is representative of the peaks obtained after considerable experimentation to reduce tailing (i.e., a peak with a long extended side). To reduce the severe tailing originally observed, teflon tubing was used to replace as much stainless steel tubing as possible in the chromatograph and all unnecessary void volume between

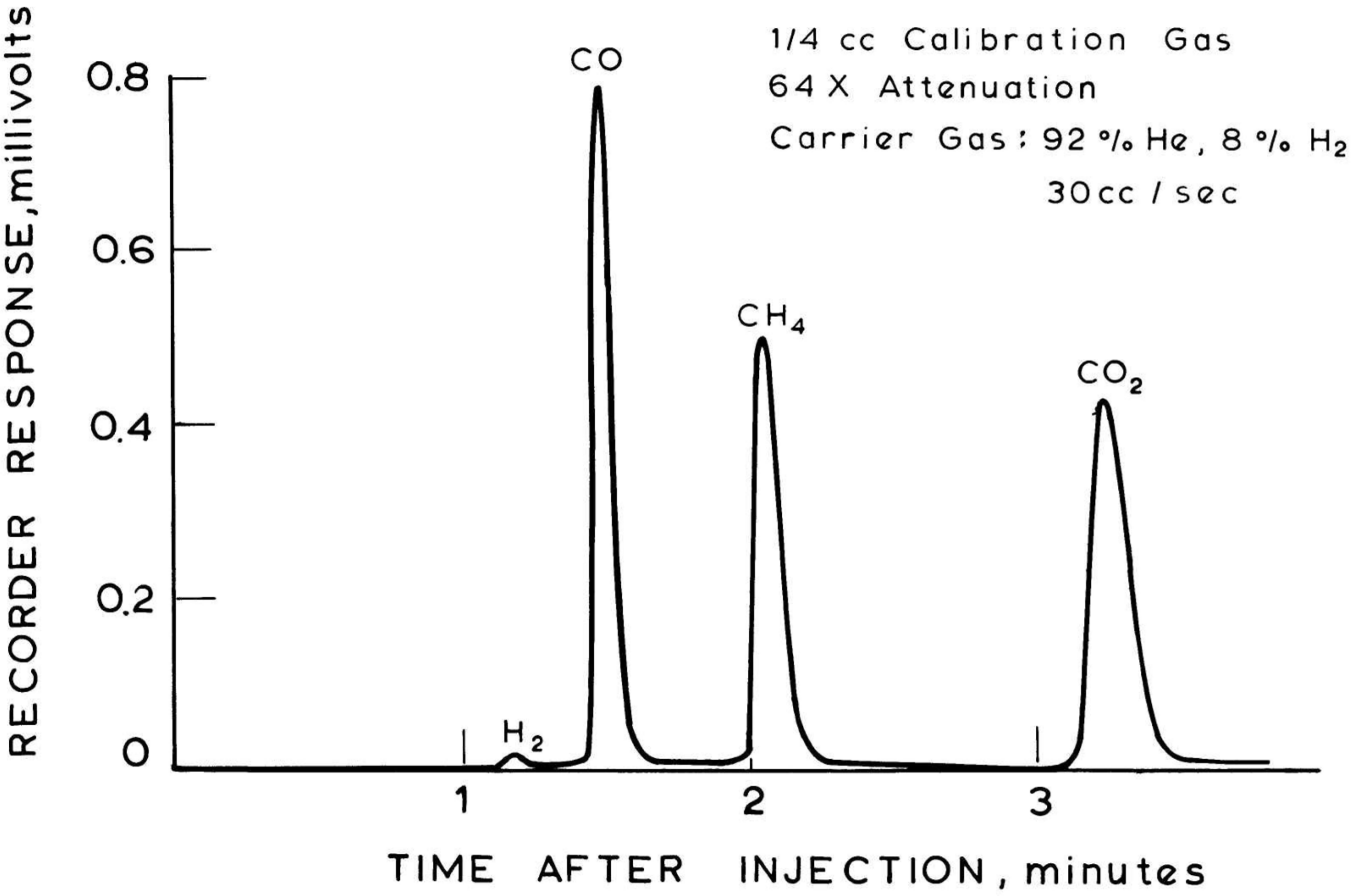


FIGURE 27, TYPICAL CHROMATOGRAM, H_2, CO, CH_4, CO_2

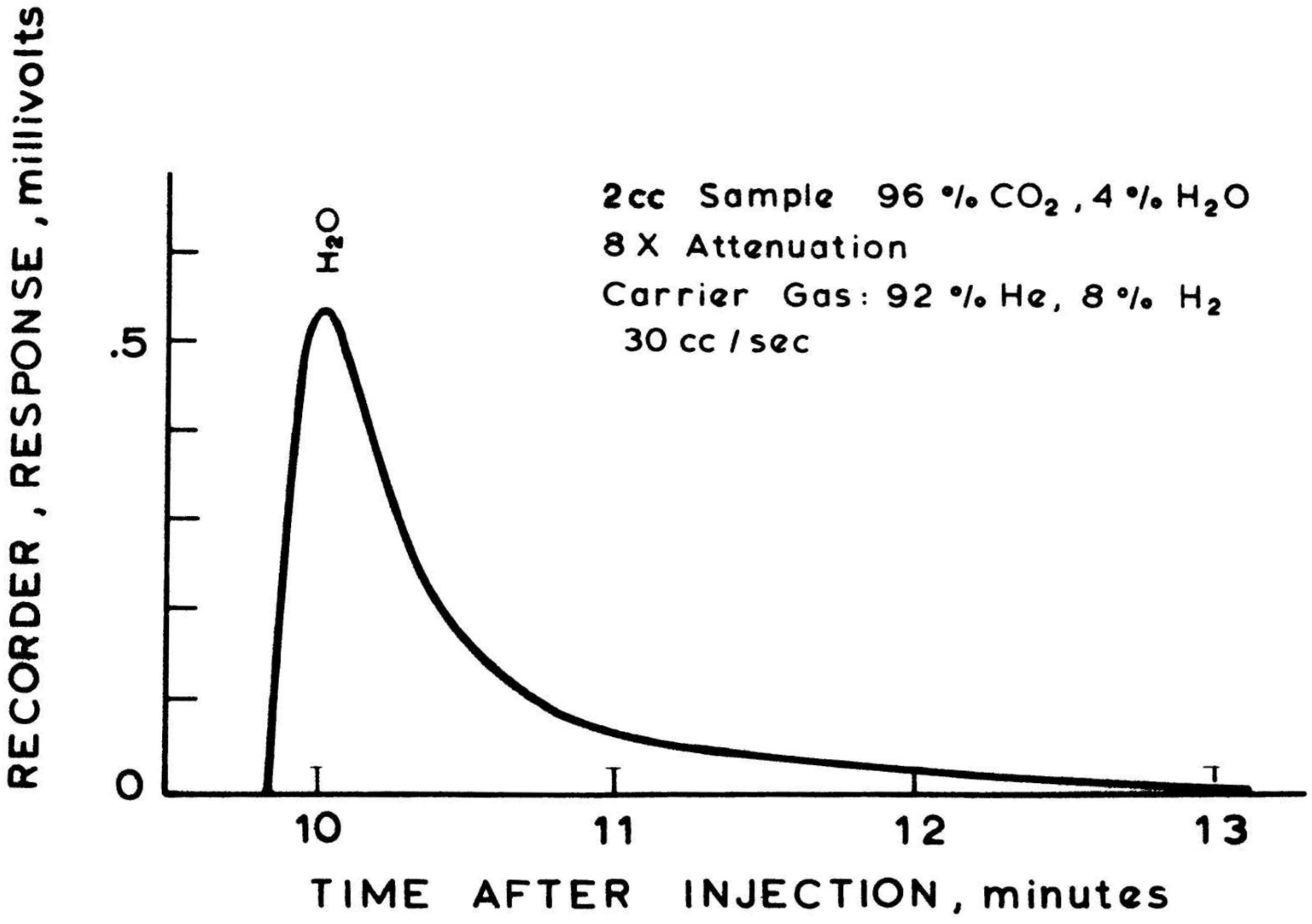


FIGURE 28, TYPICAL CHROMATOGRAM: H_2O

the column and detector was eliminated as recommended by Hollis and Hayes (1966).

3.2 Apparatus Operational Checks

Each of the separate parts of the apparatus was tested prior to start of experimentation to ensure proper operation and to determine the precision and accuracy of measuring devices.

3.2.1 Reactant Gas Preparation

The only devices requiring calibration in the reactant gas preparation system were the capillary flowmeters. These were calibrated using either a wet-test meter at high flow rates or a soap film flowmeter at low flow rates. Calibration curves were prepared for each flowmeter. All calibration curves were linear over the measured range.

Mass flow regulator operation was satisfactory. No fluctuations or drift in flow rate were detectable on the capillary flowmeters even over several hours of operation. Any component gas stream could be turned on or off without affecting the flow of the other streams.

3.2.2 Thermogravimetric Reactor

The accuracy of the furnace temperature controller was checked by operating the furnace with a chromel-alumel thermocouple mounted in the normal catalyst position and with nitrogen flowing through the reactor. The thermocouple reading was continuously recorded on a Brown multipoint recorder. The controller maintained constant reactor temperature within 0.5 K. Unstable controller operation was noted only when gas flow was reduced to 1 cc/sec or lower. The use of a chromel-alumel thermocouple probe allowed determination of a furnace profile along the length of the furnace. In the 3.5-cm center section of the furnace when the catalyst was positioned, the temperature profile had slight curvature but did not vary by more than ± 2 K. Large temperature gradients were found near both ends of the cylindrical furnace. It was found during the above experiments that the furnace temperature could be set to within 20 K of predetermined temperature by using the controller setpoint alone. Use of both the multipoint recorder and minor readjustments of the controller setpoint knob allowed the desired temperature to be set ± 1 K (see Appendix 8.2.2 for additional details).

The catalyst carrier weighing procedure was checked by repeated weighing of the empty catalyst carrier whose weight was known. During the check the reactor and furnace were at operating temperature and a nitrogen stream was used to simulate reactant gases. It was found that the catalyst carrier could be weighed accurately with a precision of 0.4 mg (1.8%) and with the largest observed deviation in eight readings being 5 mg.

3.2.3 Gas Analysis

Although the gas chromatograph would separate all five components in the gas mixture, preliminary runs indicated that several modifications were required. The first problem was to increase the separation between the hydrogen and carbon monoxide peaks so as to permit polarity switching of the gas chromatograph output signal without interfering with the electronic integrator operation. Although decreasing oven temperature improved the separation between these peaks, it also increased the retention time and led to excessive tailing of the water peak. Operating the gas chromatograph oven at 70°C was found to be a compromise in that it gave 10-sec separation between the hydrogen and carbon monoxide peaks and a total analysis time for all components of about 12 min.

Separation of water from other components using the Poropak Q packing was found to be quite good. However, tailing was found to be quite severe under most circumstances. This problem was eliminated by using some of the suggestions of Hollis and Hayes (1966). These included elimination of the sample injection ports, use of teflon instead of stainless steel for column tubing, and shortening of tubing between the end of the analytical column and the chromatograph detector. After incorporation of these changes, tailing of the water peak was reduced. Operating conditions for the chromatograph are shown in Table 2.

Table 2. Chromatograph Operating Conditions

Sample Size	0.25 ml
Carrier gas flow rate	20 cc/min
Column operating temperature	70°C
Detector operating temperature	200°C
Detector filament current	200 mamp

The gas chromatograph was checked for accuracy and precision by analyzing two calibration gas standards. The calibration gases, both supplied by Matheson Gas Products, were certified to be of the concentrations shown in Table 3.

Table 3. Concentrations of Calibration Gas Standards (mole %)

	Calibration Gas I	Calibration Gas II	
H_2	balance	29.1	± 2% of value
CO	24.91 ± 0.02%	29.4	
CH_4	24.97 ± 0.02%	21.4	
CO_2	24.94 ± 0.02%	14.8	
C_2H_2	0.0	5.3	

The concentration in each of the calibration gases was determined by injecting a sample of the gas, recording the component peak areas, and determining concentration of a given species knowing the peak area of an identical sample of the pure component gases. Calculation of each of the component concentrations (except hydrogen) was by the absolute method described by Dal Nogare and Juvet (1962). Hydrogen was determined by using a calibration curve as recommended by Purcell and Ettre (1965). The concentrations thus determined were accurate within 1% and had a precision of 0.8%.

3.3 Procedure

3.3.1 Catalyst Preparation and Startup

Steel wool manufactured by the American Steel Wool Co., Long Island City, N.Y., was the catalyst in all experimental runs. The concentration of alloying elements in the steel wool was 0.36 wt % C, 0.70 wt % Mn, 0.04 wt % P, 0.018 wt % S., and 0.4 ppm N. The BET surface area of the catalyst was determined to be 389 cm^2/g from the adsorption of krypton at liquid nitrogen temperatures. Approximately 250 mg of Grade 2 steel wool was cut, weighed, and placed between two quartz wool plugs in the reactor catalyst carrier. The length of catalyst carrier packed with steel wool was 2.5 cm. Thus, the total volume occupied by the catalyst was about 7.8 cm^3.

The catalyst, catalyst carrier, and other parts required to hang the catalyst carrier in the reactor were weighed. These same pieces were reweighed after assembly to ensure that all pieces had been assembled properly. By subtracting this initial weight from all subsequent weighings, the weight of carbon deposited on the catalyst could be determined.

After assembly of the reactor and furnace, the inlet gas stream was turned on and 20-30 cc/sec of hydrogen were passed over the catalyst. The furnace temperature controller was set to the approximate operating temperature, and the power to the furnace heater turned on. The furnace required about 20 min to come to operating temperature. While the reactor was heating to operating temperature, the chromatograph recorder and integrator were turned on. Several calibration gas samples were injected into the chromatograph to check on the analytical equipment.

After the furnace had come to temperature and calibration gas samples were analyzed, the inlet gas stream was changed from pure hydrogen to the desired concentration by adjusting the flow controllers to the desired component flow rates. The pressure differential across the capillary flowmeters for each component in the gas stream was recorded. From the inlet flow rates obtained for each component, the inlet concentration of each component could be calculated. Unless otherwise specified, the total gas flow rate for all experiments was 20 cm^3/sec (STP).

3.3.2 Reactor Operation

During reactor operation a gas sample of either the inlet or outlet gas was taken approximately every 15 min. A sample was taken by evacuating the gas sample loop system and then opening the toggle valve corresponding to the desired gas stream. The loop was then reevacuated and refilled a second time. After the sample loop was filled, the toggle valve was closed and the pressure in the sample loop recorded. Then the sample valve was turned, injecting the sample into the chromatograph. The chromatogram for each sample taken was recorded and the area under each peak determined by an electronic integrator.

The gas sample composition was determined by injecting a sample of the gas, recording the component peak areas, and determining concentration of a given species knowing the peak area of an identical sample of calibration gas. Calculation of each of the component concentrations (except hydrogen) was done using the absolute method described by Dal Nogare and Juvet (1962). Hydrogen was determined by using a calibration curve as recommended by Purcell and Ettre (1965). The concentrations thus determined were accurate within 1% and had a precision of 0.8%.

The catalyst carrier was weighed approximately every half hour. To weigh the catalyst carrier, the vent fan and inlet gas flow were shut off, the catalyst carrier was lifted from its support by the connecting rod, and the carrier was suspended from the balance by a piece of monofilament fishing line. The weight of the catalyst carrier was recorded, the catalyst carrier was replaced on its support, and the vent fan and gas flow turned on. This entire operation took less than one minute to complete.

Reactor temperature, gas sample valve temperature, and ambient temperature were recorded continuously on a multipoint recorder throughout all runs.

4. RESULTS

A summary of the experimental operating conditions is contained in Appendix 8.4.1 The experimental data obtained during reactor operation are tabulated in Appendix 8.4.2. The data were transferred to punched IBM data cards for tabulation and data conversion on an IBM 1130 computer. The raw input data consisting of digital integrator readings, catalyst carrier weight readings, and capillary flowmeter manometer readings were converted to gas phase concentration, amount of carbon deposited, and inlet flow rates by the computer program. A copy of the program listing is found in Appendix 8.4.3. The output of the computer program for each run consists of three pages as shown in Tables 4, 5, and 6 with the data and run number listed at the top of each page. The first page, as shown in Table 4, is a tabulation of the raw data, in this case, for Run 20. The first four columns on the page list, respectively, the time of day on a 24-hr clock, the gas sample number, the differential pressure between atmospheric and the gas sample loop pressure before sample injection, and a code number indicating the type of data. The single digit code is as shown in Table 7.

Table 7. Code Number

1.	Digital Integrator Output: Calibration Gas Sample
2.	Digital Integrator Output: Pure Hydrogen Gas Sample
3.	Digital Integrator Output: Water Saturated Gas Sample
4.	Digital Integrator Output: Reactor Inlet Gas Sample
5.	Digital Integrator Output: Reactor Outlet Gas Sample
6.	Capillary Flowmeter Manometer Readings, cm of Manometer Fluid
7.	Weight of Catalyst Carrier and Sample, g
8.	Reactor Temperature Setpoint Reading, °C

```
                    DATA TAKEN DURING RUN  20 ON 18 JUL 74

TIME SAMP     DELP IGAS       H2        CO       CH4       CO2       H2O          C
 921    1     1.00    1   5047.0  241234.0  196032.0  266043.0       0.0
 928    2     1.00    1   4639.0  221724.0  183329.0  248465.0       0.0
 935    3     0.00    1   5085.0  239036.0  197283.0  267333.0       0.0
 941    4     1.00    1   4687.0  223009.0  186894.0  250005.0       0.0
 958    5     0.00    2  29594.0       0.0       0.0       0.0       0.0
1010    6     0.00    2  26612.0       0.0       0.0       0.0       0.0
1653   33     0.00    3      0.0       0.0       0.0 1062723.2   27311.0
1726   35    -1.00    3      0.0       0.0       0.0 1059382.2   26360.0

 948                  6     48.0       0.0       0.0       0.0       0.0

 949                  8    550.0
 958    5     0.00    4  29594.0       0.0       0.0       0.0       0.0
1010    6     0.00    4  26612.0       0.0       0.0       0.0       0.0
1030                  7                                                      31.860
1034    7     0.00    5  29639.0       0.0       0.0       0.0       0.0
1041    8     0.00    5  26698.0       0.0       0.0       0.0       0.0
1058                  7                                                      31.862

1103                  6     16.0      34.0       0.0       0.0       0.0
1105    9     0.00    4  11892.0  489823.0       0.0      57.0       0.0
1111   10     0.00    4  10809.0  466730.0       0.0       0.0       0.0
1118   11     0.00    4  11988.0  490473.0       0.0       0.0       0.0
1127   12    -1.00    5  10462.0  470067.0       0.0     153.0    7508.0
1131                  7                                                      31.907
1141   13     0.00    5  11629.0  496561.0       0.0     357.0    2443.0
1149                  7                                                      31.930
1155   14    -1.00    5  10732.0  471768.0       0.0    4191.0    2059.0
1210   15    -2.00    5  11778.0  493446.0       0.0     570.0    3297.0
1214                  7                                                      31.966
1224   16    -2.00    5  10733.0  466865.0       0.0     314.0    2115.0
1246                  7                                                      32.024
1254   18    -2.00    5  10700.0  470590.0       0.0    1327.0    2826.0
1308   19    -2.00    5  11748.0  494290.0     140.0     604.0    3269.0
1312                  7                                                      32.077
1321                  7                                                      32.161
1323   20    -2.00    5  10708.0  467203.0       0.0     472.0    4647.0
1337   21    -1.00    5  11705.0  493655.0      52.0     716.0    4849.0
1353   22    -1.00    5  10648.0  464616.0       0.0     656.0    5078.0
1408   23    -2.00    5  11632.0  493374.0       0.0    1127.0    7245.0
1412                  7                                                      32.280
1424   24    -1.00    5  10733.0  467852.0       0.0    1190.0    7683.0
1428                  7                                                      32.374

1428                  6     32.0       0.0       0.0       0.0       0.0

1439                  6     16.0       0.0       0.0      30.0       0.0
1443   25     0.00    4  11208.0    1384.0       0.0  566316.1       0.0
1452   26     0.00    4  10391.0     323.0       0.0  543034.1       0.0
1500                  7                                                      32.371
1504   27     0.00    5   9409.0   52267.0      18.0  519333.0   42078.0
1525   28    -1.00    5   8543.0   53948.0       0.0  491666.0   42720.0
```

Table 4. Sample Raw Data

```
                              DATA TAKEN DURING RUN  20 ON 18 JUL 74


THE CALIBRATION GASES ARE KNOWN TO BE
                      IGAS         H2        CO        CH4        CO2        H2O
                         1      25.17     24.94     24.97      24.94       0.00
                         2     100.00      0.00      0.00       0.00       0.00
                         3       0.00      0.00      0.00      96.76       3.23

CALIBRATION GAS SAMPLES FOR THIS RUN WERE ANALYSED AS

TIME SAMP        DELP IGAS         H2        CO        CH4        CO2       H2O          C
 921    1        1.00    1      25.19     25.16     24.93      24.90      0.00
 928    2        1.00    1      25.23     24.84     24.94      24.95      0.00
 935    3        0.00    1      25.19     24.88     24.94      24.97      0.00
 941    4        1.00    1      25.18     24.74     25.17      24.89      0.00
 958    5        0.00    2     100.00      0.00      0.00       0.00      0.00
1010    6        0.00    2     100.00      0.00      0.00       0.00      0.00
1653   33        0.00    3       0.00      0.00      0.00      96.89      3.10
1726   35       -1.00    3       0.00      0.00      0.00      96.99      3.00

THE RELATIVE CALIBRATION
AREA COEFFICENTS ARE      0.019677  0.997533  0.739083  1.000000  0.802260  0.027196

 ATMOSPHERIC PRESSURE WAS  759.96 .

 THE WEIGHT OF CATALYST INITIALLY CHARGED TO THE REACTOR IS  0.252 GRAMS.

 THE GROSS WEIGHT OF THE CATALYST CARRIER AND SUSPENSION MECHANISM IS  31.843 GRAMS.
```

Table 5. Sample Calibration Data

Table 6. Summary of Experimental Operating Conditions and Results for Run 20

```
                                      DATA TAKEN DURING RUN  20 ON 18 JUL 74

TIME SAMP        DELP IGAS        H2          CO          CH4          CO2          H2O           C

 948 CHANGED INLET GAS TO    100.00        0.00         0.00         0.00         0.00             TOTAL FLOW 29.7 CC/SEC (STP)

 949 REACTOR TEMPFRATURE 550. DEGREES CENTIGRADE

 958    5        0.00    4   100.00        0.00         0.00         0.00         0.00
1010    6        0.00    4   100.00        0.00         0.00         0.00         0.00
1030                                                                                          0.016 GRAMS CARBON DEPOSITED
1034    7        0.00    5   100.00        0.00         0.00         0.00         0.00
1041    8        0.00    5   100.00        0.00         0.00         0.00         0.00
1059                                                                                          0.019 GRAMS CARBON DEPOSITED

1103 CHANGED INLET GAS TO     49.98       50.01         0.00         0.00         0.00             TOTAL FLOW 19.8 CC/SEC (STP)
1105    9        0.00    4    49.06       50.93         0.00         0.00         0.00
1111   10        0.00    4    48.39       51.60         0.00         0.00         0.00
1118   11        0.00    4    49.02       50.97         0.00         0.00         0.00
1127   12       -1.00    5    47.12       51.93         0.00         0.01         0.92
1131                                                                                          0.063 GRAMS CARBON DEPOSITED
1141   13        0.00    5    48.12       51.55         0.00         0.03         0.28
1149                                                                                          0.086 GRAMS CARBON DEPOSITED
1155   14       -1.00    5    47.66       51.67         0.00         0.41         0.25
1210   15       -2.00    5    48.46       51.10         0.00         0.05         0.38
1214                                                                                          0.123 GRAMS CARBON DEPOSITED
1224   16       -2.00    5    48.09       51.61         0.00         0.03         0.26
1246                                                                                          0.180 GRAMS CARBON DEPOSITED
1254   18       -2.00    5    47.74       51.77         0.00         0.13         0.34
1308   19       -2.00    5    48.36       51.18         0.01         0.05         0.37
1317                                                                                          0.233 GRAMS CARBON DEPOSITED
1321                                                                                          0.317 GRAMS CARBON DEPOSITED
1323   20       -2.00    5    47.87       51.50         0.00         0.04         0.57
1337   21       -1.00    5    48.24       51.12         0.00         0.06         0.56
1353   22       -1.00    5    47.87       51.43         0.00         0.06         0.62
1408   23       -2.00    5    47.97       51.07         0.00         0.10         0.83
1412                                                                                          0.437 GRAMS CARBON DEPOSITED
1424   24       -1.00    5    47.67       51.26         0.00         0.11         0.94
1429                                                                                          0.530 GRAMS CARBON DEPOSITED

1428 CHANGED INLET GAS TO    100.00        0.00         0.00         0.00         0.00             TOTAL FLOW 19.8 CC/SEC (STP)

1439 CHANGED INLET GAS TO     49.80        0.00         0.00        50.19         0.00             TOTAL FLOW 19.9 CC/SEC (STP)
1443   25        0.00    4    46.91        0.14         0.00        52.94         0.00
1452   26        0.00    4    46.52        0.03         0.00        53.43         0.00
1500                                                                                          0.527 GRAMS CARBON DEPOSITED
1504   27        0.00    5    40.97        5.45         0.00        48.65         4.91
1525   28       -1.00    5    40.11        5.94         0.00        48.66         5.27
1532                                                                                          0.530 GRAMS CARBON DEPOSITED
1544   29       -2.00    5    40.07        6.27         0.00        47.77         5.87
1603   30       -1.00    5    39.57        6.49         0.00        48.16         5.77
1607                                                                                          0.534 GRAMS CARBON DEPOSITED
1618   31       -2.00    5    39.26        6.77         0.00        47.16         6.79
1631                                                                                          0.536 GRAMS CARBON DEPOSITED
```

In the next five columns are digital integrator chromatograph responses for each of the components specified at the column heading. The last column is the gross catalyst carrier weight.

The second and third pages, Tables 5 and 6, show converted output where the raw data have been replaced by gas phase concentrations in mole percent, the net weight of carbon deposited in grams, and gas flow rates in cm^3/sec at standard temperature and pressure. The second page, Table 5, shows these data for the analysis of calibration gas mixtures while the third page shows the data obtained during reactor operations. With the calibration data, the known concentrations of the calibration mixtures are listed. Samples of calibration gas I listed in Table 4 and samples of pure hydrogen were required to calibrate the response of the analytical equipment and then analyze the reactor operating data. Samples of gas saturated with water were not taken for all runs but were taken for a sufficient number of runs to ensure that the water analysis was accurate. The third output page, as shown in Table 6, lists all of the reactor operating data in the order that they were recorded or changed.

4.1 H_2-CO Mixtures - Carbon Deposition

As previous studies had indicated that a number of reactions were occurring simultaneously in the Bosch process, experimental runs were made with binary gas mixtures. The first binary gas mixtures investigated were those of hydrogen and carbon monoxide. From the studies of Walker et al. (1959), it was expected that these would deposit carbon more rapidly than other mixtures. Figure 29 shows the amount of carbon deposited on 250 mg of fresh steel wool catalyst as a function of time for a typical run. As can be seen, the amount of carbon deposited during the early portion of the run is

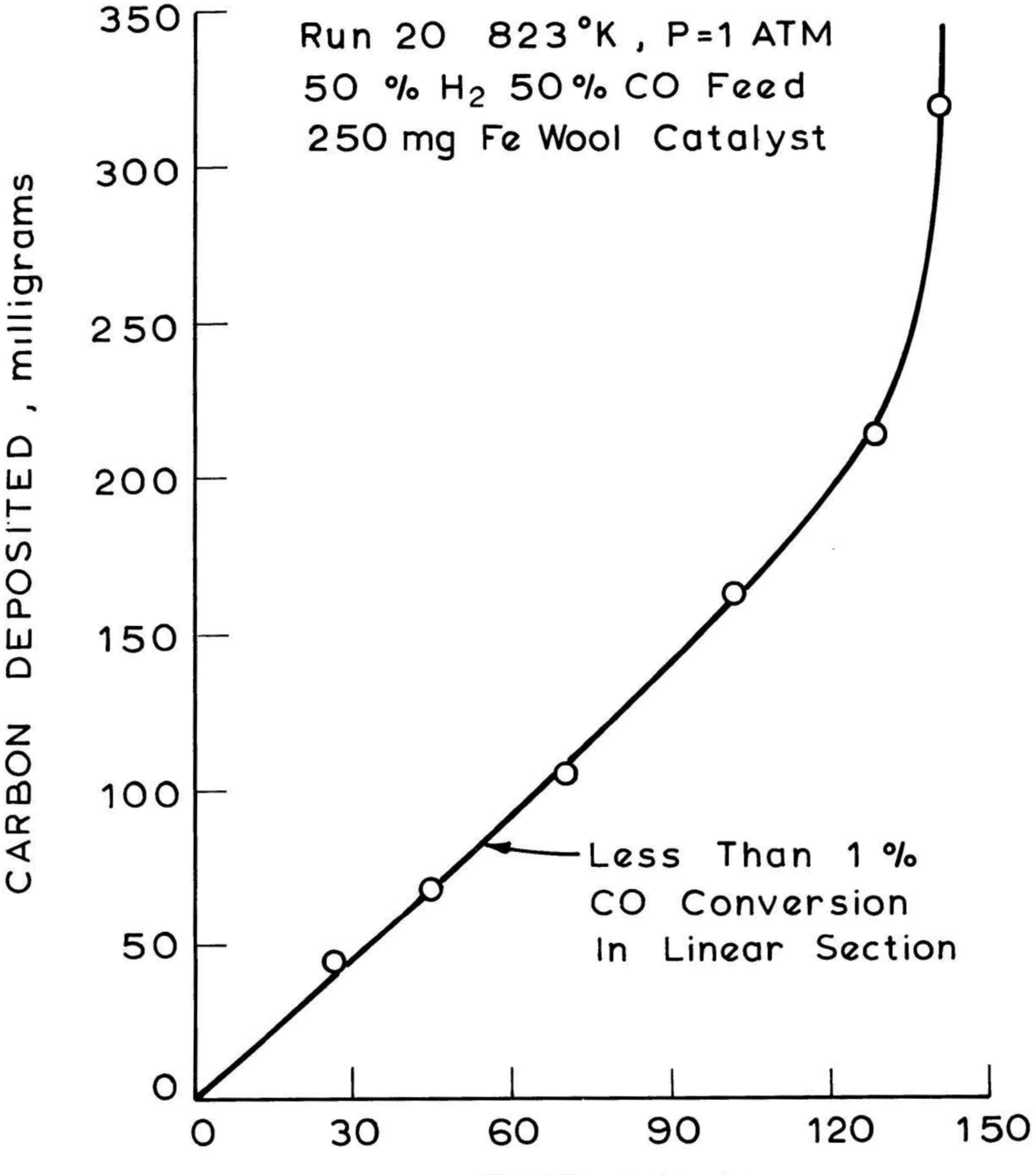


FIGURE 29 CARBON DEPOSITION DURING STARTUP WITH CO - H_2 FEED

approximately a linear function of time. However, the amount of carbon deposited is not a linear function of time over long periods, but, rather, shows an increasing rate of deposition as more carbon is deposited. During the same period that the data shown in Fig. 29 were taken gravimetrically, the reactor exit gas analysis indicated up to 0.37 mole % water and up to 0.41 mole % carbon dioxide. From the data, no determination could be made as to whether the carbon deposition process was a combination of reactions (C) and (D) in parallel or reactions (B) and (D) in series.

$$2CO \rightarrow CO_2 + C \qquad (C)$$

$$CO + H_2 \rightarrow H_2O + C \qquad (D)$$

$$H_2O + CO \rightarrow CO_2 + H_2 \qquad (B)$$

To determine whether the initial catalyst condition influenced the carbon deposition rate, 250 mg of fresh steel wool catalyst were oxidized in the reactor using a flowing stream of carbon dioxide at 823 K for one hour in Run 49. After a 30-min helium purge, a 25% carbon monoxide - 75% hydrogen mixture was passed over the catalyst. The subsequent carbon deposition was an order of magnitude faster than that for the same mixture over an untreated catalyst as is shown in Fig. 30. Concentrations of water and carbon dioxide in the reactor outlet were 4.8 and 1.7%, respectively. Similar but less pronounced results were apparent in Runs 15 and 16.

The physical change in the catalyst responsible for the increase in carbon deposition rate is readily seen in Figs. 31, 32, and 33. Figure 31 shows several strands of the untreated catalyst at low magnification. Although the edges of the steel wool band appear rough, the wide-flat

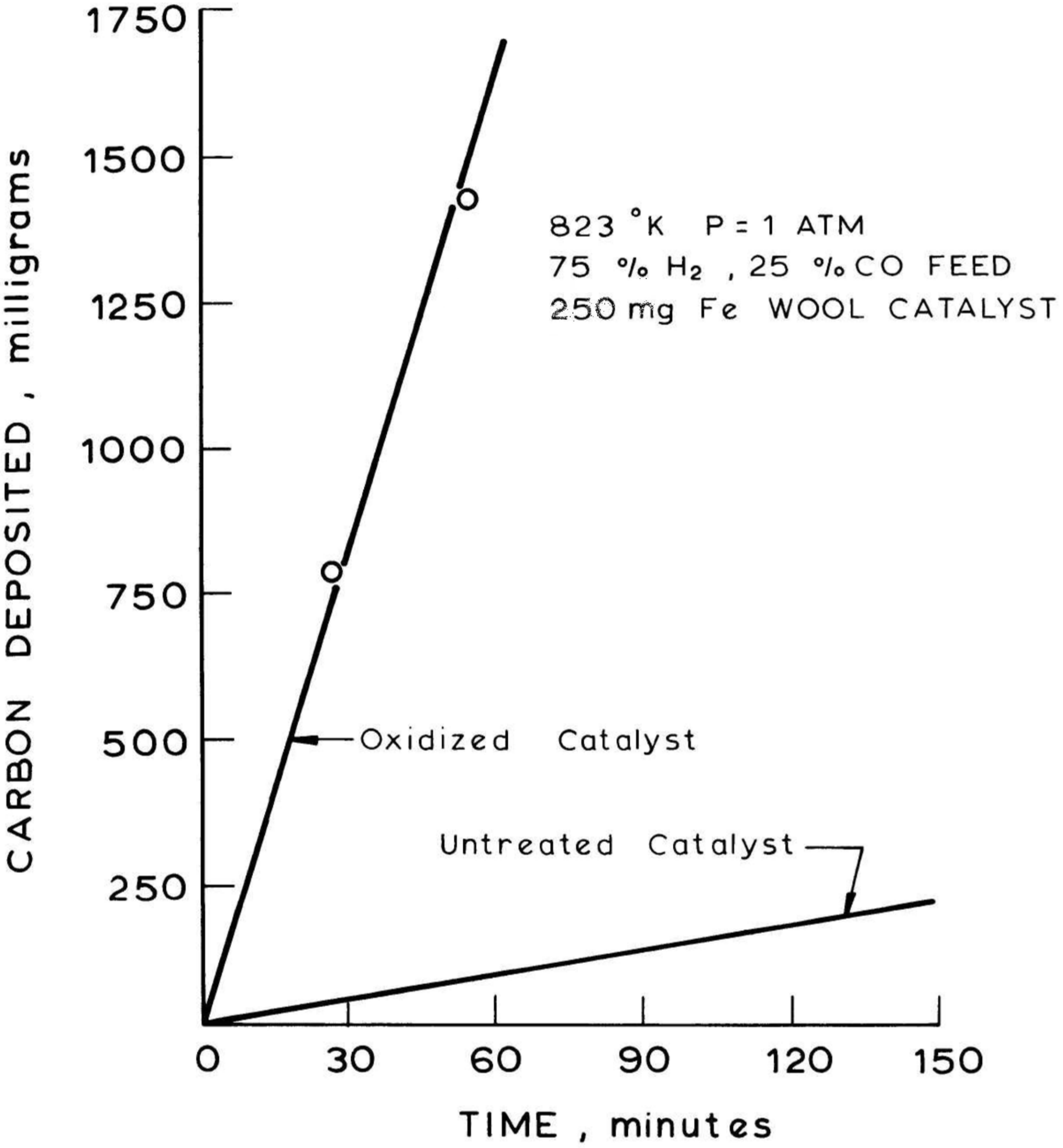


FIGURE 30, CARBON DEPOSITION DURING START UP WITH AN OXIDIZED CATALYST

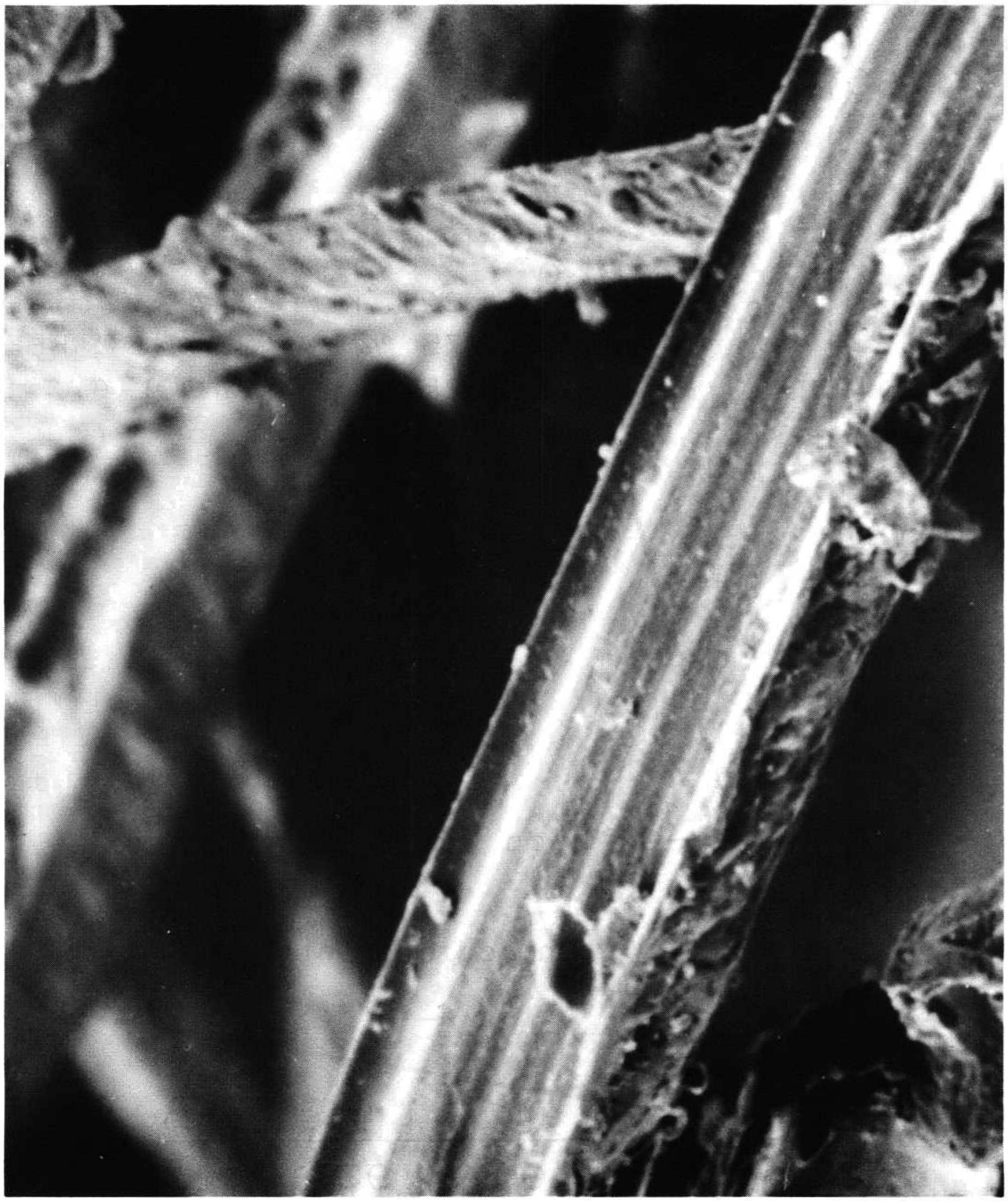


Figure 31 Untreated Steel Wool, 200 X

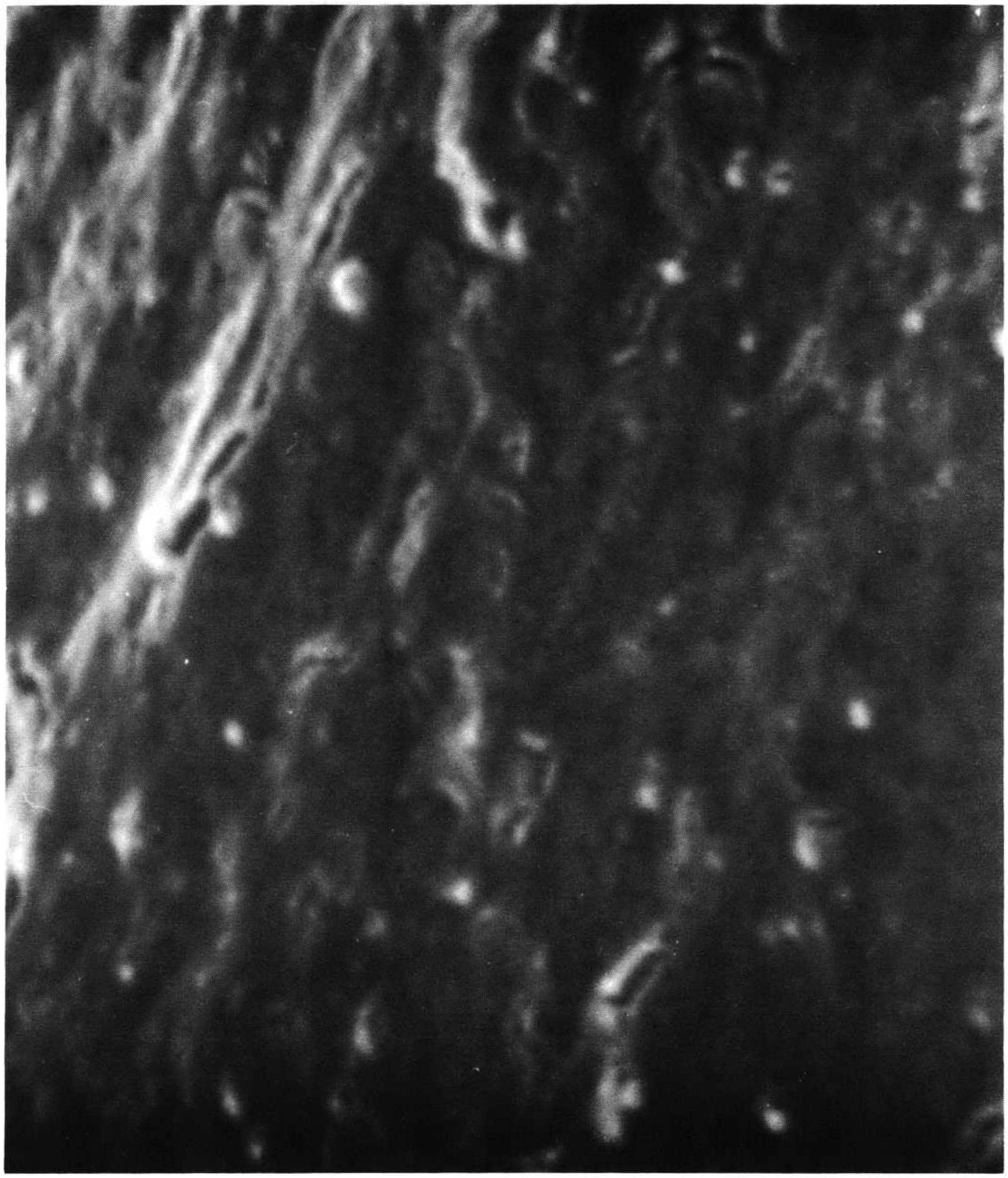


Figure 32 Untreated Steel Wool, 6000 X

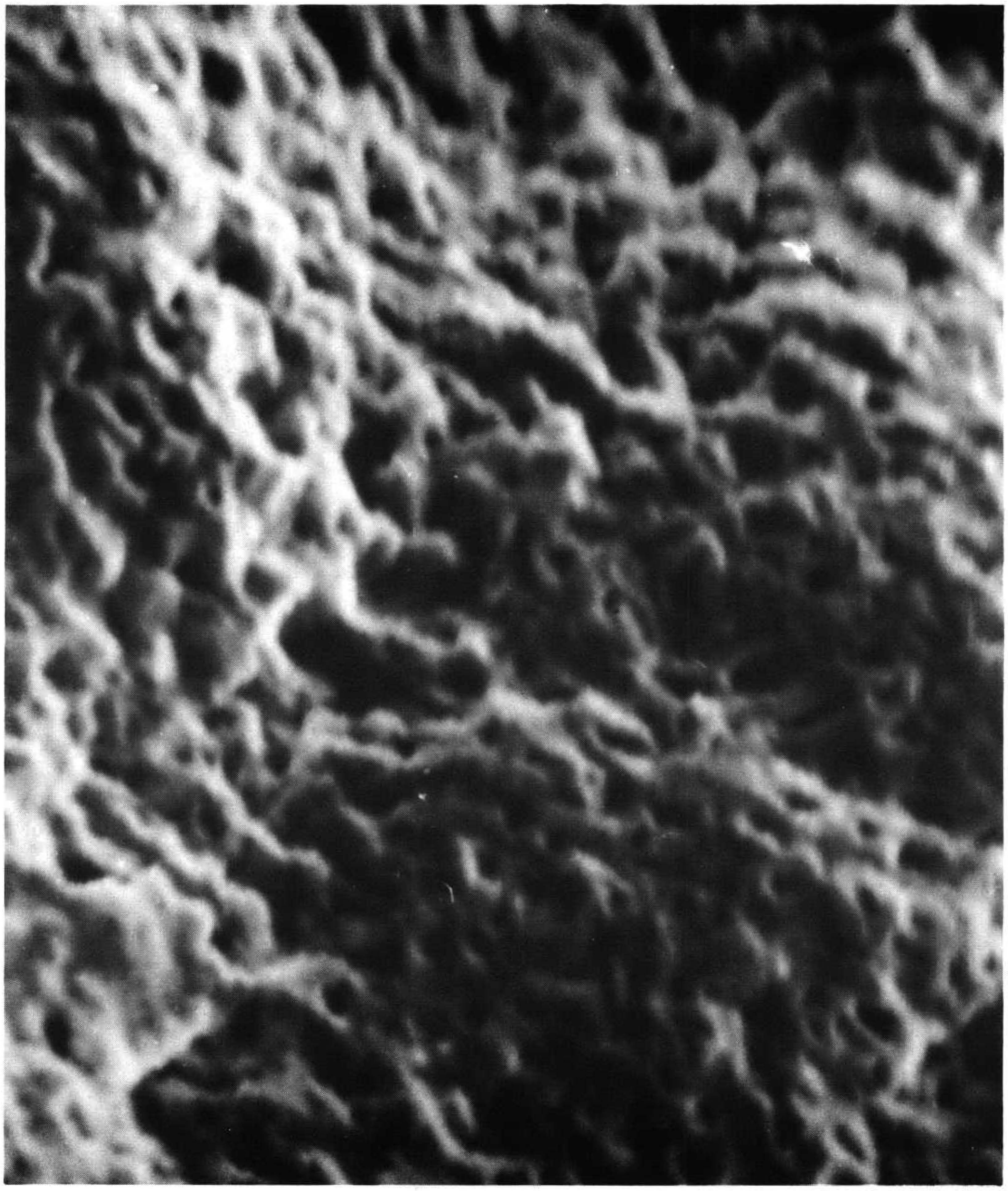


Figure 33, Oxidized Steel Wool, 6000 X

portion of the band is fairly smooth. In Fig. 32, a photograph of this same section at higher magnification is shown. The surface appears flat with some cracks evident. Figure 33 shows a similar area at high magnification taken of an oxidized catalyst after oxidation in CO_2 but before exposure to an H_2/CO feed mixture. In this photograph the surface appears rough and porous. It is possible that the oxidized surface increased the carbon deposition rate either by providing higher specific area or by providing a surface which readily forms the iron or iron carbide crystallites described by Ruston (1966, 1969).

In all other experiments, a stream of dry hydrogen was passed through the reactor and over the fresh steel wool catalyst to prevent catalyst oxidation as the reactor was heated. When the reactor temperature was stable at 823 K, a CO-H_2 mixture was passed over the catalyst. The amount of carbon deposited on the catalyst was recorded at various times. The results of seven experiments in which a 50% H_2-50% CO mixture was passed over the reduced catalyst are shown in Fig. 34. Similar results from nine other experiments for mixtures containing 25, 10, and 5% CO in hydrogen are shown in Fig. 35.

For each set of experimental data shown in Figs. 34 and 35, the rate of carbon deposition was determined graphically from the slope of the initial linear portion of the curves. The resulting values of carbon deposition rate were correlated with hydrogen and carbon monoxide partial pressures using a least-squares technique. The best resulting correlation was:

$$\text{rate (gmole/cm}^2\text{-sec)} = 4.3 \times 10^{-8} \, (P_{CO}P_{H_2})^{0.42 \pm 0.10} \qquad (4)$$

where the component partial pressures are in atmospheres. The rates corresponding to the values from this correlation for the experimental gas mixtures are shown as dashed lines in Figs. 34 and 35.

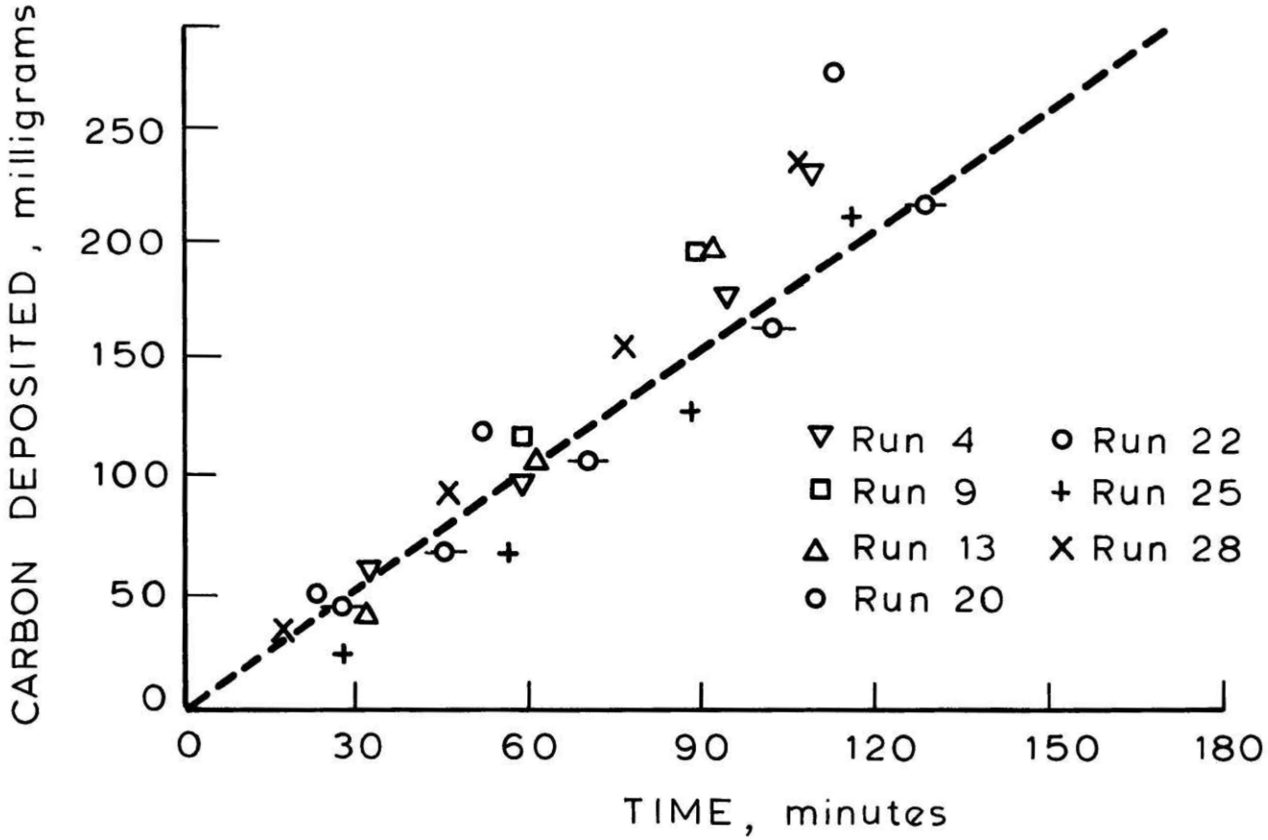


FIGURE 34, CARBON DEPOSITED FROM 50 % H_2 , 50 % CO MIXTURE AT 823 °K

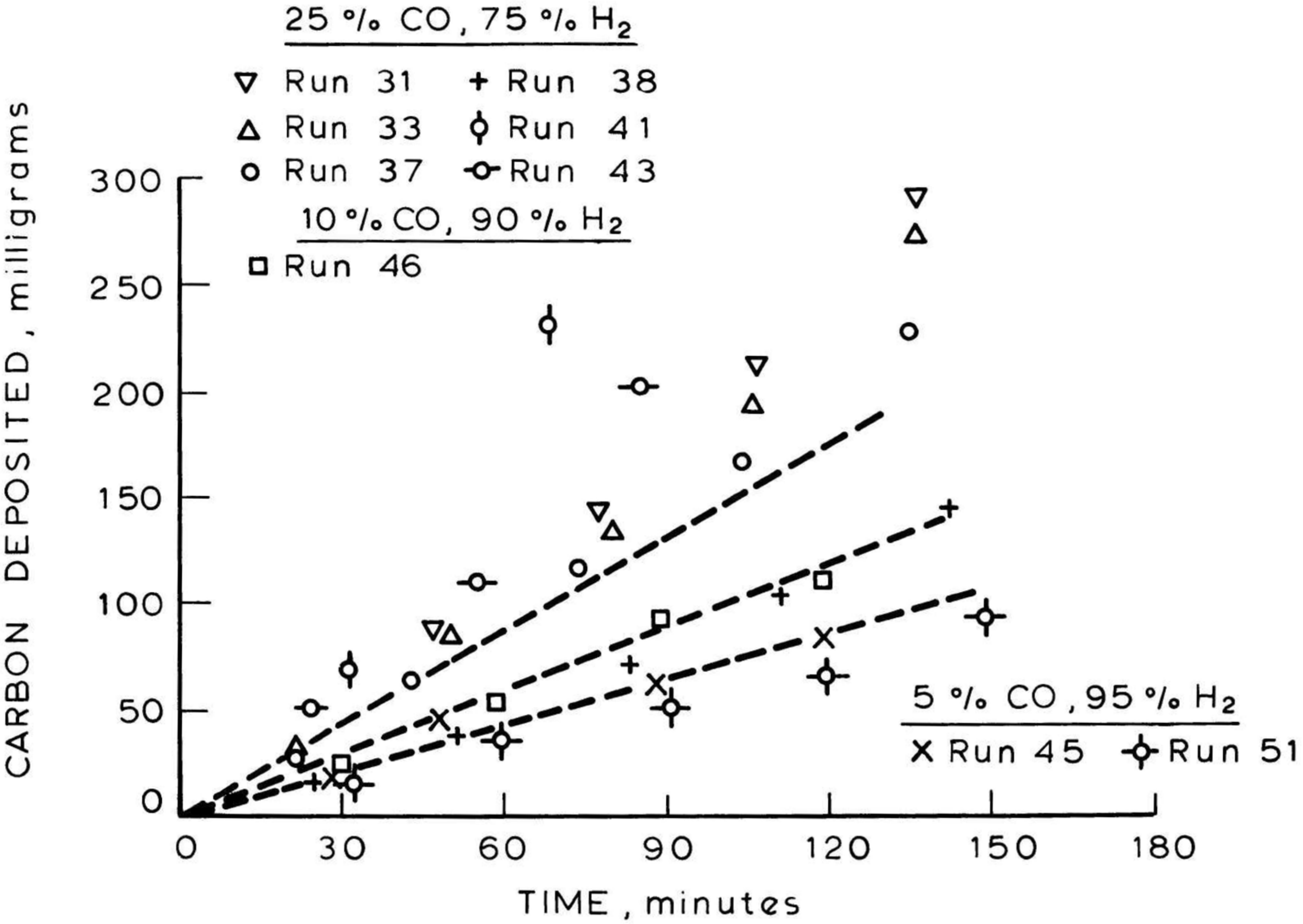


FIGURE 35. CARBON DEPOSITED FROM GAS MIXTURES CONTAINING 25, 10, AND 5 % CO IN HYDROGEN AT 823°K

One additional experiment, Run 39, at 773 K with a 25% CO-75% H_2 mixture permitted calculation of an approximate activation energy. Using the graphically determined carbon deposition rate of 0.76 mg/min at 773 K and the corresponding value of the correlation for the carbon deposition rate at 823 K, the activation energy was calculated to be approximately 70 kJ/mole.

Some limitations in the experimental data are apparent. The first is the scatter in the carbon deposition data presented in Figs. 34 and 35. In Fig. 34, for example, although the nominal operating conditions of the reactor did not change, the graphically determined rate of carbon deposition varied by as much as 50% above or below the mean rate. Thus, the range of rates encountered with a 50% CO-50% H_2 mixture overlapped the range of rates encountered with a 25% CO-75% H_2 mixture. Moreover, if the rate is assumed to vary with the square root of the partial pressures of carbon monoxide and hydrogen, only a 15% difference in rates would be expected between the 50% CO and 25% CO mixtures. Thus, a least-squares technique was required to correlate the data, and standard statistical techniques were used to evaluate the correlations. The multiple correlation coefficient was chosen as the criteria for comparison of the correlations.

Two-constant correlations of the form

$$r = kP^a$$

were used to correlate the rate with either the hydrogen or with the carbon monoxide partial pressures alone; multiple correlation coefficients of 0.48 and 0.78, respectively, indicate a statistically significant correlation with each variable at a confidence level above 90%. A similar two-constant equation using the product of the hydrogen and carbon monoxide partial pressures as the independent variable yielded the correlation shown as Eq. (4) with a multiple correlation coefficient of 0.75. Thus, the correlation is statistically significant with a probability of less than 0.001 that a larger value of the correlation coefficient will be obtained. A three-constant equation in which the exponents of the carbon monoxide and hydrogen partial pressures were allowed to vary independently was obtained; however, the correlation coefficient was smaller than that for the two-constant equation. Hence, the three-constant equation was disregarded.

Carbon deposition from mixtures of carbon monoxide and hydrogen on an iron catalyst has been discussed by Everett (1967). His results for gas mixtures with carbon monoxide to hydrogen partial pressure ratios near 1.0 indicated that carbon deposition rate was linearly dependent on carbon monoxide concentration. However, the same result was not found for mixtures with very high carbon monoxide to hydrogen partial pressure ratios. The results of Everett for both ratios of partial pressures are consistent with an approximately half-order dependence each on hydrogen and carbon monoxide partial pressure. The agreement in the form of the dependence in both sets of data lends additional support to the significance of the correlation.

4.2 H_2-CH_4 Mixtures

In Run 5, the reaction of methane and hydrogen mixtures on a Bosch catalyst was investigated by passing several hydrogen-methane mixtures over 250 mg of steel wool catalyst with approximately 400 mg of deposited carbon at 823 K. The results of this run are shown in Fig. 36. The points plotted are the net amount of carbon deposited on the catalyst at specific times during the experiment. In the early part of the run an inlet stream of pure hydrogen was fed to the reactor and the amount of deposited carbon decreased

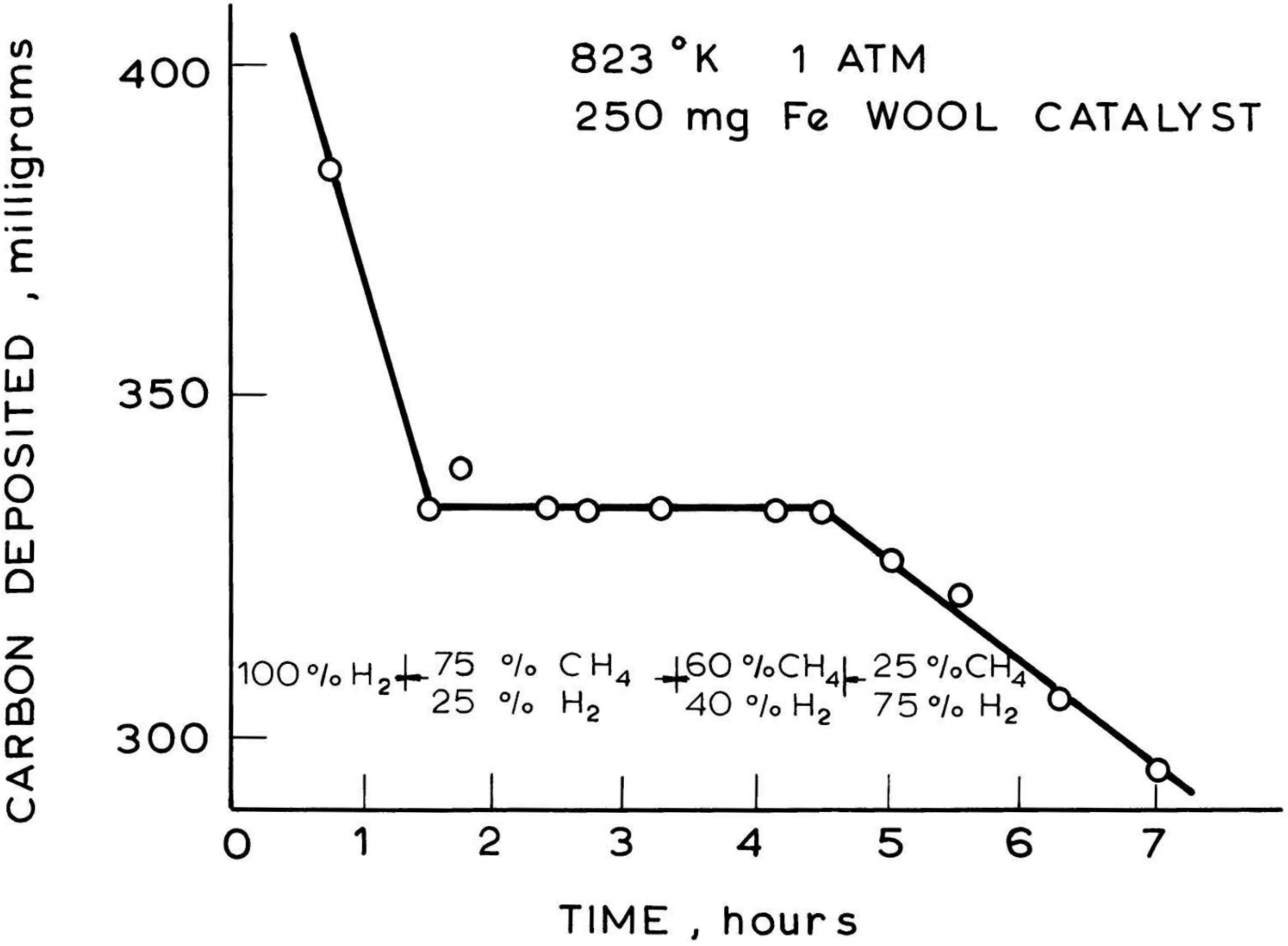


FIGURE 36, CARBON DEPOSITION FROM H_2 - CH_4 MIXTURES sharply. The reactor exhaust contained between 0.17 to 0.27 mole % methane indicating that carbon was being removed from the catalyst and converted to methane. However, when the methane concentration in the inlet gas was increased to 60 or 75%, the amount of carbon deposited remained constant. During this same period, the inlet and outlet gases were identical in composition within the limits of analytical accuracy. Thus, with more than 60% methane in the gas phase, all carbon forming or consuming reactions stopped. Changing the inlet gas composition to 25 mole % methane and 75% mole % hydrogen caused the amount of carbon deposited to decrease again.

At 823 K the equilibrium constant for reaction (E) is 0.966

$$C + 2H_2 \rightarrow CH_4 \tag{E}$$

while the equilibrium constant for reaction (J) is 2.48

$$Fe_3C + 2H_2 \rightarrow 3Fe + CH_4 \tag{J}$$

according to Browning et al. (1950). The equilibrium concentrations of methane for these two reactions would then be 38 and 53%, respectively.

As methane formation is possible by either reactions (E) or (J), Run 48 was performed to determine whether methane would form from free carbon at an appreciable rate in the absence of iron. In this experiment, 425 mg of activated charcoal (finer than 200 mesh with a BET area of ∿850 m^2/g) were charged to the reactor. The reactor was heated to 823 K in a flowing stream of hydrogen. No methane was detectable in the reactor exhaust gas. Thus, reaction (J) is the probable source of methane. However, since the amount of carbon removed by pure hydrogen (>75 mg carbon) exceeds that which could form a stoichiometric carbide, Fe_3C, with all the iron present (17 mg carbon), formation of methane from a carbide would require simultaneous formation of the carbide from the iron and carbon present.

No carbon deposited from mixtures rich in methane. This experimental observation indicates that the point at which carbon deposition ceases may not correspond to a reaction equilibrium. In most reaction equilibria, the equilibrium point may be reached from either side. It is possible in this case that carbon deposition does occur, but rapidly covers the catalyst surface stopping reaction. As the amount of carbon required to cover completely the iron surface area is below the sensitivity of the gravimetric technique employed, such a process would not be experimentally observable.

From this information several conclusions can be drawn:

- For gas mixtures on the methane-rich side of the equilibrium concentration, no carbon formation is observed experimentally. Nor is there any decomposition of methane to form carbon.
- For gas mixtures on the hydrogen-rich side of equilibrium concentration, hydrogen reacts (probably with iron carbide) to form methane.

4.3 CO-CO_2 Mixtures: The Effect of an Oxidized Catalyst Surface

In Runs 6 and 7, experiments were also performed to study the reactions of carbon monoxide and carbon dioxide mixtures. The results shown in Fig. 37 were obtained by passing various mixtures over 250 mg of steel wool catalyst and approximately 700 mg of deposited carbon at 823 K. As can be seen, an inlet gas composition of 50 mole % each of carbon monoxide and carbon dioxide caused no observable change in total weight of carbon deposited. Also, no change in gas composition through the reactor was observed. However, when a gas mixture containing 55 or 60 mole % carbon monoxide was fed to the reactor, no consistent weight gain or loss was observed, although both losses and gains were noted. One difficulty leading to these uncertain

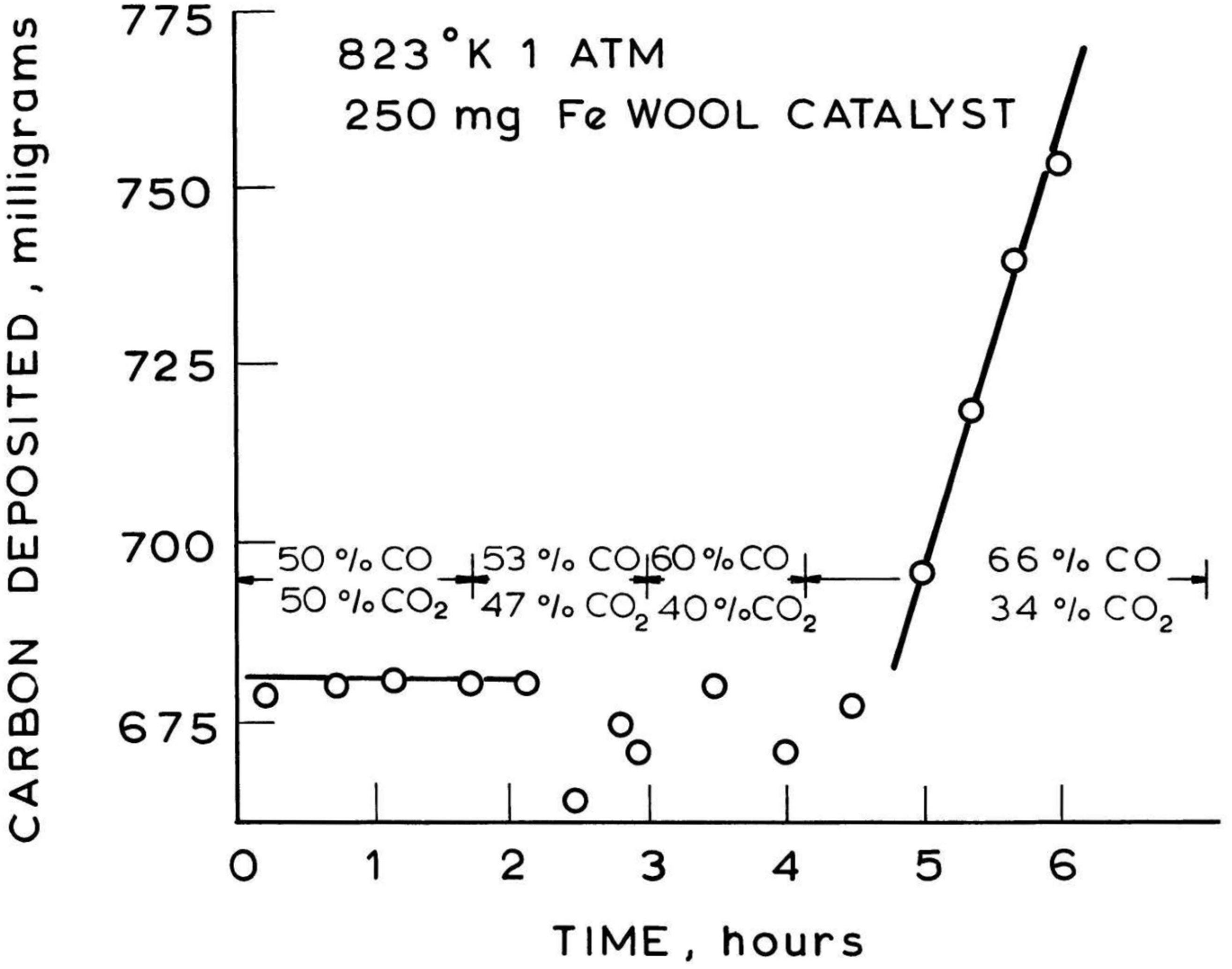


FIGURE 37, CARBON DEPOSITION FROM CO - CO_2 MIXTURES observations is that weight gain can be caused either by carbon deposition or by oxidation of the catalyst by reaction (L):

$$\frac{3}{4}Fe + CO_2 \rightarrow CO + \frac{1}{4}Fe_3O_4 \qquad (L)$$

The equilibrium constant for reaction (L) at 823 K is 1.11 corresponding to an equilibrium mole fraction of CO of 53%. When a gas stream containing 66 mole % carbon monoxide was fed to the reactor, a large, rapid weight gain occurred clearly indicating carbon deposition. The equilibrium constant for reaction (C) at 823 K is 48.8 corresponding to an equilibrium

$$2CO \rightarrow CO_2 + C \qquad (C)$$

mole fraction of CO of 13%.

From these data the following conclusions can be drawn:

- For gas mixtures on the CO_2-rich side of the equilibrium concentration, no reaction other than catalyst oxidation occurs. No carbon is removed.
- For gas mixtures on the CO-rich side of the equilibrium concentration, carbon deposition occurs.
- For gas compositions very close to equilibrium, no distinction could be made between carbon deposition and catalyst oxidation using the experimental apparatus.
- Although carbon deposition by reaction (C) is possible under all the experimental conditions shown in Fig. 16, no carbon deposition occurs when the catalyst is expected to be oxidized by reaction (L).

4.4 H_2-CO_2 Mixtures: Reverse Water-Gas Shift Reaction and Surface Area Effects

The next binary gas mixture studied in the experimental reactor was an equimolar mixture of hydrogen and carbon dioxide. From the results of Kusner (1962), it was expected that the reverse water-gas shift reaction,

$$H_2 + CO_2 \rightarrow CO + H_2O \qquad \text{(B)}$$

would proceed slowly over a low surface area iron catalyst such as steel wool. Indeed, when a gas stream containing 50% hydrogen and 50% carbon dioxide was passed over a fresh steel wool catalyst at 823 K, the product water and carbon monoxide were barely detectable (0.02%) in the reactor outlet stream as shown in Run 14.

However, with the same amount of iron catalyst after deposition of approximately 500 mg of carbon, reactor outlet concentrations of 5 to 7% each carbon monoxide and water were obtained with the same feed mixture in Runs 10, 11, and 12. No carbon was deposited. As the same weight of catalyst is present in all four experiments, it is obvious that the formation of deposited carbon on the catalyst has a large effect on its activity with respect to the reverse water-gas shift reaction.

This increase in activity resulting from carbon deposition can be hypothesized to result from several alternative causes. First, it might be suggested that the surface area of the deposited carbon was a catalyst for the reverse water-gas shift reaction. However, if this were the case, one would expect activated carbon with a large surface area to also be catalytic.

Alternatively, one might suggest that the active surface area of the catalyst had been increased during the deposition of carbon on the catalyst.

To determine which of these hypotheses was true, the following experiment was performed in Run 48. Approximately 425 mg of activated charcoal (finer than 200 mesh, with a BET area of $\sim$850 m^2/g) was charged to the reactor, and the reactor was heated to 823 K in a flowing stream of hydrogen. No methane was observed in the exhaust gas. The inlet gas was changed to 75% hydrogen and 25% carbon monoxide and only barely detectable amounts (<0.07 mole %) of carbon dioxide and water were found in the exhaust gas. The inlet gas was then changed to 50% hydrogen and 50% carbon dioxide, and less than 0.33 mole % carbon monoxide and water were observed in the exhaust gas. As the reaction rate of each of the reactions

$$C + 2H_2 \rightarrow CH_4 \tag{E}$$

$$CO + H_2 \rightarrow C + H_2O \tag{D}$$

$$CO_2 + H_2 \rightarrow CO + H_2O \tag{B}$$

is slower by at least an order of magnitude than the same reaction over a similar Bosch catalyst with approximately one fifth the carbon surface area, one can conclude that the carbon surface area is not influencing the rate of observed reaction. Hence, the iron must be responsible for the observed reaction rate increase. This conclusion, along with the experimentally observed increase in the carbon deposition rate and reverse water-gas shift rate as carbon is deposited, leads to the conclusion that the catalytic iron surface area increases by some mechanism in the process of carbon deposition. This observation is not unreasonable and can also be substantiated by calculations estimating the amount of iron surface area present. For example, if the steel wool is initially considered to be an infinitely long ribbon of thickness, t, the surface area per unit mass, S, can be shown to be

$$S = \frac{2}{t\rho}$$

Using a typical value for t and ρ (1.3 μm, 7.6 g/cm^3) one finds that the surface area of #2 steel wool should be about 200 cm^2/g. The BET surface area was experimentally determined to be 389 cm^2/g. Thus, if the initial catalyst charge is 0.25 g, the initial iron surface area would be 97 cm^2.

After carbon deposition, however, iron is present not only as steel wool fibers but also dispersed in the carbon product as iron or iron carbide. Transmission electron photomicrographs have shown that the iron is dispersed in the carbon in segments which have approximately the same dimensions as the carbon. On the basis of one gram of carbon-iron ribbon containing x_{Fe} weight fraction iron, the iron surface area is

$$A_{Fe} = x_{Fe}S_{Fe} = x_{Fe}\left(\frac{2}{t_{Fe}\rho_{Fe}}\right)$$

and the carbon surface area is

$$A_C = (1 - x_{Fe})S_C = (1 - x_{Fe})\left(\frac{2}{t_C\rho_C}\right)$$

As the ribbon thickness appears to be constant in electron photomicrographs,

$$t_{Fe} = t_C$$

Hence,

$$\frac{A_{Fe}}{A_C} = \frac{x_{Fe}}{1 - x_{Fe}} \frac{\rho_C}{\rho_{Fe}}$$

Taking the values reported by MacIver and Emmett (1955) for the total surface area (145 m^2/g) and weight fraction iron (7%) as typical of Bosch carbons, the iron surface area in 0.5 g of deposited carbon is found to be 1.2 m^2. Thus, one would expect that the iron surface area has increased by a factor of 120 during the carbon deposition. This factor is approximately equal to the observed increase in the water-gas shift reaction rate.

As the above estimation assumes that the major portion of the product carbon is in the form of carbon fibers or ribbons, a scanning electron microscope was also employed to photograph the carbon deposited on the catalyst surface. Figures 38 and 39 show typical photographs of the product carbon. Figure 38 shows the catalyst surface entirely covered with a mass of fibrous carbon growth. Figure 39 shows the fibers at much higher magnification. From the photograph, the diameter of a fiber is calculated to be $\sim 4 \times 10^{-5}$ cm (0.4 μm).

Since equipment was not available to make direct measurements of iron surface area in this investigation, the change in catalytic surface area leads to the conclusion that the data obtained may help qualitatively to determine the effects of gas composition and temperature on reaction rates but cannot be used to specify quantitatively the catalytic reaction rates. One exception, however, is that reaction rate data may be obtained from the initial portions of the experimental runs. That is, the initial rate of carbon deposition can be determined as a function of temperature and gas composition where the initial surface area is fixed.

In spite of the complications introduced by the changing catalytic surface area, several interesting comparisons can be made from the experimental data. For example, a comparison can be made of the relative rates of the carbon deposition reaction and the water-gas shift reaction from the rates observed on fresh catalysts. For the carbon deposition reaction at 823 K, the rate of reaction, using Eq. (4) and the measured BET surface area,

Figure 38 Carbon Deposited on Catalyst
560 X

Figure 39 Carbon Fibers ,7800 X

is 2 x 10^{-8} gmole/cm^2-sec for a gas mixture containing 50% H_2 and 50% CO. For a similar mixture containing 50% H_2 and 50% CO_2 (negligible water), the observed rate of the water-gas shift reaction on a fresh catalyst (Run 14) is 2 x 10^{-9} gmole/cm^2-sec. Thus, one can see that both reactions may be significant depending on the gas phase concentration of the reactants.

Similarly, from the data shown in Fig. 36, the maximum rate of formation of methane on a catalyst with 0.35 g of deposited carbon is approximately 1.5 x 10^{-6} gmole/sec. Over a similar catalyst, the typically observed rate of the reverse water-gas shift reaction was 4.5 x 10^{-5} gmole/sec. Thus, the methane forming reaction in the Bosch process is significantly slower than either the carbon forming or reverse water-gas shift reactions.

4.5 H_2-CO_2 Mixtures: Reverse Water-Gas Shift Reaction, Heat and Mass Transfer Effects

Since the conversion of carbon dioxide to carbon monoxide by the reverse water-gas shift reaction was rapid over a steel wool catalyst with deposited carbon, additional experiments at various temperatures and two other flow rates were performed to determine the effects of heat and mass transfer on the observed reaction rate. In Runs 34 and 35, the inlet reactor temperature was varied from 673 to 823 K in 25 K increments. A 47% H_2, 53% CO_2 feed mixture flowed through the reactor at a constant total flow rate of 20 cc/sec (STP). The conversion of CO_2 expressed as the percentage of inlet CO_2 converted to CO is shown as a function of reciprocal of the reactor inlet temperature in Fig. 40. Also shown is the conversion that would be expected at equilibrium in the same temperature range. The experimentally measured conversions at low conversion (below 5%) represent experimental reactor operation in a region where reactor operation may be assumed to be differential; that

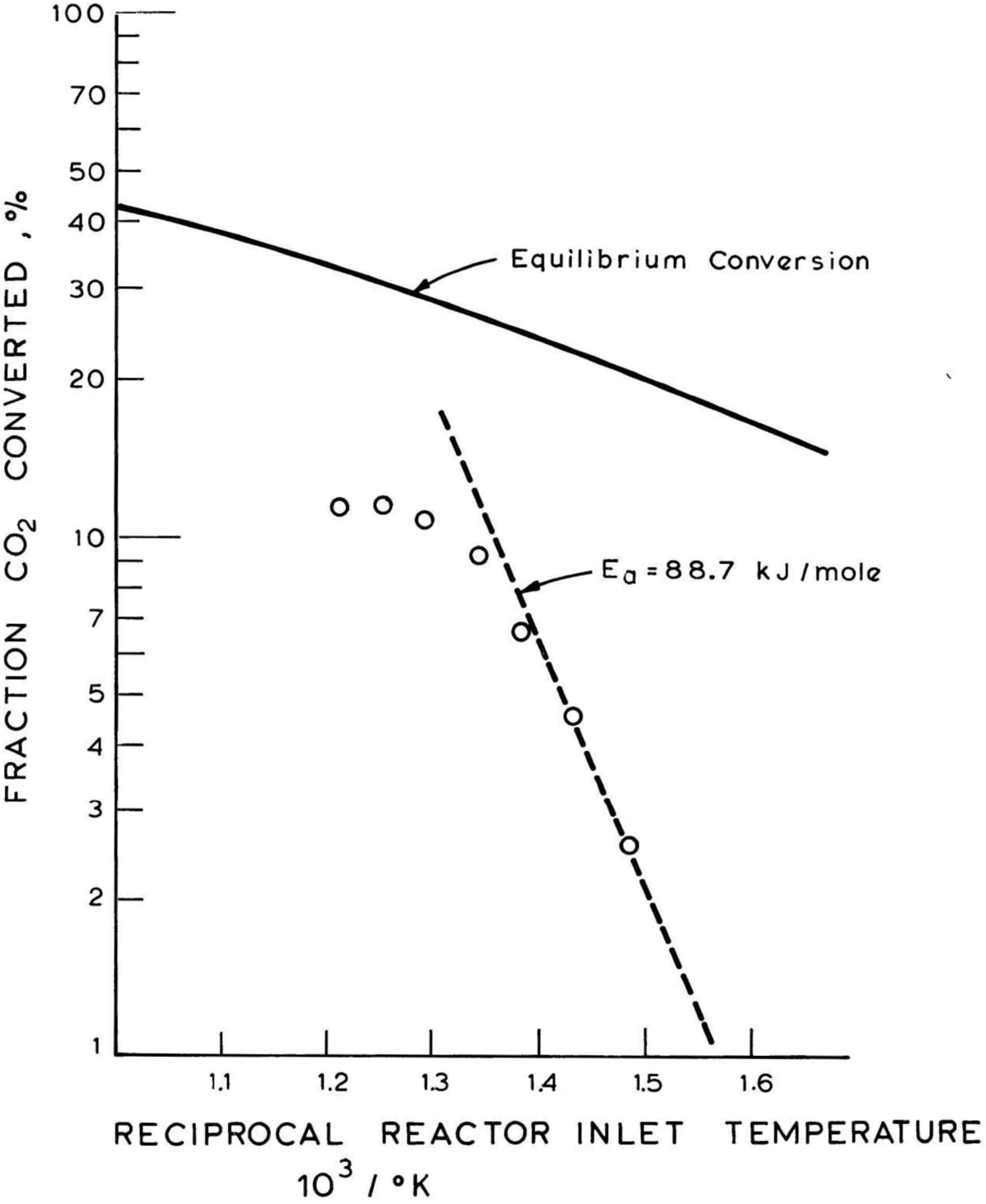


FIGURE 40, EFFECT OF TEMPERATURE ON SHIFT CONVERSION is, the gas phase concentrations may be assumed to be constant through the reactor and the conversion in the reactor is directly proportional to the reaction rate. Hence, the activation energy for the reaction may be determined from the slope of the dotted line in Fig. 40. The dotted line shown represents an activation energy of 88.7 kJ/mole. No previous experimental measurements of the activation energy of the reverse water-gas shift reaction have been reported and thus no direct comparison with other results is possible. However, if the transformation of the reactants into the products on the catalyst surface is assumed to occur in a single activated step, then the activation energy of the reverse reaction (i.e., the water-gas shift reaction) can be calculated from the activation energy of the forward reaction and the known enthalpy change which occurs when the reactants are converted to products. Thus, the activation energy for the water-gas shift reaction is computed to be 125.5 kJ/mole from the observed activation energy of the reverse water-gas shift reaction (88.7 kJ/mole) and the known enthalpy of reaction (36.8 kJ/mole). The activation energy for the water-gas shift reaction was reported to be

110.8 kJ/mole	Ruthven (1968)
114.6 kJ/mole	Bohlbro (1961)
123.0 kJ/mole	Podolski and Kim (1974)
133.9 kJ/mole	Mars (1961)

Hence, the calculated activation energy for the water-gas shift reaction based on the observed activation energy of the reverse reaction is in good agreement with that reported by other authors.

As temperature is increased and observed conversions exceed 5%, the observed rate of conversion does not continue to increase toward equilibrium conversion. As indicated in Appendix 8.1.2, mass transfer is not expected to be limiting the conversions even at 823 K. Under the same conditions, it can be shown that heat transfer from the reactor furnace to the catalyst carrier is expected to limit conversion. Indeed, for the two highest conversions shown in Fig. 40 at 798 and 823 K, the adiabatic temperature drop from the reactor inlet to the reactor outlet is calculated to be 75 K. Moreover, if the catalyst bed is assumed to be isothermal and if heat transfer from the furnace to the catalyst bed is limited by radiation between the catalyst carrier and the reactor support tube, a minimum temperature difference of 13 K would be required. The reactor operation at these high conversions is probably intermediate between the extremes of isothermal and adiabatic operation. Hence, the reactor outlet temperature is expected to have been somewhere between 13 and 75 K below the reactor inlet temperature. Unfortunately, it was not possible to position a thermocouple at the reactor outlet without interfering with gravimetric determination of catalyst weight. Thus, reactor outlet temperature was not measured.

Run 17 was initially intended to demonstrate the absence of any mass transfer limitation on the reverse water-gas shift conversion. In this experiment, the conversion of a 47% H_2, 53% CO_2 feed mixture was determined at 823 K for total gas feed rates of 10 and 2 cc/sec (STP). The overall conversions obtained at the two flow rates were 10 and 22%, respectively. Thus, the process limiting conversion in this experiment is, again, heat transfer from the reactor furnace to the catalyst carrier; and, no conclusion on the role of mass transfer from the bulk gas phase to the catalyst surface can be made on the basis of this experiment.

4.6 H_2-H_2O and CO_2-H_2O Mixtures

At the start of Runs 30 and 42, a hydrogen stream saturated with water at 294 K was passed over a catalyst with more than 0.5 g of deposited carbon at 823 K. In both cases, a loss of 12 mg of carbon from the catalyst carrier was observed over a half hour period. No CO, CH_4, or CO_2 was observed in the outlet gas stream even though this carbon loss should yield detectable (0.06%) amounts of gaseous products.

In Run 44, both pure carbon dioxide and carbon dioxide saturated with water at 294 K were passed over a catalyst with approximately 0.35 g of deposited carbon at 823 K. No consistent weight gain or loss was observed and neither hydrogen, nor carbon monoxide, nor methane were detected in the reactor exhaust. From these experiments, it would appear that the reactions

$$H_2O + C \rightarrow CO + H_2$$

and

$$CO_2 + C \rightarrow 2CO$$

do not proceed at detectable rates under the experimental conditions employed. This observation is consistent with the rate expressions for these reactions determined by Wicke _et_ _al_. (1966) which predict reaction rates at least four orders of magnitude below the minimum detectable rates for this experimental apparatus.

4.7 Multicomponent Gas Mixtures

Several experiments were performed to determine the relative effects of the reactions which are major components of the Bosch process. For these experiments, both the reaction temperature and relative concentration of the reactants were varied. The most prominent effect was that of temperature.

In Run 26, the formation of methane from pure hydrogen flowing over an iron catalyst containing 700 mg of deposited carbon was not detectable at 673 K. In Run 27, methane formation was detectable at 748 K with ∿0.07 mole % CH_4 at the reactor outlet with a simultaneous carbon loss rate of 0.38 mg/min. At 823 K approximately 0.22 to 1.5% methane is found in the reactor outlet mixture as shown in Runs 5 and 19, respectively. The addition of approximately 3% water to the hydrogen stream was observed to stop methane formation as shown in parts of Runs 29 and 30. Methane formation was observed at 823 K in the presence of water from feed gas streams containing 95% H_2, 2% CO, and 3% H_2O and 91% H_2, 5% CO, and 3% H_2O in Run 29. It would appear that under these circumstances methane formation is possibly by reactions (M) and (J) and that water inhibits reaction (J).

$$3H_2 + CO \rightarrow CH_4 + H_2O \tag{M}$$

Finally, it should be noted that the observed rate of methane production exceeds the observed rate of carbon deposition for both the H_2-CO-H_2O mixtures investigated in Run 29 and the H_2-CO-CO_2-H_2O mixtures investigated in Run 30.

In Run 26, carbon formation from a 50% H_2, 50% CO feed mixture was found to be undetectable at 673 K. In Run 27, the same gas feed mixture produced detectable amounts of water and carbon dioxide in the reactor effluent (0.60 and 0.15 mole %, respectively) and a carbon deposition rate of 3.2 mg/min at 748 K. In Run 40, the effect of carbon dioxide concentration on the carbon deposition rate was investigated at 773 K. The carbon deposition rate from a feed mixture containing 74% hydrogen and

26% carbon monoxide was found to be 1.3 x 10^{-6} gmole/sec. After changing the feed mixture to 73% H_2, 10% CO, 17% CO_2, the carbon deposition rate dropped to 9.7 x 10^{-7} gmole/sec over the same catalyst. The decrease in the carbon deposition rate, however, is not significantly different from that expected by the reduction in CO partial pressure alone assuming the carbon deposition rate depends on the square root of the hydrogen and carbon monoxide partial pressures. Hence, it is concluded that CO_2 exhibits no pronounced inhibition of the carbon deposition reaction.

Water, on the other hand, appears to reduce the carbon deposition rate in a manner similar to that shown by Karcher and Glaude. This fact becomes apparent when the ratio of the carbon deposition rate to the methane formation rate is examined at several values of water partial pressure. First, for all carbon depositions on a fresh catalyst, carbon deposition occurs at the rate given by Eq. (4). During the period that carbon is depositing at the observed rate, no detectable methane occurs in the reactor outlet while the water concentration corresponding to carbon deposition from a 50% H_2, 50% CO mixture at 823 K is ∿0.26% H_2O. That is, at this low value of water concentration, carbon deposition is fast relative to methane production. Over a catalyst where a significant amount of carbon deposition has occurred and the catalytic surface area has been increased, the water-gas shift reaction is so rapid that outlet water conditions are significantly higher (i.e., ∿5-10%). For these mixtures when sufficient CO (∿10%) is available to make carbon deposition measurable, the carbon deposition rate and the methane production rate are within a factor of two of each other as shown in Runs 29, 30, 36, and 37. Under these same circumstances the rate of the reverse water-gas shift reaction is normally at least one order of magnitude faster as is evident in Runs 29, 30, 36, and 37.

In several of the experiments cited above, carbon deposition is observed under conditions where the ratio of the hydrogen partial pressure to the water partial pressure at the reactor outlet is as low as 8.1. Karcher and Glaude reported that at ratios below 20, carbon deposition at 823 K was suppressed. Hence, it is possible that the low carbon deposition rates relative to the methane formation rates may be due to inhibition of carbon deposition by water near the reactor outlet. This argument is qualitative, however, and requires substantiation by experiments with increased values of the partial pressure ratio below 20 at the reactor <u>inlet</u>. The interpretation of the observations is also complicated by the fact that in some of the experiments the reverse water-gas shift conversions are high so that heat transfer effects may also be important.

In summary, the initial rate of carbon deposition on a reduced iron catalyst has been found to depend on the product of hydrogen and carbon monoxide partial pressures to the 0.42 ± 0.10 power. This result is consistent with the experimental data of Everett (1967) and Everett and Kinsey (1965). Moreover, no carbon deposition was observed from $CO-CO_2$ mixtures when the iron surface was expected to be oxidized instead of reduced by reaction (L). The observed rates for carbon deposition and for the reverse water-gas shift have been shown to be within an order of magnitude of each other for similar but not identical conditions. The maximum rate of the methane-forming reaction has been shown to be significantly slower than the reverse water-gas shift reaction when no water is present but of the same order of magnitude when approximately 5% water is present. Moreover, the formation of metal carbide has been indicated to be an intermediate process in the formation of methane from carbon. In addition, more data on the change of catalyst surface area during carbon deposition are required to determine quantitatively the kinetic parameters of the Bosch process.

5. APPLICATION OF RESULTS

The experimental results indicate the causes of some problems previously experienced with prototype Bosch reactors. For example, Holmes et al. (1970) noted that at least 1.5 hr was required to start an experimental Bosch recycle reactor using a feed mixture of hydrogen and carbon dioxide with a steel wool catalyst. From a similar feed mixture over a steel wool catalyst, the conversion realized in a single-pass experimental reactor was shown in this investigation to be extremely low. Thus, one would expect many passes of the gas mixture through a recycle reactor would be required to form carbon monoxide in sufficient quantities to initiate carbon deposition.

To overcome the difficulties in starting a reactor which operates as shown in Figs. 1 and 41, an alternative scheme as shown in Fig. 42 could be used. In this process, a feed mixture containing two moles of hydrogen for each mole of carbon dioxide is fed to a reverse water-gas shift reactor at 922 K. Using a pelleted iron powder catalyst with high specific surface area, Kusner (1962) has shown that the shift reaction rate at 922 K over an active catalyst is limited only by mass transfer of reactants from the gas phase to the catalyst surface. The product stream from the shift reactor is then fed to a recuperative heat exchanger where water is condensed and separated. If it is assumed that equilibrium is reached in the shift reactor, 0.562 moles of water would be obtained per mole of CO_2 fed. The remaining gas stream containing 18 mole % carbon dioxide, 59 mole % hydrogen, and 23 mole % carbon monoxide (on a dry basis) may then be fed to a recycle reactor at 823 K to produce both carbon and water as shown in Fig. 42.

This operating scheme has several advantages. First, 28% of the water

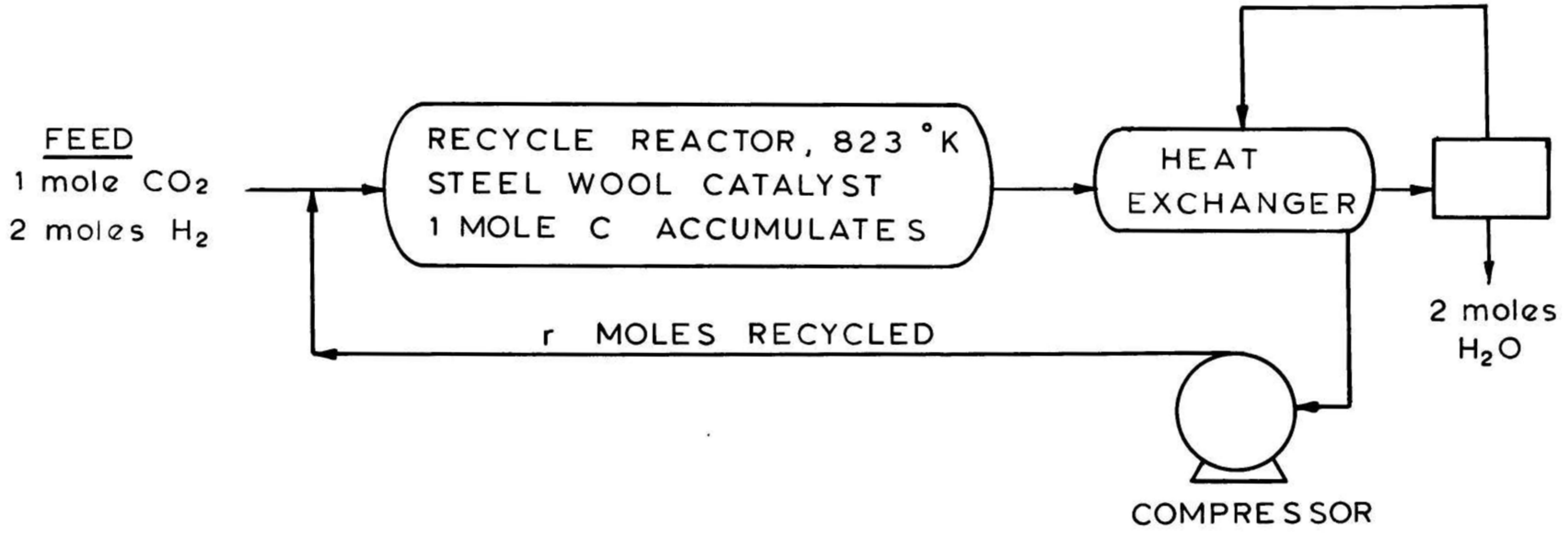


FIGURE 41, THE BOSCH RECYCLE REACTOR

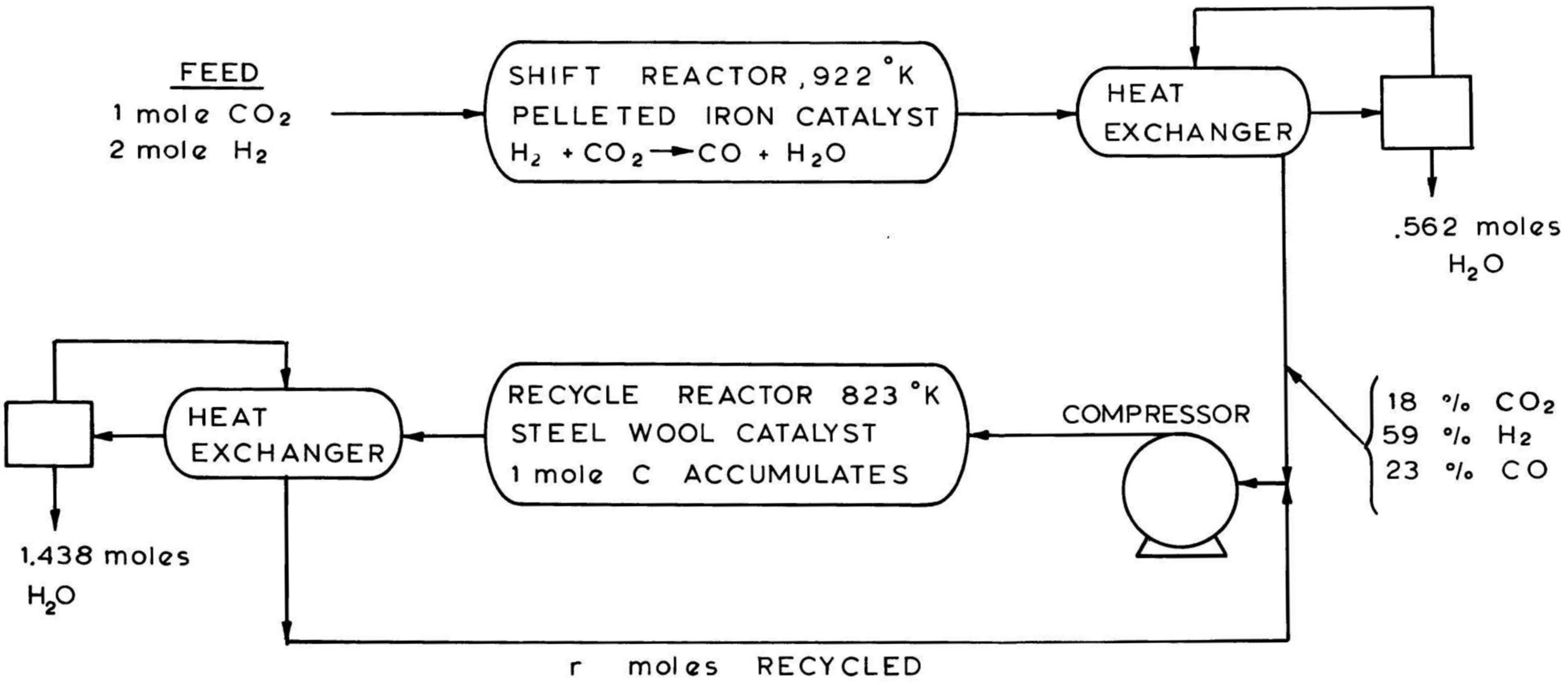


FIGURE 44, ALTERNATIVE BOSCH PROCESS FLOWSHEET

formed in the overall process can be recovered after one pass through the shift reactor. Secondly, a rapid start of the recycle reactor should be achievable by using the H_2-CO-rich stream from the shift reactor and a catalyst activation procedure such as surface oxidation by carbon dioxide. Additionally, the flowsheet shown in Fig. 42 can be simplified by employing only the second heat exchanger for both reactors; that is, the product stream from the shift reactor could be introduced directly into the recycle loop after the recycle reactor and before the heat exchanger as shown in Fig. 43. Finally, even more favorable yields of water and carbon monoxide are obtainable by increasing the shift reactor temperature. It should be noted that higher water yields could also be obtained by increasing the H_2/CO_2 ratio of the feed mixture. However, this would lead to accumulation of hydrogen in the second recycle reactor requiring an occasional reactor purge and, thus, a more complicated operation. To increase the H_2/CO_2 ratio above two without purging, a hydrogen separator, such as a palladium-silver semipermeable membrane, could be added as illustrated in Fig. 44. The excess hydrogen would be recycled to the shift reactor inlet.

The experimental results also indicate that methane is formed from the reaction of hydrogen with the carbide present when carbon is deposited on the steel wool catalyst. Thus, in any recycle loop, such as those shown in Figs. 41 through 44, when methane is not removed, an accmumlation of methane in the recycle loop must be expected. Based on the data obtained using binary mixtures and the results of Browning _et_ _al_. (1950), the concentration of methane in the recycle stream would be expected to increase at least until reaching a concentration corresponding to equilibrium for reaction (E). Since kinetic data are not yet sufficient to evaluate the feasibility of single-pass reactor(s) to form carbon and water, the disadvantages of recycling methane

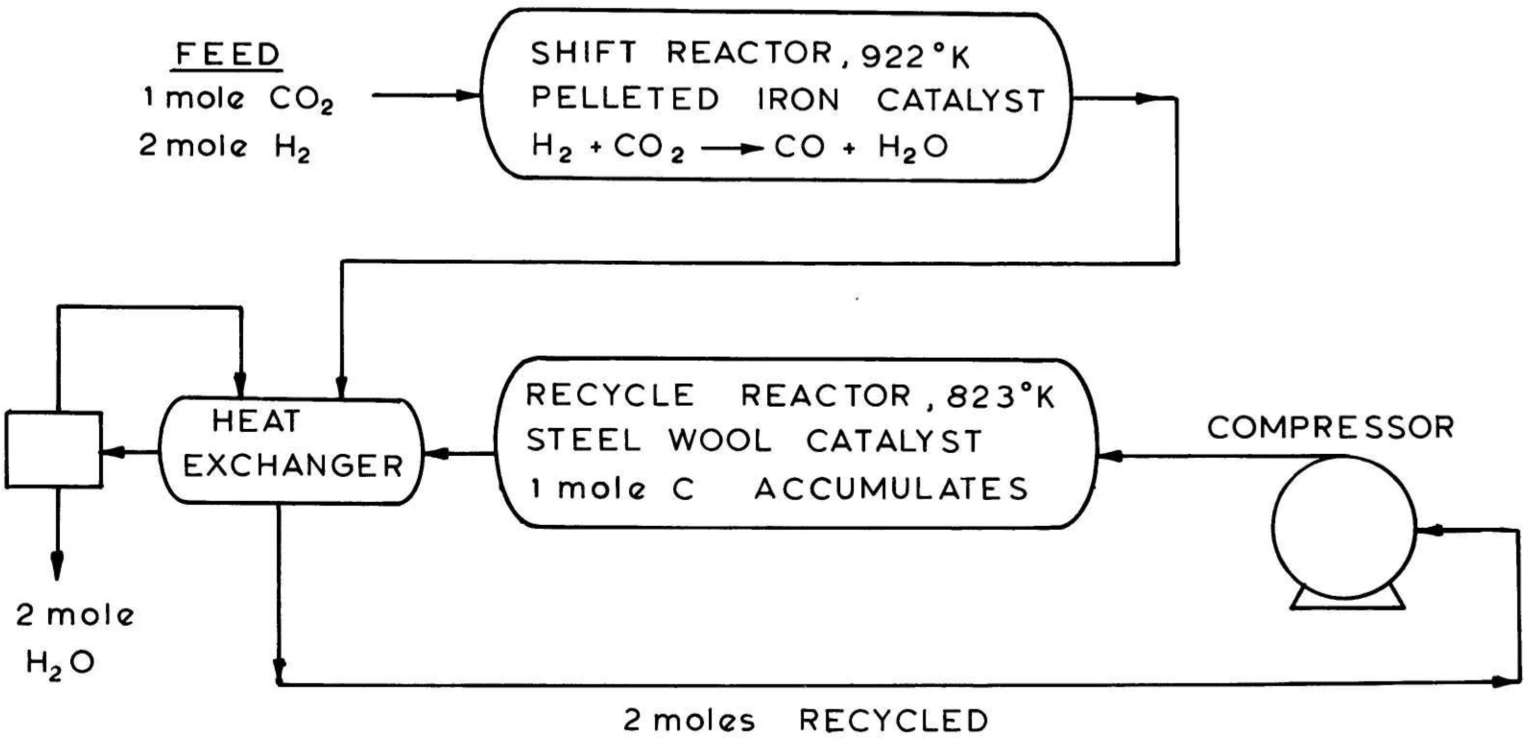


FIGURE 43, ALTERNATIVE BOSCH PROCESS FLOWSHEET

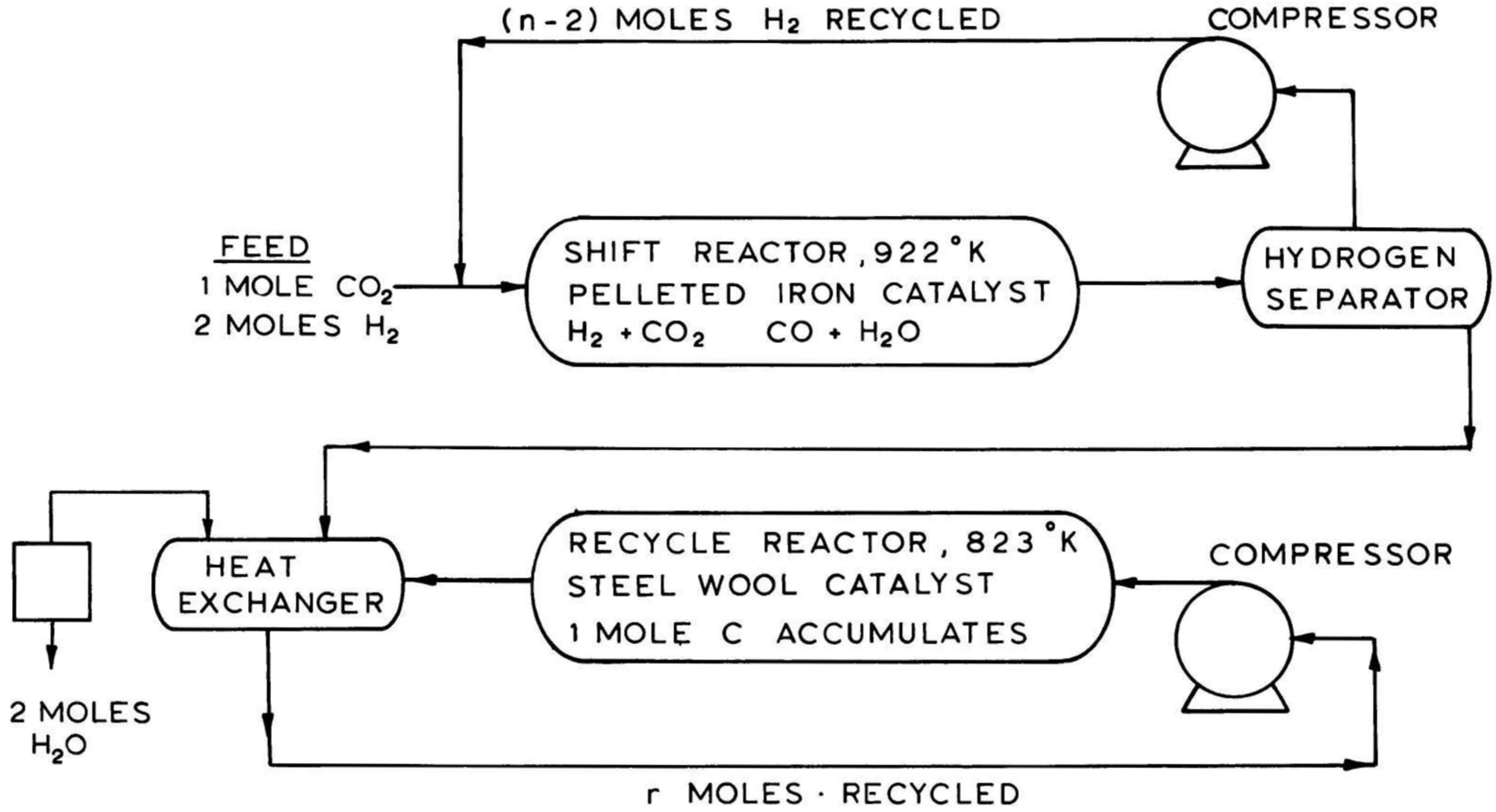


FIGURE 42, ALTERNATIVE BOSCH PROCESS FLOWSHEET

through the second reactor must be accepted.

To evaluate the advantages of the various flowsheets presented in Figs. 41 through 44, the mass balances expected at equilibrium conversion (the most favorable operating conditions achievable) were calculated for each flowsheet. In all cases, it was assumed that, in a reverse water-gas shift reactor, equilibrium conversion was obtainable without carbon deposition and without methane formation. Thus, the outlet composition of the reverse water-gas shift reactor depended only on the reactor temperature and H_2/CO_2 feed ratio. The inlet H_2/CO_2 ratio was assumed to be two in all cases where a hydrogen separator and hydrogen recycle were not employed. The outlet composition of the Bosch reactor was assumed to be the equilibrium mixture expected at the $Fe\text{-}Fe_3O_4$(or FeO)-H_2-CO-CH_4-CO_2-H_2O equilibrium or C-H_2-CO-CH_4-CO_2-H_2O equilibrium where applicable. The water separation system was assumed to be 100% efficient. In each case, the number of moles of reactants recycled in the Bosch recycle loop is calculated as a function of the adjustable processing parameters: the reverse water-gas shift reactor temperature, the Bosch reactor temperature, and the H_2/CO_2 ratio of the feed to the water-gas shift reactor. The results of this calculation are presented graphically in Fig. 45.

In Fig. 45 the two solid lines represent the number of moles, r, of gas which must be recycled in the Bosch reactor loop per mole of inlet CO_2. The upper solid line represents the amount of recycle required if a Bosch reactor is operated without a reverse water-gas shift prereactor as shown in Fig. 41 but at a temperature as shown on the abscissa; the lower line represents the amount of recycle required with the addition of a prereactor operating at the same temperature. If the temperature of the water-gas shift reactor is increased above the temperature of the Bosch reactor, the minimum recycle required decreases slightly as indicated in Fig. 45 by the

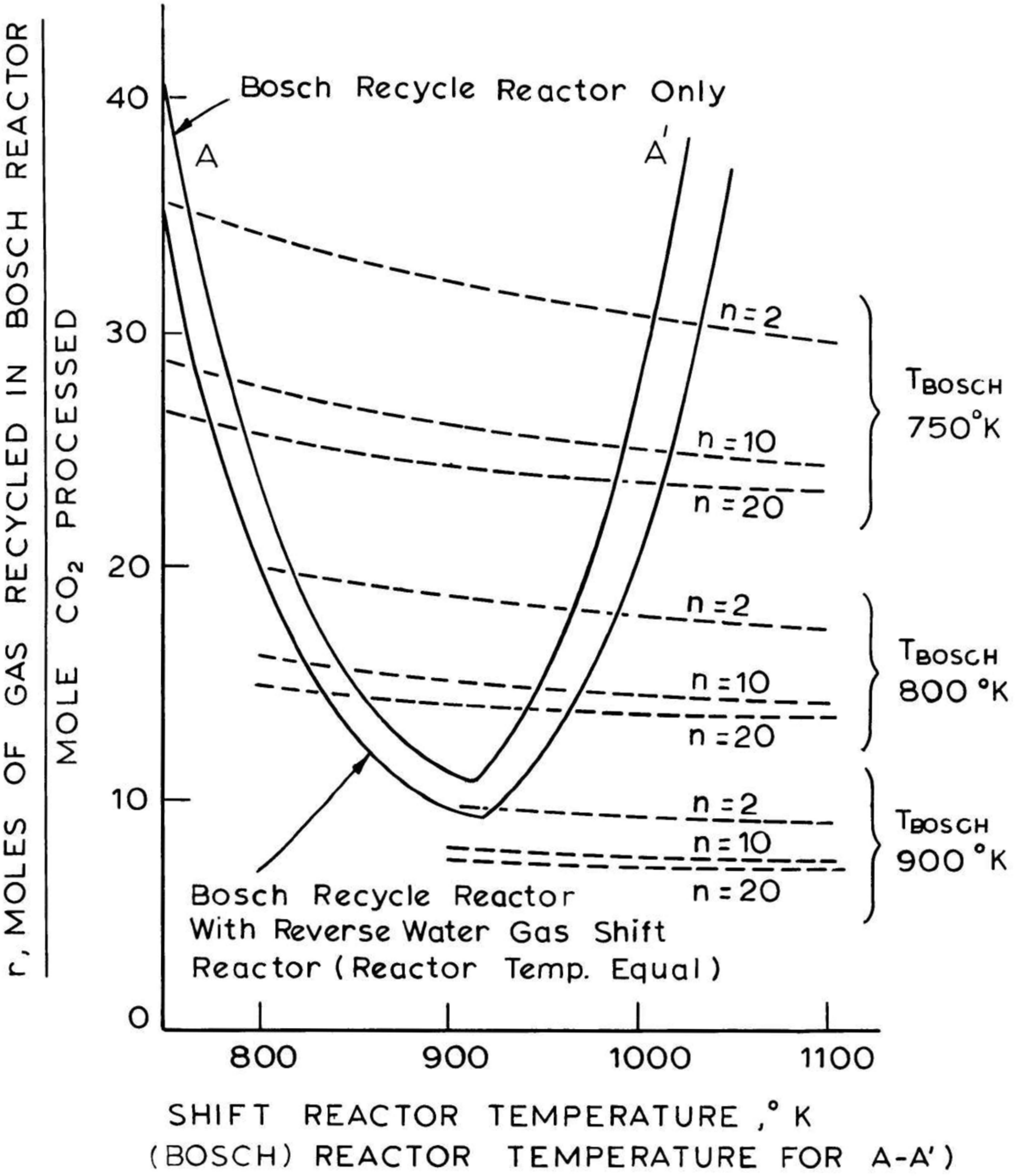


FIGURE 45, EFFECT OF PROCESS OPERATING PARAMETERS dotted lines corresponding to an H_2/CO_2 feed ratio, n, of two as indicated in the flow diagrams of Figs. 42 and 43. Finally, if an H_2/CO_2 feed ratio above two is employed with hydrogen recycle as shown in Fig. 44, the required recycle decreases as shown by the dotted lines for H_2/CO_2 feed ratios of 10 and 20.

The recycle required for the flowsheets shown in Figs. 41 and 42 decreases rapidly with increasing temperature up to approximately 900 K. As shown in Fig. 45, the addition of the reverse water-gas shift prereactor decreases the required recycle by 21% at 800 K and 14% at 900 K. Increasing the reverse water-gas shift reactor temperature to 1100 K results in an additional 11% decrease at 800 K and an additional 8% decrease at 900 K. The largest single factor decreasing the required amount of recycle, however, is the Bosch reactor temperature.

The use of increased H_2/CO_2 ratios for the reverse water-gas shift reactor is also shown to decrease the number of moles of material that must be recycled through the Bosch reactor as shown in Fig. 45. This decrease is accomplished, however, by the addition of a hydrogen recycle loop. For reactor temperatures above 800 K, the number moles of hydrogen that must be recycled exceeds the decrease in the number of moles that must be recycled through the Bosch reactor. For some reactor operating conditions below 800 K, the total number of moles to be recycled, n+r-2, decreases for values of n larger than 2 and then increases as n becomes exceedingly large. This means that a reactor cycle such as shown in Fig. 45 can be optimized for the minimum value of n+r-2 if the Bosch reactor will operate at temperatures below 800 K and if operations at such low temperature are favored from other weight, volume, or power considerations.

Finally, there is a minimum value of r for the flowsheets shown in

Figs. 41 through 43. This minimum occurs at a reactor temperature of 915 K for these flowsheets at atmospheric pressure. At this temperature, the composition of the gaseous effluent from the Bosch reactor becomes determined by the $C-H_2-CO-CH_4-CO_2-H_2O$ equilibrium rather than the $Fe-Fe_3O_4$(or $FeO)-H_2-CO-CH_4-CO_2-H_2O$ equilibrium. As shown in Fig. 16, at 800 K and atmospheric pressure, the curves describing carbon-gas phase equilibrium and iron-iron oxide equilibrium intersect. As temperature is increased above 800 K, however, the curve describing the carbon-gas phase equilibrium moves upward in the diagram while the curve describing the iron-iron oxide-gas phase equilibrium moves downward. The intersection point of the two curves, point b, moves from left to right. The minimum shown in Fig. 45 occurs when the intersection point, b, crosses a line describing the O/H operating ratio of the Bosch reactor. The O/H ratio in the Bosch recycle loops shown in Figs. 41-44 is constrained by mass balances at steady state to be 0.5. Point b lies on an operating line corresponding to this O/H ratio at 915 K at atmospheric pressure. Hence, for temperature below 915 K, the Bosch reactor effluent at equilibrium corresponds to the gas phase in equilibrium with solid phases of iron and iron oxide. At temperatures above 915 K, the effluent at equilibrium corresponds to the gas phase in equilibrium with solid carbon. Description of the calculation procedures and computer programs employed in calculating the results shown in Fig. 45 is contained in Appendix 8.3.

In conclusion, each of the reactor flow schemes shown in Figs. 41-44 has advantages and disadvantages. The final selection and optimization of the proposed schemes will require an analysis of the aggregate weight, volume, and power requirements of the various flowsheets. At this point, however, the verification of the suggested equilibrium limitation imposed by an oxidized catalyst surface for a gas phase containing all of the expected recycle components should be demonstrated for a wide range of O/H operating ratios.

6. CONCLUSIONS

1. The initial rate of carbon deposition on a steel wool catalyst is

$$\text{rate (gmole/cm}^2\text{-sec)} = 4.3 \times 10^{-8} \, (P_{CO}P_{H_2})^{0.42\pm0.10}$$

where the component partial pressures are in atmospheres and the area is the initial iron surface area. The activation energy for this reaction is ∿70 kJ/mole.

2. The iron catalyst surface area available for reaction appears to increase during the carbon deposition process. This conclusion is based on observed increases in reaction rates and on the surface area calculated from BET total surface area of the product carbon, iron content of the product carbon, and transmission electron photomicrographs of the iron distribution in the product carbon. No direct measurements of active metal surface area were made.

3. After carbon deposition had occurred on the steel wool catalyst, the rates of the reverse water-gas shift reaction and carbon deposition reactions were sufficiently fast to be influenced by heat transfer into or out of the experimental reactor.

4. Several alternative flowsheets for the Bosch process have been developed. Based on the observed rates of reactions occurring on a Bosch catalyst, the rate of methane formation in the recycle reactor cannot be assumed to be small. As iron oxide surfaces do not appear to catalyze carbon formation, the minimum required Bosch reactor recycle rates have been calculated on the basis that the reactor effluent will approach gas phase concentrations expected in the appropriate Fe-Fe_3O_4(or FeO)-H_2-CO-CH_4-CO_2-H_2O and C-H_2-CO-CH_4-CO_2-H_2O equilibria.

7. RECOMMENDATIONS

1. The experimental reactor should be modified to permit higher water concentration in the feed mixture to the reactor.

2. Additional experiments should be performed with mixtures close to the equilibrium gas phase composition expected for the Fe-Fe_3O_4(or FeO)-H_2-CO-CH_4-CO_2-H_2O system to verify the hypothesis that no carbon formation occurs when the catalyst surface is expected to be oxidized.

3. An energy balance for alternative Bosch process flowsheets should be performed to aid in evaluation.

8. APPENDIX

8.1 Supplementary Detail

8.1.1 Mass Transfer Limitations in the Experiments by Walker at al. (1959)

The data shown in Fig. 6 of Walker *et al*. (1959) are for a series of experiments at 801 K with a feed gas containing 97.8% CO and 2.2% H_2, and feed flow rates from 0.29 to 5.80 cc/sec. For the data points corresponding to a feed flow rate of 5.80 cc/sec, a carbon deposit of ∿12 g was observed in 400 min corresponding to a carbon deposition rate of 4.16×10^{-5} gmole/sec. The deposition rate that would be expected if mass transfer of carbon monoxide to the catalyst surface were the limiting step in the reactor process can be approximated in the following manner. The reactor flow configuration is assumed to be as described by Walker *et al*. and shown in Fig. 46. The superficial mass flow rate of inlet gas is

$$G = 5.8\ \text{cm}^3/\text{sec}(1\ \text{mole}/22{,}400\ \text{cm}^3)(28\ \text{g/mole})(4/\pi)\frac{1}{(2.5\ \text{cm})^2}$$

$$= 1.48 \times 10^{-3}\ \text{g/cm}^2\text{-sec}$$

and the superficial molar flow rate is

$$G_M = 5.2 \times 10^{-5}\ \text{moles/cm}^2\text{-sec}$$

At 801 K the viscosity of pure carbon monoxide is

$$\mu = 2.10 \times 10^{-5}\ \text{g/cm-sec}$$

Thus, the Reynolds number in the combustion tube based on tube diameter is approximately

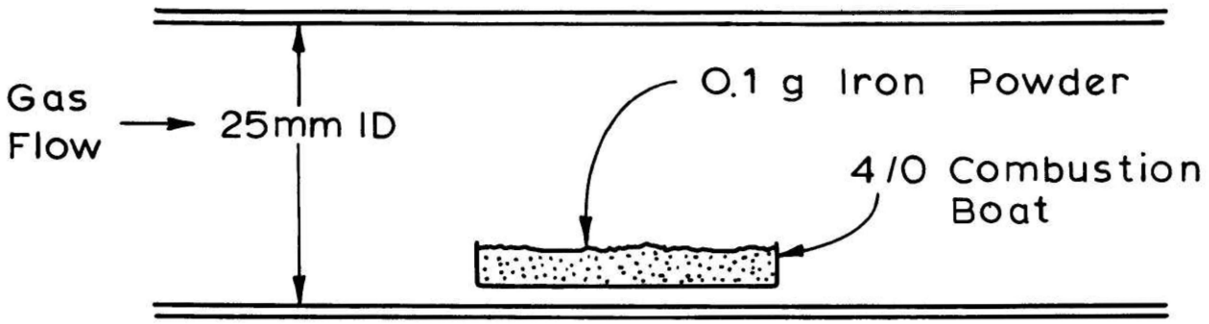


FIGURE 46 EXPERIMENTAL REACTOR FLOW CONFIGURATION OF (WALKER et al 1959)

$$Re_D = \frac{DG}{\mu} = \frac{(2.5\ \text{cm})(1.48 \times 10^{-3}\ \text{g/cm}^2\text{-sec})}{2.10 \times 10^{-5}\ \text{g/cm-sec}} = 175$$

and the flow is laminar.

If it is assumed that the catalyst is completely contained, the combustion boat containing the iron powder can be modeled as a flat plate in the laminar gas stream with mass transfer occurring at the top surface only. For this model the results of Polhausen and Colburn as reported in Sherwood and Pigford (1952), Eq. (103) apply

$$j_D = \frac{k_G P_{BM}}{G_M} Sc^{2/3} = 0.66\ Re_x^{-1/2}$$

where Re_x is the Reynolds number based on the length of the flat plate. As the length of the combustion boat was approximately 3 cm,

$$Re_x = \frac{LG}{\mu} = \frac{(3\ \text{cm})(1.48 \times 10^{-3}\ \text{g/cm}^2\text{-sec})}{2.10 \times 10^{-5}\ \text{g/cm-sec}} = 211$$

Hence,

$$k_G = 0.66\left(\frac{G_M}{P_{BM}}\right) Re_x^{-1/2}\ Sc^{-2/3}$$

Assuming that mass transfer is the limiting step, the surface concentration of CO at 801 K should be approximately equal to its equilibrium (Fe-Fe_3O_4-C-gas) value of 0.488 atm. Thus,

$$P_{BM} = \frac{0.978 - 0.488}{\ell n(0.978/0.488)} = 0.70\ \text{atm}$$

$$k_G = 0.66\left(\frac{5.2 \times 10^{-5}\ \text{gmole/cm}^2\text{-sec}}{0.70\ \text{atm}}\right)(211)^{-1/2}(0.7)^{-2/3}$$

$$= 4.28 \times 10^{-6}\ \text{mole/cm}^2\text{-sec-atm}$$

For the nominal surface area of the 4/0 combustion boat, 1.8 cm^2, and the largest expected logarithmic mean partial pressure difference, 0.70 atm, the maximum expected mass transfer rate would be

$$\text{rate} = k_G a\ \Delta P_{\ell m} = (4.28 \times 10^{-6})(1.8)(0.70)$$

$$= 5.4 \times 10^{-6}\ \text{gmole/sec}$$

Since the observed "reaction rate" cannot exceed the maximum mass transfer rate, it is possible that the observed reaction was limited by mass transfer from the bulk gas phase to the top surface of the combustion boat. The calculated mass transfer rate exceeds the observed reaction rate by about one order of magnitude. This may be because the flat plate model is not appropriate or the estimation of the combustion boat dimensions may be inaccurate.

Alternatively, the observed reaction rate may also be limited by reaction equilibria. For example, in the experiment mentioned above, if the reactor exhaust corresponded to the gas phase in equilibrium with Fe, Fe_3O_4, and β-graphite, the exhaust gas composition would be

H_2	2.5%			
CO	48.8%		C	38.9%
CH_4	0.1%	or	H	2.6%
CO_2	48.0%		O	58.4%
H_2O	0.6%			

Each mole of inlet gas mixture contains 0.978 moles C, 0.978 moles O, and 0.044 moles H. The C/H ratio in the exhaust is

$$\frac{C}{H} = \frac{38.9}{2.6} = 14.96$$

If x moles of carbon deposit in the reactor per mole of feed gas mixture, then by a carbon balance

$$\frac{0.978 - x}{0.044} = 14.96$$

or

$$x = 0.32$$

Thus, the observed carbon deposition rate would be expected to be

$$\left(5.8\ \frac{\text{cc feed mixture}}{\text{sec}}\right)\left(\frac{\text{1 mole feed}}{\text{22,400 cc}}\right)\left(\frac{\text{0.32 moles C deposited}}{\text{mole feed mixture}}\right)$$

$$= 8.27 \times 10^{-5}\ \text{gmole/sec}$$

This rate is within a factor of two of the observed rate.

8.1.2 Mass Transfer Limitations in This Work - Water-Gas Shift Reaction

To determine whether the conversions observed in the experimental reactor are limited by mass transfer of the reactants to the catalyst surface or by the kinetic rate of reaction at the catalyst surface, one can compare the observed reaction rate with the calculated rate of mass transfer for a given model of the gas-catalyst contacting. As long as the calculated rate of mass transfer exceeds the observed reaction rate, the reaction may be assumed to be kinetically controlled. The largest observed rate of reaction for the reverse water-gas shift reaction was obtained with an iron catalyst upon which carbon had been deposited as discussed in Sect. 4.4. Although the catalytic surface area has been shown to increase during carbon deposition, the catalytic surface area available for reaction will be assumed to be equal to the original catalyst surface area ($\sim 100\ \text{cm}^2$) to calculate a conservative estimate of the mass transfer rate.

The steel wool catalyst will be modeled as woven screens or an assemblage of cylindrical surfaces oriented normal to the gas flow in the reactor. The characteristic diameter of the cylinders will be taken as 0.0254 cm (0.01 in.) which is intermediate between the maximum and minimum dimensions of a steel wool fiber. From the experimental data of Run 11, the total gas flow rate is 20 cc/sec, inlet composition approximately 50% H_2-50% CO_2, and outlet composition approximately 45% H_2, 45% CO_2, 5% CO, and 5% H_2O. (Nominal values are used for simplicity of computations.) The internal diameter of the catalyst carrier is 20 mm so that the superficial gas velocity at reaction conditions in the catalyst section is

$$u \;=\; (20\ \text{cc/sec})\left(\frac{823\ \text{K}}{273\ \text{K}}\right)\frac{4}{\pi(2\ \text{cm})^2} \;=\; 19\ \text{cm/sec}$$

and the average gas density is

$$\rho \;=\; \frac{1}{V} \;=\; \frac{P}{RT} \;=\; \frac{1\ \text{atm}}{(82\ \frac{\text{cc-atm}}{\text{K-mole}})(873\ \text{K})} \;=\; 1.4 \times 10^{-5}\ \text{mole/cm}^3$$

The average molecular weight of the gas is

$$M_{av} \;=\; \frac{2 + 44}{2} \;=\; 23$$

so that

$$\rho \;=\; 1.4 \times 10^{-5}(23) \;=\; 3.2 \times 10^{-4}\ \text{g/cm}^3$$

The viscosity of hydrogen is 175 x 10^{-6} g/cm-sec at 823 K. The viscosity of carbon dioxide is 345 x 10^{-6} g/cm-sec at 823 K. Assuming that the viscosity of a 50/50 mixture is the average of these two values, the reactant mixture viscosity is 260 x 10^{-6} g/cm-sec. Hence, the Reynolds number based on steel wool fiber diameter is

$$Re = \frac{Du\rho}{\mu} = \frac{(2.54 \times 10^{-2}\ \text{cm})(19\ \text{cm/sec})(3.2 \times 10^{-4}\ \text{g/cm}^3)}{260 \times 10^{-6}\ \text{g/cm-sec}} = 0.59$$

Using the correlation of Satterfield and Cortez (1970) for the mass transfer coefficient from a gas phase to woven wire screens

$$j_D = 0.865\ Re^{-0.648} = 0.865(0.59)^{-0.648} = 1.2$$

where:

$$j_D = St\ Sc^{2/3} = \frac{k_G P}{G_M}\left(\frac{\nu}{\mathcal{D}_{CO_2-H_2}}\right)^{2/3}$$

Thus,

$$k_G = \frac{j_D G_M}{P}\left(\frac{\mathcal{D}_{CO_2-H_2}}{\nu}\right)^{2/3} = \frac{j_D u\rho}{M_{av}P}\left(\frac{\mathcal{D}_{CO_2-H_2}}{\nu}\right)^{2/3}$$

From molecular theory, the value of $\mathcal{D}_{CO_2-H_2}$ is

$$\mathcal{D}_{12} = \frac{0.001858\ T^{2/3}[(M_1 + M_2)/M_1M_2]^{1/2}}{P[\frac{1}{2}(\sigma_1 + \sigma_2)]^2\ \Omega_D}$$

where

$$\frac{T}{\sqrt{(\varepsilon_1/k)(\varepsilon_2/k)}} = \frac{823}{\sqrt{(195.2)(59.7)}} = 7.62$$

and thus $\Omega_D = 0.77$. At 823 K for a gas mixture of hydrogen and carbon dioxide,

$$\mathcal{D}_{CO_2\text{-}H_2} = \frac{0.001858(823)^{3/2}(\frac{46}{88})^{1/2}}{[\frac{1}{2}(3.941 + 2.827)]^2(0.77)} = \frac{(0.001858)(23{,}610)(0.72)}{(11.45)(0.77)}$$

$$= 3.58 \text{ cm}^2/\text{sec}$$

Thus,

$$k_G = \frac{(1.2)(19 \text{ cm/sec})(3.2 \times 10^{-4})}{(23)(1)}[(3.58)\ \frac{3.2 \times 10^{-4} \text{ g/cm}^3}{260 \times 10^{-6} \text{ g/cm-sec}}]^{2/3}$$

$$= 3.17 \times 10^{-4}(4.40)^{2/3} = 8.52 \times 10^{-4} \text{ moles/cm}^2\text{-atm-sec}$$

At the reactor inlet and outlet the CO_2 partial pressure driving forces are 0.17 and 0.12 atm, respectively. Hence, the log mean driving force is

$$\Delta P_{\ell m} = \frac{0.17 - 0.12}{\ell n(\frac{0.17}{0.12})} = 0.14 \text{ atm}$$

Hence, the expected overall mass transfer rate is

$$N = (8.52 \times 10^{-4} \frac{\text{mole}}{\text{cm}^2\text{-atm-sec}})(0.14 \text{ atm})(100 \text{ cm}^2)$$

$$= 1.19 \times 10^{-2} \text{ mole/sec}$$

The observed reaction rate for a fresh catalyst is, from Run 14, assuming differential conversion

$$\text{rate} \approx (0.0002)(10 \text{ cc/sec})(1 \text{ mole/22,400 cc}) = 9 \times 10^{-8} \text{ mole/sec}$$

or from Run 15 with ∿850 mg of carbon deposited, the observed reaction rate is

$$\text{rate} = (0.06)(10\ \text{cc/sec})(1\ \text{mole}/22{,}400\ \text{cc}) = 2.7 \times 10^{-5}\ \text{mole/sec}$$

As both of these calculated rates are significantly below the expected mass transfer rate, the observed rates are concluded to be kinetically controlled.

8.1.3 Heat Transfer Limitation of Reverse Water-Gas Shift Reaction

As indicated in Sect. 4.5, , the conversion, $\Delta n/n$, observed for a 47% H_2, 53% CO_2 feed mixture at 823 K is 12%. The enthalpy change for reaction, ΔH_r, at this temperature is 8800 kcal/mole CO_2. On a basis of one mole of CO_2 fed to the reactor, 0.12 moles of H_2 and CO_2 are converted to CO and H_2O. If this conversion occurs adiabatically, the observed temperature change. ΔT, would be,

$$\Delta T = \frac{\Delta n_r \Delta H_r}{\Sigma n_i C_{p_i}}$$

Assuming that the total heat capacity of the reactants is equal to the heat capacity of the products, the sum of the heat capacities is

$$\Sigma n_i C_{p_i} = (1\ \text{mole}\ CO_2)(12.32\ \frac{\text{cal}}{\text{mole-K}}) + (0.89\ \text{mole}\ H_2)(7.1\ \frac{\text{cal}}{\text{mole-K}})$$

$$= 18.7\ \text{cal/K}$$

and

$$\Delta T = \frac{(0.12)(8800)(1.89)}{18.7} = 107\ \text{K}$$

If the reactor is to be operated isothermally, heat must be supplied to the reactor at the rate

$$Q = (0.12\ \frac{\text{moles CO}_2\text{ converted}}{\text{mole inlet CO}_2})(8800\text{ cal/mole CO}_2)$$

$$\times\ (\frac{\text{1 mole inlet CO}_2}{\text{1.89 moles feed}})(\frac{\text{1 mole feed}}{\text{22,400 cc(STP)}})(\frac{\text{20 cc (STP)}}{\text{sec}})$$

$$= 0.50\text{ cal/sec}$$

At steady state heat must be transferred at this rate from the furnace walls to the reactor support tube and from the reactor support tube to the catalyst carrier and from the catalyst carrier to the catalyst bed. If the catalyst carrier is assumed to be isothermal at 823 K, the temperature gradient at the reactor tube wall can be calculated.

$$\frac{dT}{dL} = \frac{Q/a}{k} = \frac{(0.5\text{ cal/sec})/(16\text{ cm}^2)}{(50 \times 10^{-5}\text{ cal/cm-sec-K})} = 62.5\text{ K/cm}$$

8.2 Equipment Calibration

8.2.1 Determination of Gas Phase Composition

Inlet and outlet streams of the experimental reactor were sampled periodically as outlined in Sect. 3. The samples were analyzed with a gas chromatograph and digital integrator. The gas chromatograph was checked for accuracy and precision by analyzing two calibration gas standards. The calibration gases, both supplied by Matheson Gas Products, were certified to be of the concentrations shown in Table 2 as indicated in Sect. 3.

The concentration in each of the calibration gases was determined by injecting a sample of the gas, recording the component peak areas, and determining the concentration of a given species knowing the peak area of an identical sample of the pure component gases. Calculation of each of the component concentrations (except hydrogen) was by the absolute method described by Dal Nogare and Juvet (1962). Hydrogen was determined by using an empirical calibration curve as recommended by Purcell and Ettre (1965).

Dal Nogare and Juvet (1962) have reported that the peak area of a component in a chromatogram is directly proportional to the amount of that component in the sample as long as precise control is maintained on all detector and column operating variables. Under these circumstances, the number of moles of component i, n_i, is related to the component i peak area, a_i, by the equation

$$n_i = k_i a_i$$

The only variable which was not automatically controlled in the analytical technique described in Sect. 3 was the pressure in the calibrated volume gas sample loop. Instead, the pressure differential between the gas sample loop and atmospheric pressure (usually 0.5 cm of mercury or less) was measured and the digital integrator peak area was corrected to atmospheric pressure as

$$a_i = a_{i,\text{uncorrected}}\left(\frac{P_{atm} - \Delta P}{P_{atm}}\right)$$

The values of k_i were determined prior to each run by injecting several samples of calibration gas with the calibrated gas sample valve and recording the component peak areas. As the volume of the sample valve loop, V_{sv}, and concentration of the calibration gas mixture, $C_{i,cm}$, are known, the k_i may be calculated as

$$k_i = \frac{C_{i,cm} V_{sv}}{a_i}$$

To determine the constant k_i for water, a similar procedure was employed in which the calibration standard was prepared by passing a stream of carbon dioxide through a series of water spargers and noting the dew point of the mixture. Water concentration in the standard was calculated from the vapor pressure of water at the dew point temperature assuming that the carbon dioxide-water gas mixture behaved as an ideal gas.

From data presented by Dietz (1967), the relative calibration area coefficients, k_i°, defined by the equation

$$k_i^\circ = \frac{k_i}{k_{CO_2}}$$

are expected to be 0.875, 0.743, and 0.687 for carbon monoxide, methane, and water, respectively. The relative area calibration coefficients were calculated for each run as a check on the calibration procedure.

Purcell and Ettre (1965) have shown that hydrogen may be determined quantitatively by gas chromatography with thermal conductivity detectors by using an 8.5% H_2/91.5% He carrier gas. The relationship between hydrogen concentration and peak area was found to be non-linear and calibration curves were recommended. To determine the calibration curve for hydrogen, various known quantities of hydrogen were injected into the gas chromatograph and the digital integrator peak area recorded. The digital integrator peak area was found to provide a linear relationship over two orders of magnitude (0.02 - 2 cc H_2) with the amount of hydrogen injected when plotted on log-log paper. The slope of the line on log-log paper was 1.3, indicating that the relationship between hydrogen concentration and peak area was non-linear as reported. Subsequently, prior to each run, the calibration curve for hydrogen was determined by injecting several samples each of pure hydrogen and a prepared calibration mixture (25.18% hydrogen) and fitting a line by least-squares technique to the empirically observed relationship

$$n_{H_2} = k_{H_2} a_{H_2}^{b}$$

The concentration of each component in a sample was then determined by calculating

$$c_i = \frac{n_i}{\sum_i n_i}$$

after all the values of k_i and the value of b had been determined.

8.2.2 Temperature Profile in Experimental Reactor

Several preliminary experiments were performed to determine whether the temperature profile within the reactor was steady and uniform. For these experiments, the reactor and furnace were assembled as for all kinetic experiments except that the suspension rod for the catalyst carrier was removed. Removal of the suspension rod allowed insertion of a thermocouple probe through the weighing port of the reactor to determine the axial, centerline reactor temperature profile. Measurements with the probing thermocouple near the center of the furnace in a flowing stream of carbon dioxide indicated that the temperature was stable within ± 1 K when the setpoint was 773 K with a flow rate of 13 cc/sec. When the reactor flow was reduced to 6.5 cc/sec CO_2, the temperature was again stable ± 1 K. When the flow was further reduced to 1 cc/sec, the temperature oscillated regularly ± 3 K. With the setpoint temperature at 673 K, the temperature oscillated regularly ± 5 K at gas flow rates of 6.5 and 13 cc/sec. Thus, it was apparent that temperature regulation in the reactor was degraded as either temperature level or flow rate was reduced. Since the reactor was subsequently operated at temperatures at or above 773 K with total gas flow rates of approximately 20 cc/sec, temperature control stability to within ± 1 K was expected. Indeed, in subsequent kinetic experiments, transient output from a thermocouple mounted immediately below the catalyst section was observed only when the reactor gas flow was temporarily interrupted to measure the catalyst weight or when the setpoint of the temperature controller was changed.

The uniformity of the axial reactor temperature profile was checked by moving the thermocouple probe in successive 2.5-cm increments from one end of the reactor to the other. During the probing, the temperature controller setpoint and gas flow rate were constant. Temperature profiles were obtained for gas flow rates of 15 cc/sec (100% CO_2) and 30 cc/sec (50% CO_2, 50% He). The results of this experiment are plotted in Fig. 47 as the observed temperature as a function of height above the reactor furnace floor. Also shown are the region in which the catalyst sample is situated and the position of the controller thermocouple for these experiments. It is apparent from Fig. 47 that the axial temperature is constant within ± 2 K in the region where the catalyst is contained and that there are large temperature gradients near the ends of the furnace. The temperature in the center of the reactor is also not sensitive to the changes of gas flow rate or composition for the two profiles. One noticeable problem, however, is the temperature difference between the location of the controller thermocouple (13.5 cm above the furnace floor) and the catalyst region (17.5 - 21.0 cm above the furnace floor). To eliminate this 10 K temperature offset, the controller thermocouple was raised to a point 15 cm above the furnace floor prior to kinetic experiments.

8.2.3 Analysis of Steel Wool Catalyst

The catalyst was obtained from a single box of grade 2 American Steel Wool, manufactured by the American Steel Wool Co., Orchard St., Long Island City, NY 11101. Correspondence with the company indicated that the steel wool is manufactured by a continuous shaving process from wire stock. Typical chemical analysis of the wire stock was stated to be

Alloy Element	Concentration (wt %)
C	0.11
Mn	0.78
P	0.050

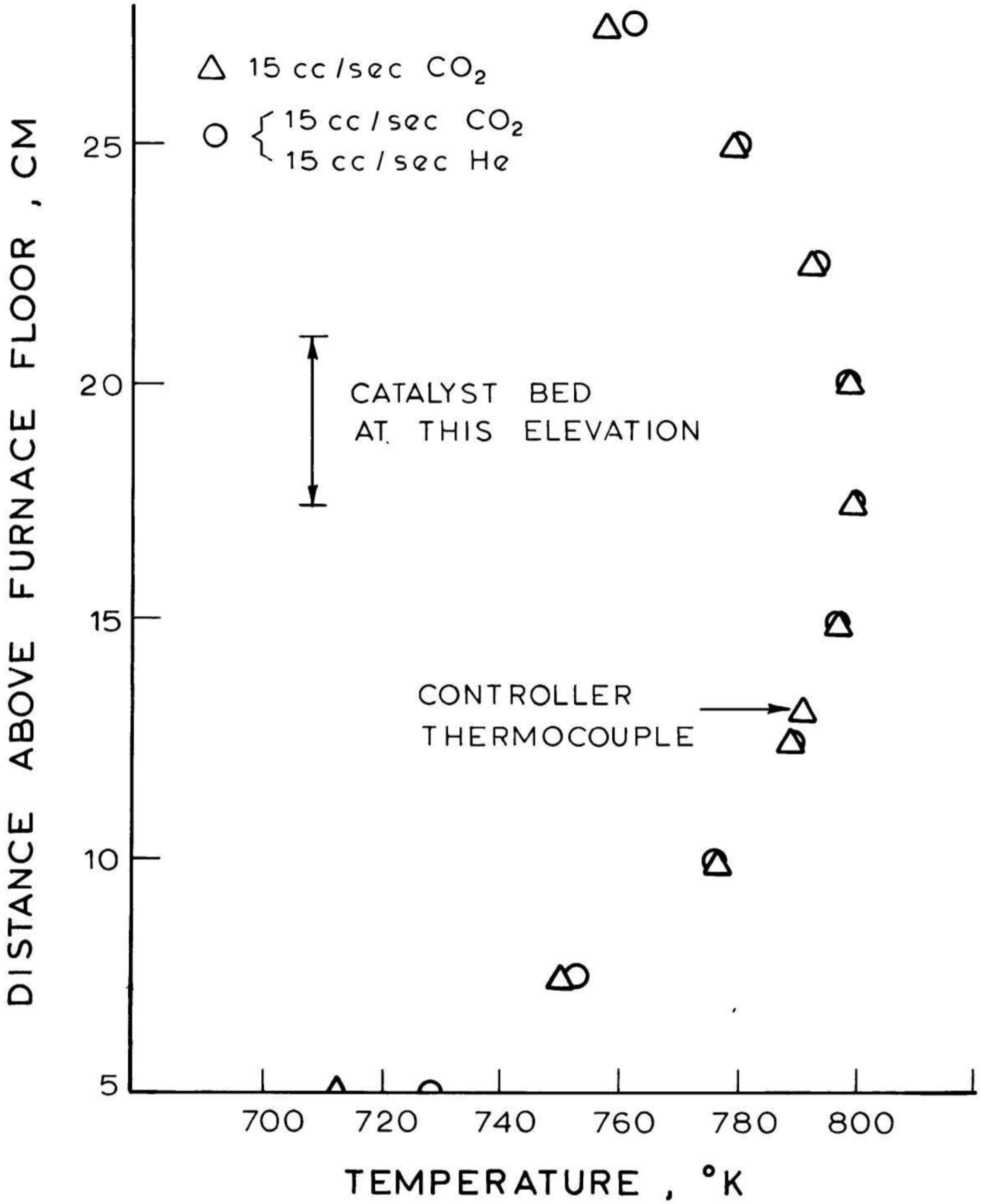


FIGURE 47, REACTOR TEMPERATURE PROFILE

Alloy Element	Concentration (wt %)
S	0.017
N	0.012

A sample of the steel wool was also analyzed by the MIT Material Sciences Dept., Control Analysis Facility, and found to contain

Alloy Element	Concentration (wt %)
C	0.36
Mn	0.70
P	0.04
S	0.018
N	0.4×10^{-5}

The surface area of the steel wool was measured by the BET method with krypton adsorption at liquid nitrogen temperatures and found to be 389 cm^2/gm. Surface areas estimated from scanning electron photomicrographs of single steel wool strands were in the range 180 to 395 cm^2/gm.

8.3 Calculations

8.3.1 Equilibrium Calculations

8.3.1.1 General Approach. The numerical methods employed by Tevebaugh and Cairns (1964, 1965) to calculate CHO gas phase compositions in equilibrium with carbon were followed in calculating the solid-gas phase reaction equilibria presented. The general approach of this technique is to reduce algebraically the equations describing the reaction equilibrium to a single polynomial in one unknown. The polynomial may then be solved by a conventional numerical technique such as Newton-Raphson iterative search. The algebraic reduction procedure is then reversed to solve for the other variables.

For example, consider the equilibrium between a solid phase of β-graphite and a gas phase containing H_2, CO, CH_4, CO_2 and H_2O. Application of the phase rule indicates that the number of variables required to specify an equilibrium state for this system of two phases (solid graphite and gas) and six components (C, H_2, CO, CH_4, CO_2, and H_2O) is

$$V = C - P + 2 = 6 - 2 + 2 = 6$$

After specifying the temperature, five variables remain. Let the remaining five constraints be the pressure, the O/H ratio of the gas phase, and the fact that the three independent reactions (E), (B), and (M) are at equilibrium. The equilibrium state of the system is now fixed by the five simultaneous, non-linear equations in five unknowns:

$$P = P_{H2} + P_{CO} + P_{CH_4} + P_{CO2} + P_{H2O} \tag{5}$$

$$K_1 = \frac{P_{CH_4}}{P_{H_2}^2} = f_1(T) \qquad (6)$$

$$K_3 = \frac{P_{H_2O}P_{CO}}{P_{H_2}P_{CO_2}} = f_3(T) \qquad (7)$$

$$K_6 = \frac{P_{CH_4}P_{H_2O}}{P_{CO}P_{H_2}^3} = f_6(T) \qquad (8)$$

$$\left(\frac{O}{H}\right)_{\text{gas phase}} = \frac{P_{CO} + 2P_{CO_2} + P_{H_2O}}{2P_{H_2} + 2P_{H_2O} + 4P_{CH_4}} \qquad (9)$$

By successive algebraic substitution, one may arrive at an equation of the form

$$C_o + C_1P_{H_2} + C_2P_{H_2}^2 + C_3P_{H_2}^3 + C_4P_{H_2}^4 + C_5P_{H_2}^5 + C_6P_{H_2}^6 = 0 \qquad (10)$$

where C_o through C_6 are constants which may be expressed as functions of the specified parameters P, K_1, K_3, K_6, and the O/H ratio in the gas phase. The derivative of Eq. (10) is

$$C_1 + C_2P_{H_2} + C_3P_{H_2}^2 + C_4P_{H_2}^3 + C_5P_{H_2}^4 + C_6P_{H_2}^5 = 0 \qquad (11)$$

Since both the value of the function, Eq. (10), and its derivative, Eq. (11), can be computed, the Newton-Raphson iterative search procedure may be employed to find the root of Eq. (10). As there are five roots to Eq. (10), the proper root must be selected. The proper root will be a real number with a value between zero and the value of the total pressure, and with a value such that the inversion of the algebraic reduction procedure results in values of P_{CO}, P_{CH_4}, P_{CO_2}, and P_{H_2O} which are also real, positive and between zero and the value of the total pressure.

For equilibrium between a gas phase containing the same five components and the two solid phases α-iron and magnetite, Fe_3O_4, the phase rule indicates that six variables are required to fix the equilibrium state of the system. After specifying the temperature, five parameters are sufficient to fix the final equilibrium state of the system. Specifying the total pressure, C/H ratio in the gas phase, and the fact that reactions (L), (M), and (I) with equilibrium constants, K_5, K_6, and K_4, respectively, are at equilibrium, results in the following five simultaneous, non-linear equations in five unknowns:

$$P = P_{H_2} + P_{CO} + P_{CH_4} + P_{CO_2} + P_{H_2O} \tag{5}$$

$$K_4 = \frac{P_{H_2}}{P_{H_2O}} = f_4(T) \tag{12}$$

$$K_5 = \frac{P_{CO}}{P_{CO_2}} = f_5(T) \tag{13}$$

$$K_6 = \frac{P_{CH_4}P_{H_2O}}{P_{CO}P_{H_2}^3} = f_2(T) \tag{8}$$

$$\left(\frac{C}{H}\right)_{\text{gas phase}} = \frac{P_{CO} + P_{CO_2} + P_{CH_4}}{2P_{H_2} + 2P_{H_2O} + 4P_{CH_4}} \tag{14}$$

Solution of these equations is accomplished by the same numerical procedure.

Under conditions where the above two equilibria have at least one common solution, an equilibrium is possible between three solid phases (graphite, α-iron, and magnetite, Fe_3O_4) and a gas phase containing H_2, CO, CH_4, CO_2, and H_2O. In these circumstances, the phase rule indicates again that six parameters are required to specify the equilibrium state of the system. In this case, however, the equilibrium state is described by the point of intersection of the equilibrium curves determined for the C-H_2-CO-CH_4-CO_2-H_2O and the Fe-Fe_3O_4(FeO)-H_2-CO-CH_4-CO_2-H_2O equilibria.

8.3.1.2 Construction of CHO Triangular Diagrams. A computer program, BOSCH1, was written to perform the necessary equilibrium calculations and to draw CHO triangular diagrams on a CALCOMP plotter. A program listing is contained in the following section. Program execution proceeds as described in the following paragraphs.

Pressure and temperature are specified as constants. The subroutine KEQUIL(T) is called. This subroutine calculates the values of the equilibrium constants, K_1, K_2, K_3, K_4, K_5, and K_6 at temperature, T, for the reactions

$$C(\beta\text{-graphite}) + 2H_2 \rightarrow CH_4$$

$$2CO \rightarrow C(\beta\text{-graphite}) + CO_2$$

$$H_2 + CO_2 \rightarrow CO + H_2O$$

$$H_2O + \frac{3}{4} Fe \rightarrow H_2 + \frac{1}{4} Fe_3O_4$$

$$CO_2 + \frac{3}{4} Fe \rightarrow CO + \frac{1}{4} Fe_3O_4$$

and

$$CO + 3H_2 \rightarrow CH_4 + H_2O$$

respectively. The equilibrium constants are calculated from values of component free energies of formation tabulated in the JANAF Thermochemical

Tables (1971) and interpolated to the specific temperature. For temperatures above 860 K, constants K_4 and K_5 are calculated to correspond to reactions

$$H_2O + Fe \rightarrow H_2 + FeO$$

and

$$CO_2 + Fe \rightarrow CO + FeO$$

respectively.

The coordinates of points on the axes of the triangular diagram are computed in x-y coordinates and drawn by the CALCOMP plotter. Symbols are located on the triangular diagram at the CHO compositions corresponding to the compounds methane, water, carbon monoxide, and carbon dioxide. The apexes are labeled C, H, and O, and a figure title is drawn on the CALCOMP plot. The lines corresponding to the $C-H_2-CO-CH_4-CO_2-H_2O$ and $Fe-Fe_3O_4$(or $FeO)-H_2-CO-CH_4-CO_2-H_2O$ equilibria are drawn on the triangular diagram in that order.

To draw the line corresponding to the graphite-gas phase equilibrium, the computer program calculates the hydrogen and methane partial pressures for the equilibrium between a solid graphite phase and a gas phase containing only hydrogen and methane,

$$P_{H_2} = \frac{-1 + \sqrt{1 + 4PK_1}}{2K_1} \qquad (15)$$

The hydrogen and methane partial pressures fix the CHO composition of the point located at the intersection of the C-H axis of the triangular diagram and the $C-H_2-CO-CH_4-CO_2-H_2O$ equilibrium line. The equilibrium line is drawn starting from this point.

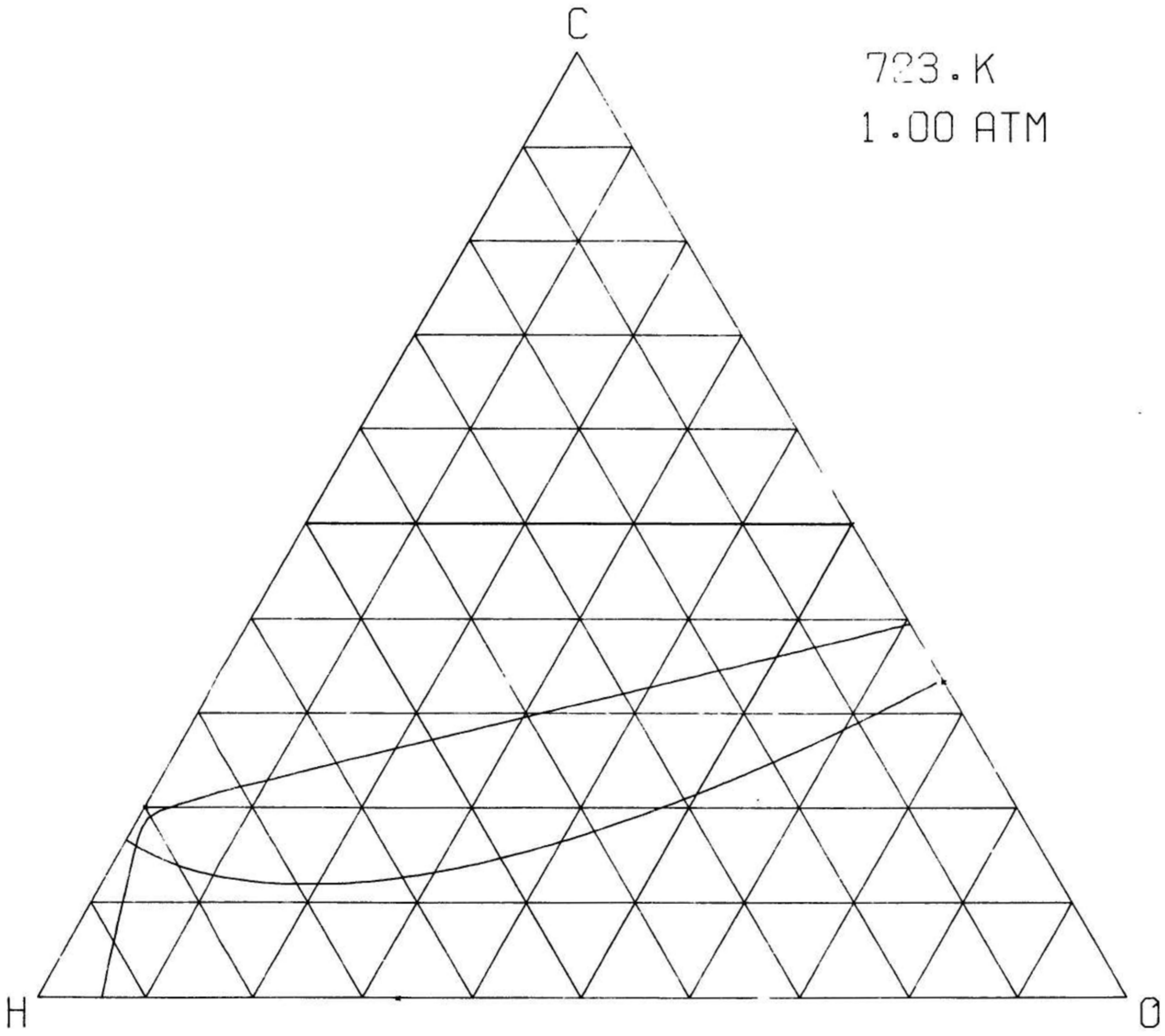
The subroutine CEQ(P, T, ROH, PI, C, H, O) has the pressure, temperature, and O/H ratio of the gas phase as input parameters and calculates the component partial pressures and CHO composition of the gas phase at the $C-H_2-CO-CH_4-CO_2-H_2O$ equilibrium. The subroutine is employed to calculate these values in an iterative fashion by successively replacing the gas phase O/H ratio in the list of input parameters. In this manner, starting with a large O/H ratio (∿99) and successively reducing the O/H ratio to a near zero value (∿0.01), the equilibrium CHO composition is determined and the line drawn on triangular coordinates starting from the intercept on the C-H axis and proceeding toward the C-O axis.

At each step in the above procedure, the subroutine RTNI, a standard IBM Scientific Subroutine, determines the root (hydrogen partial pressure) of the sixth order polynomial by the Newton-Raphson iterative search technique. The value of the hydrogen partial pressure from Eq. (15) is used as the initial estimate of the root to start the procedure. The last computed value of the hydrogen partial pressure is taken as the initial estimate in calculating the root at all subsequent O/H gas phase ratios.

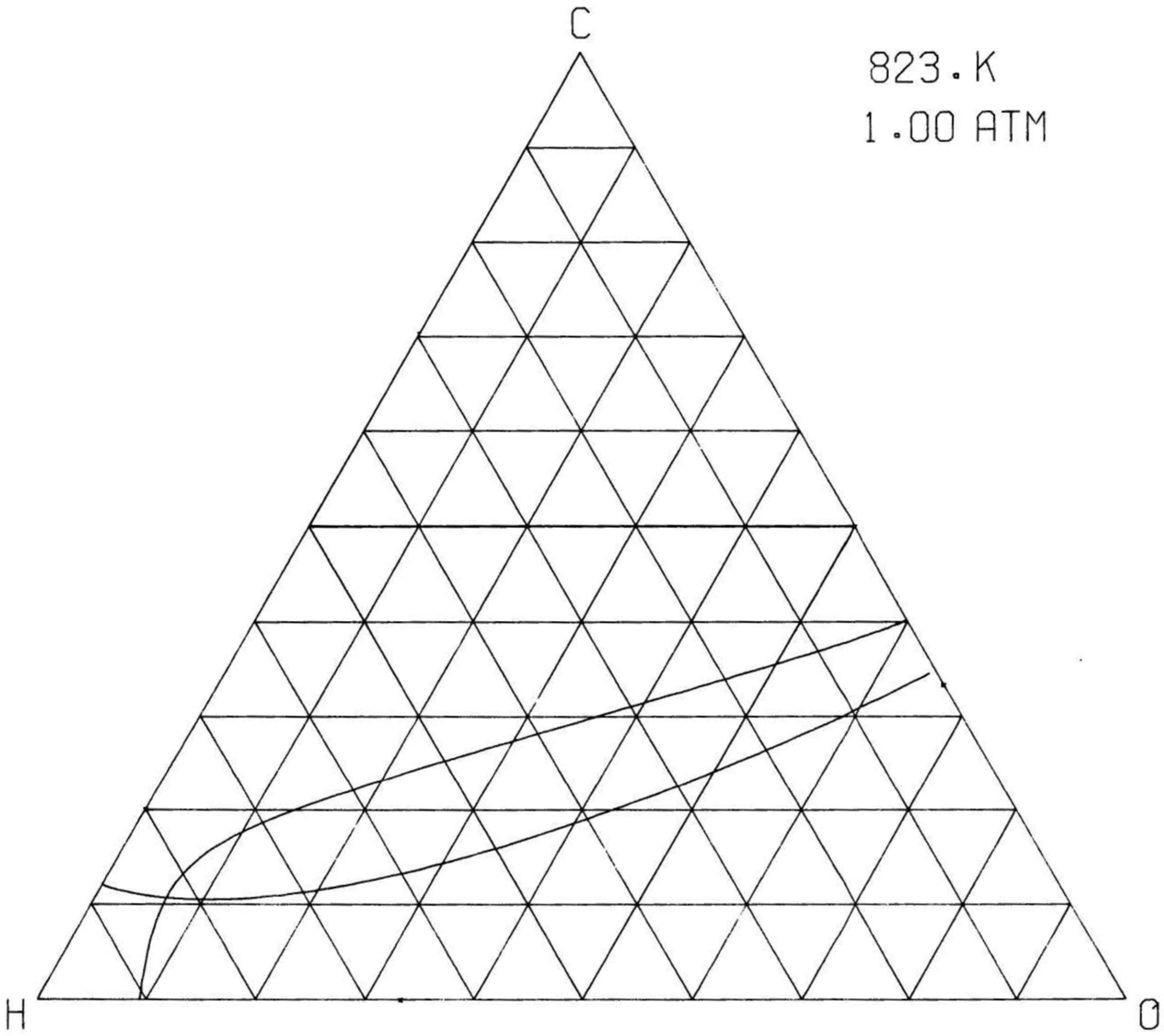
A similar procedure is then repeated to calculate the $Fe-Fe_3O_4$(or FeO)-$H_2-CO-CH_4-CO_2-H_2O$ equilibrium line with the Subroutine OXEQ(P, T, RCH, PI, C, H, O). After calculating the two equilibrium lines, the program proceeds to calculate and to draw the diagram for the next set of specified temperature and pressure.

Sample diagrams produced by the program are shown in Figs. 48 through 51.

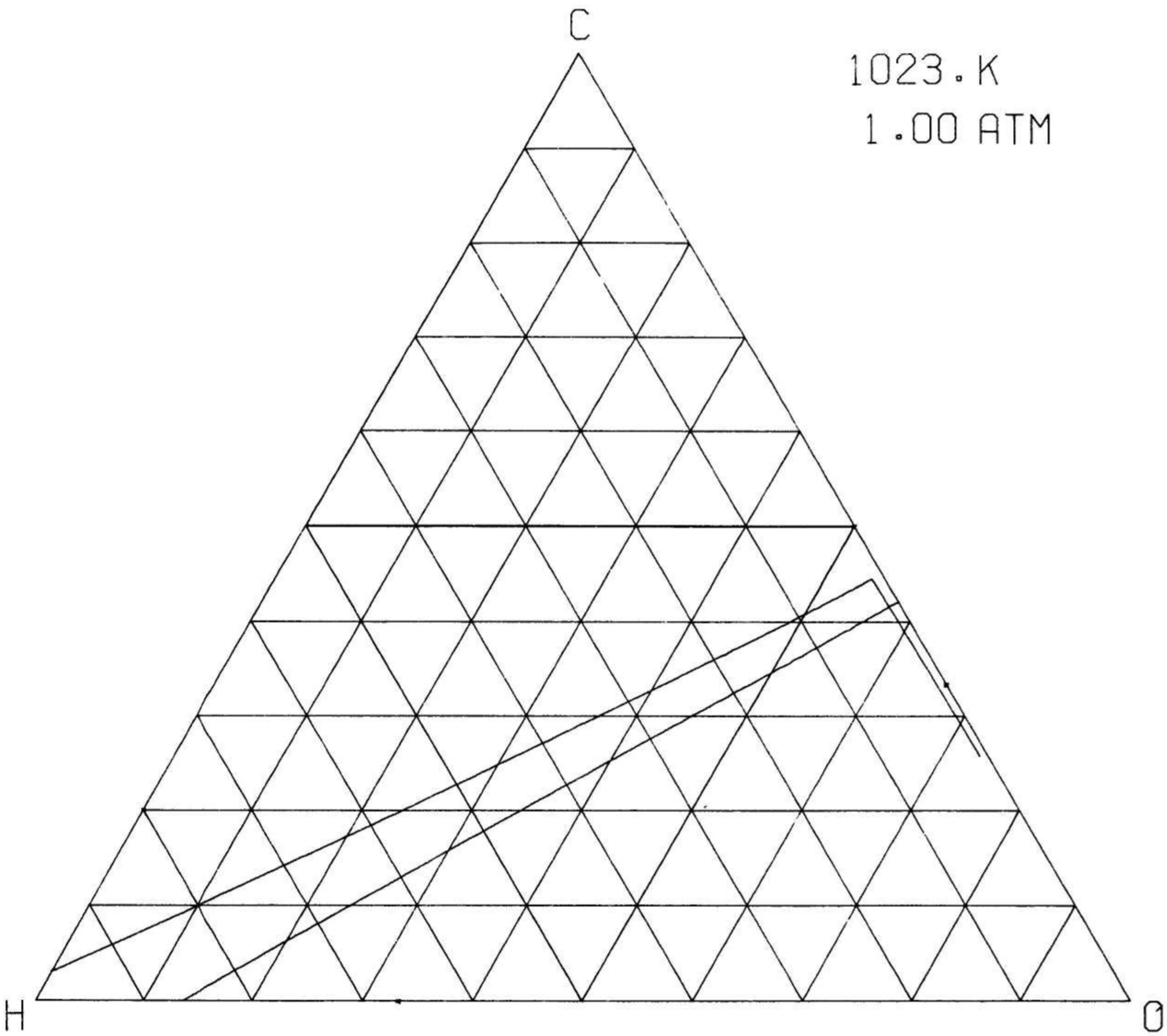
8.3.1.3 BOSCH1 Listing. A listing of the program BOSCH1 follows:



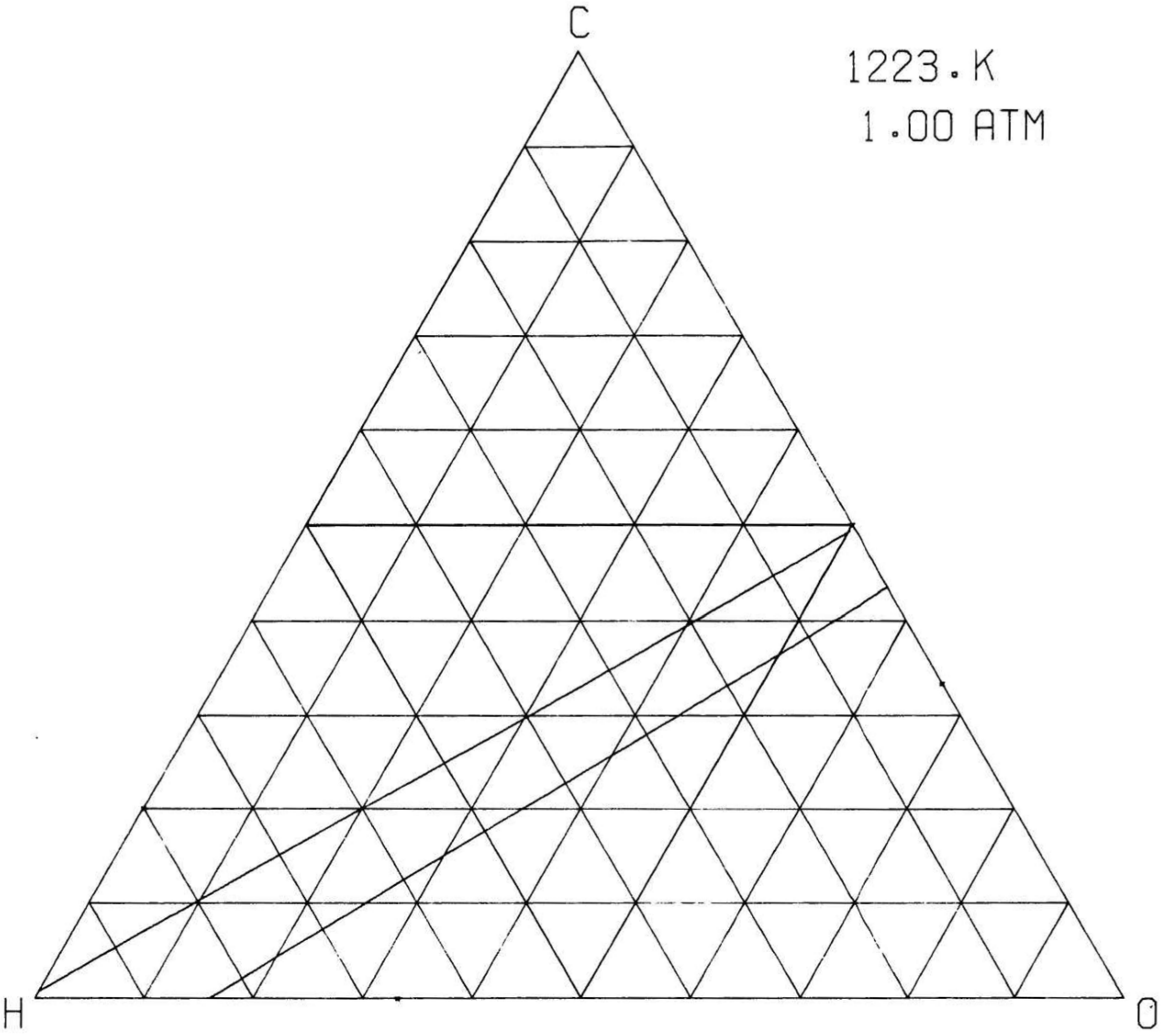
IRON - IRON OXIDE - GRAPHITE - GAS EQUILIBRIA



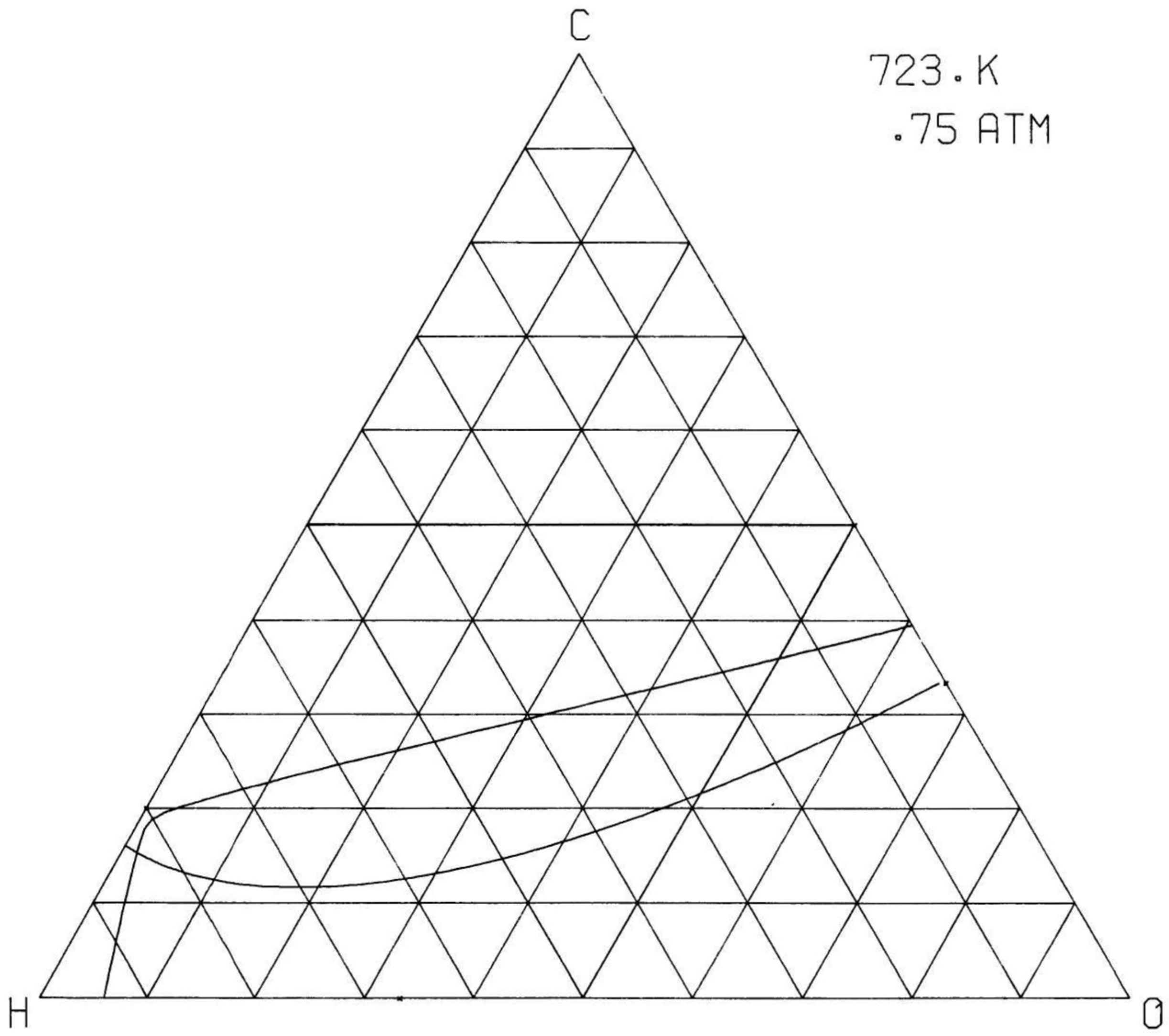
IRON - IRON OXIDE - GRAPHITE - GAS EQUILIBRIA



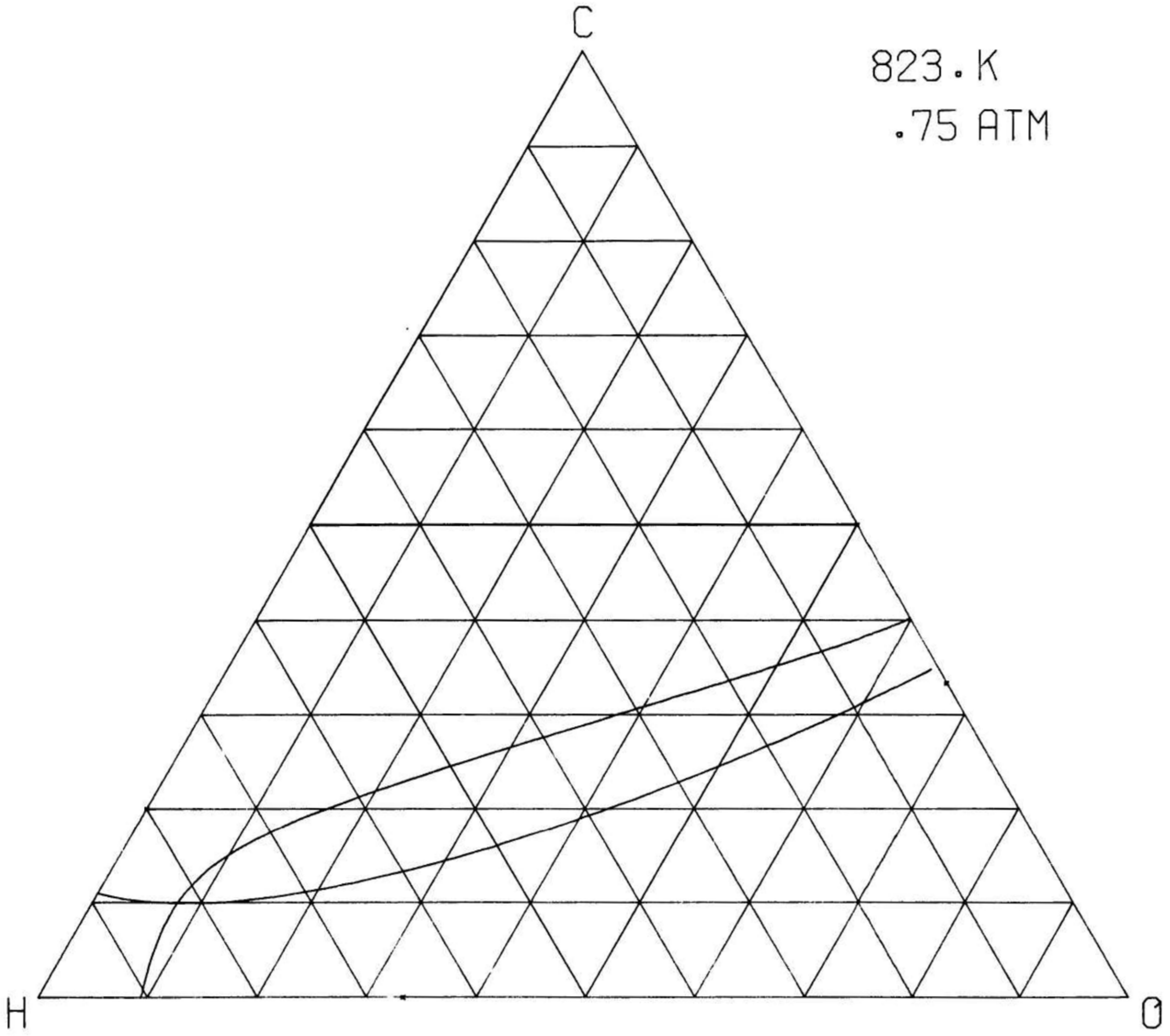
IRON - IRON OXIDE - GRAPHITE - GAS EQUILIBRIA



IRON - IRON OXIDE - GRAPHITE - GAS EQUILIBRIA



IRON - IRON OXIDE - GRAPHITE - GAS EQUILIBRIA



IRON - IRON OXIDE - GRAPHITE - GAS EQUILIBRIA

```
      DIMENSION PI(5),A(5000)
      REAL K1,K2,K3,K4,K5,K6
      COMMON/DATA/K1,K2,K3,K4,K5,K6
      COMMON/ROOT/C0,C1,C2,C3,C4,C5,C6,XST,EPS,IEND
      OPEN(UNIT=26,ACCESS='APPEND')
      CALL PLOTS(A,5000)
      P=1.00
      T=600.
    9 T=T+100.
      IF (T.GT.1400.)STOP
      CALL KEQUIL(T)
      YMAX=8.
      YY=SQRT(3.)
      DO 400 J=1,5
      RJ=J
      C=0.1*(10.-RJ)
      H=1.0-C
      O=0.0
      X=1.5+((2.*O+C)*YMAX)/YY
      Y=1.5+C*YMAX
      CALL PLOT(X,Y,3)
      IPEN=2
      DO 400 I=1,6
      GO TO (1,2,3,1,2,3),I
    1 DUMMY=H
      H=O
      O=DUMMY
      GO TO 20
    2 DUMMY=C
      C=H
      H=DUMMY
      GO TO 20
    3 DUMMY=O
      O=C
      C=DUMMY
   20 X=1.5+((2.*O+C)*YMAX/YY)
      Y=1.5+C*YMAX
      CALL PLOT(X,Y,IPEN)
      IPEN=1
  400 CONTINUE
      C=0.0
      H=1.0
      O=0.0
      DO 500 I=1,4
      DUMMY=C
      C=H
      H=O
      O=DUMMY
      X=1.5+((2.*O+C)*YMAX)/YY
      Y=1.5+C*YMAX
      CALL PLOT(X,Y,1)
  500 CONTINUE
```

```
      CALL SYMBOL(1.25,1.25,0.25,1HH,00.0,1)
      X=2.*(YMAX/YY)+1.62
      CALL SYMBOL(X,1.25,0.25,1HO,00.0,1)
      X=1.43+YMAX/YY
      Y=1.62+YMAX
      CALL SYMBOL(X,Y,0.25,1HC,00.0,1)
      CALL SYMBOL(1.5,0.5,0.25,
     1 45HIRON - IRON OXIDE - GRAPHITE - GAS EQUILIBRIA,00.0,45)
      C=0.2
      O=0.0
      X=1.5+((C+2.*O)*(YMAX/YY))
      Y=1.5+C*YMAX
      CALL SYMBOL(X,Y,0.035,10,00.0,-1)
      C=0.0
      O=1./3.
      X=1.5+((C+2.*O)*(YMAX/YY))
      Y=1.5+C*YMAX
      CALL SYMBOL(X,Y,0.035,10,00.0,-1)
      C=0.5
      O=0.5
      X=1.5+((C+2.*O)*(YMAX/YY))
      Y=1.5+C*YMAX
      CALL SYMBOL(X,Y,0.035,10,00.0,-1)
      C=1./3.
      O=2./3.
      X=1.5+((C+2.*O)*(YMAX/YY))
      Y=1.5+C*YMAX
      CALL SYMBOL(X,Y,0.035,10,00.0,-1)
      CALL PLOT(X,Y,3)
      CALL NUMBER(8.37,9.25,0.25,T,00.0,'(F5.0)',5)
      CALL SYMBOL(9.5,9.25,0.25,1HK,00.0,1)
      CALL NUMBER(8.5,8.75,0.25,P,00.0,'(F4.2)',4)
      CALL SYMBOL(9.5,8.75,0.25,3HATM,00.0,3)
      WRITE(26, 898)T,P
  898 FORMAT(1H1,///' GRAPHITE - GAS EQUILIBRIUM',4X,F5.0,' K',
     14X,F4.2,' ATMA'/)
      WRITE(26, 899)
  899 FORMAT(' O/H RATIO',2X,'PH2',5X,'PCO',5X,'PCH4',4X,'PCO2',
     1 4X,'PH2O',6X,'C',7X,'H',7X,'O')
      XST=(-1.+SQRT(1.+4.*K1*P))/(2.*K1)
      PI(1)=XST
      PI(2)=0.
      PI(3)=P-XST
      PI(4)=0.
      PI(5)=0.
      ROH=0.0
      C=(P-XST)/(2.*XST+5.*(P-XST))
      H=1.-C
      O=0.0
      WRITE(26, 901)ROH,PI,C,H,O
      X=1.5+((C+2.*O)*(YMAX/YY))
```

```
      Y=1.5+C*YMAX
      CALL PLOT(X,Y,3)
      CALL PLOT(X,Y,2)
      DO 102 I=1,99
      RI=I
      ROH=RI/(100.-RI)
      CALL CEQ(P,T,ROH,PI,C,H,O)
      X=1.5+((C+2.*O)*(YMAX/YY))
      Y=1.5+C*YMAX
      CALL PLOT(X,Y,1)
      XST=PI(1)
      WRITE(26, 901)ROH,PI,C,H,O
102   CONTINUE
      WRITE(26, 900)T,P
900   FORMAT(1H1,///' IRON - IRON OXIDE - GAS EQUILIBRIA',4X,
     1F4.0,' K',4X,F4.2,' ATMA'/)
      WRITE(26, 904)
904   FORMAT(' C/H RATIO',2X,'PH2',5X,'PCO',5X,'PCH4',4X,'PCO2',
     ! 4X,'PH2O',6X,'C',7X,'H',7X,'O')
      XST=P/(1.+(1./K4))
      C=0.0
      O=(P-XST)/(3.*P-XST)
      X=1.5+((C+2.*O)*(YMAX/YY))
      Y=1.5+C*YMAX
      CALL PLOT(X,Y,3)
      CALL PLOT(X,Y,2)
      RCH=0.
      PI(1)=XST
      PI(2)=0.
      PI(3)=0.
      PI(4)=0.
      PI(5)=P-XST
      WRITE(26,901)RCH,PI,C,H,O
      DO 100 I=1,99
      RI=I
      RCH=RI/(100.-RI)
      CALL OXEQ(P,T,RCH,PI,C,H,O)
      X=1.5+((C+2.*O)*(YMAX/YY))
      Y=1.5+C*YMAX
      CALL PLOT(X,Y,1)
      XST=PI(1)
      WRITE(26, 901)RCH,PI,C,H,O
901   FORMAT(G9.3,8F8.3)
100   CONTINUE
      PI(4)=P*(1./(1.+K5))
      PI(2)=P-PI(4)
      C=(PI(4)+PI(2))/(2.*PI(2)+3.*PI(4))
      O=1.-C
      X=1.5+((C+2.*O)*(YMAX/YY))
      Y=1.5+C*YMAX
      CALL PLOT(X,Y,1)
```

```
      CALL PLOT(X,Y,1)
      PI(1)=0.
      PI(3)=0.
      PI(5)=0.
  800 CALL PLOT(14.,0.0,-3)
      GO TO 9
      END
```

```
      SUBROUTINE RTNI(X,F,DERF,XST,EPS,IEND,IER)
      IER=0
      X=XST
      TOL=X
      CALL FCT(TOL,F,DERF)
      TOLF=100.*EPS
      DO 6 I=1,IEND
      IF(F)1,7,1
    1 IF(DERF)2,8,2
    2 DX= F/DERF
      X=X-DX
      TOL=X
      CALL FCT(TOL,F,DERF)
      TOL=EPS
      A=ABS(X)
      IF(A-1.)4,4,3
    3 TOL=TOL*A
    4 IF(ABS(DX)-TOL)5,5,6
    5 IF(ABS(F)-TOLF)7,7,6
    6 CONTINUE
      IER=1
    7 RETURN
    8 IER=2
      RETURN
      END
```

```
      SUBROUTINE FCT(X,F,DERF)
      COMMON/ROOT/C0,C1,C2,C3,C4,C5,C6,XST,EPS,IEND
      F=C0+(C1*X)+(C2*X**2.)+(C3*X**3.)
      F=F+(C4*X**4.)+(C5*X**5)+(C6*X**6.)
      DERF=C1+(2.*C2*X)+(3.*C3*X**2.)
      DERF=DERF+(4.*C4*X**3)+(5.*C5*X**4)+(6.*C6*X**5)
      RETURN
      END
```

```
      SUBROUTINE CEQ(P,T,ROH,PI,C,H,O)
      DIMENSION PI(5)
      REAL K1,K2,K3,K4,K5,K6
      COMMON/DATA/K1,K2,K3,K4,K5,K6
      COMMON/ROOT/C0,C1,C2,C3,C4,C5,C6,XST,EPS,IEND
      A=-P*K1
      B=2.*ROH
      CC=1.-B
      D=1+B
      AA=(K1*D-P*K6*CC)
      AB=(K6+K1*K1*(1.+2.*B))
      AC=K1*K6*D
      AD=-(K3*K1*K1)/(4.*K6)
      AE=-B*K1-(K1*K3/4.)*(3.-B)
      AF=-(K3*K6/4.)*CC*(3.+B)-2.*B*K1*K1-B*K6*D
      AG=-(K3/(4.*K1))*K6*K6*CC*CC*D-2.*B*K1*K6*D
      C0=A*(A+AD)
      C1=2.*A*AA+AA*AD+A*AE
      C2=2.*A*AB+AA*AA+AD*AB+AA*AE+A*AF+K1*K1*ROH*ROH
      C3=2.*A*AC+2.*AA*AB+AD*AC+AB*AE+AA*AF+A*AG+ROH*B*K1*K6*D
      C3=C3+B*B*K1*K1*K1
      C4=2.*AA*AC+AB*AB+AC*AE+AF*AB+AA*AG+(K6*ROH*D)**2
      C4=C4+(B*K1*K1)**2.+2.*B*B*K1*K1*K6*D
      C5=2*AB*AC+AF*AC+AB*AG+8.*K1*K1*K1*K6*ROH*ROH*D
      C5=C5+B*B*K1*K6*K6*D*D
      C6=AC*AC+AC*AG+(B*D*K1*K6)**2.
      EPS=P*XST*5.0E-02
      IEND=100000
      CALL RTNI(X,F,DERF,XST,EPS,IEND,IER)
      IF(IER)100,200,100
200   PI(1)=X
      PI(4)=(A+AA*X+AB*X*X+AC*X*X*X)/(K1+K6*X*D)
      PI(3)=K1*X*X
      PI(5)=(B*(1.+2.*K1*X)*X)-2.*PI(4)
      PI(5)=PI(5)/((1.+(K1/(K6*X))-B))
      PI(2)=P-PI(1)-PI(3)-PI(4)-PI(5)
      TOT=2.*(PI(1)+PI(2))+3.*(PI(4)+PI(5))+5.*PI(3)
      O=(PI(2)+2.*PI(4)+PI(5))/TOT
      H=O/ROH
      C=1.-O-H
      RETURN
100   TYPE 999,IER
999   FORMAT(' BINGO',I2)
      TYPE 998,F,X
998   FORMAT(2G15.5)
      RETURN
      END
```

```
      SUBROUTINE OXEQ(P,T,RCH,PI,C,H,O)
      DIMENSION PI(5)
      REAL K1,K2,K3,K4,K5,K6
      COMMON/DATA/K1,K2,K3,K4,K5,K6
      COMMON/ROOT/C0,C1,C2,C3,C4,C5,C6,XST,EPS,IEND
      C0=-K4*(K5+1.)*P
      C1=(K4+1.)*(K5+1.)*(2.*RCH+1.)
      C2=(4.*RCH-1.)*K4*K4*K5*K6*P
      C3=(K4+1.)*K4*K5*K6*(1.-2.*RCH)
      C4=0.0
      C5=0.0
      C6=0.0
      EPS=P*1.0E-07
      IEND=100
      CALL RTNI(X,F,DERF,XST,EPS,IEND,IER)
      IF(IER)100,200,100
  200 PI(1)=X
      PI(4)=(P-X*(1.+1./K4))/((K5+1.)+K4*K5*K6*X*X)
      PI(5)=X/K4
      PI(2)=K5*PI(4)
      PI(3)=P-PI(1)-PI(2)-PI(4)-PI(5)
      TOT=2.*(PI(1)+PI(2))+3.*(PI(4)+PI(5))+5.*PI(3)
      C=(PI(2)+PI(3)+PI(4))/TOT
      H=C/RCH
      O=1.-C-H
      RETURN
  100 TYPE 999,IER
  999 FORMAT(' BINGO',I2)
      RETURN
      END
```

```
      SUBROUTINE KEQUIL(T)
      DIMENSION GCO(15),GCH4(15),GCO2(15),GH2O(15),GFEO(15),GFE3O4(15)
      REAL K11,K12,K21,K22,K31,K32,K41,K42,K51,K52,K61,K62
      REAL K1,K2,K3,K4,K5,K6
      COMMON/DATA/K1,K2,K3,K4,K5,K6
      DATA GCO/-28741.,-30718.,-32823.,-34975.,-37144.,
     1         -39311.,-41468.,-43612.,-45744.,-47859.,
     2         -49962.,-52049.,-54126.,-56189.,-58124./
      DATA GCH4/-15400.,-13909.,-12110.,-10066.,- 7845.,
     1          - 5493.,- 3046.,-  533.,  2029.,  4625.,
     2            7247.,  9087., 12535., 15195., 17859./
      DATA GCO2/-94100.,-94191.,-94267.,-94335.,-94399.,
     1          -94458.,-94510.,-94556.,-94596.,-94628.,
     2          -94658.,-94681.,-94701.,-94716.,-94728./
      DATA GH2O/-56557.,-55635.,-54617.,-53519.,-52361.,
     1          -51156.,-49915.,-48646.,-47352.,-46050.,
     2          -44712.,-43371.,-42022.,-40663.,-39297./
      DATA GFEO/-62178.,-60299.,-58564.,-56908.,-55309.,
     1          -53752.,-52222.,-50710.,-49201.,-47686.,
     2          -46140.,-44580.,-43017.,-41470.,-39938./
      DATA GFE3O4/-259592.,-251358.,-243038.,-234820.,-226772.,
     1            -218926.,-211290.,-203874.,-196661.,-189541.,
     2            -182336.,-175096.,-167849.,-160646.,-153483./
      T1=T/100.
      I1=T1
      T1=100.*I1
      I2=I1+1
      T2=I2*100.
      R=1.987
      K11=EXP(-GCH4(I1)/(R*T1))
      K12=EXP(-GCH4(I2)/(R*T2))
      DEL=((ALOG(K12)-ALOG(K11))/((1/T2)-(1/T1)))*((1/T)-(1/T1))
      K1=EXP(ALOG(K11)+DEL)
      K31=EXP((-GH2O(I1)-GCO(I1)+GCO2(I1))/(R*T1))
      K32=EXP((-GH2O(I2)-GCO(I2)+GCO2(I2))/(R*T2))
      DEL=((ALOG(K32)-ALOG(K31))/((1/T2)-(1/T1)))*((1/T)-(1/T1))
      K3=EXP(ALOG(K31)+DEL)
      K61=EXP((-GCH4(I1)-GH2O(I1)+GCO(I1))/(R*T1))
      K62=EXP((-GCH4(I2)-GH2O(I2)+GCO(I2))/(R*T2))
      DEL=((ALOG(K62)-ALOG(K61))/((1/T2)-(1/T1)))*((1/T)-(1/T1))
      K6=EXP(ALOG(K61)+DEL)
      K2=K1*K3*K6
      IF(T.LE.800.)GO TO 10
      IF(T.LT.860.)GO TO 30
      IF(T.LT.900.)GO TO 40
      GO TO 50
   10 K41=EXP((-0.25*GFE3O4(I1)+GH2O(I1))/(R*T1))
      K42=EXP((-0.25*GFE3O4(I2)+GH2O(I2))/(R*T2))
      DEL=((ALOG(K42)-ALOG(K41))/((1/T2)-(1/T1)))*((1/T)-(1/T1))
      K4=EXP(ALOG(K41)+DEL)
      K52=EXP((-0.25*GFE3O4(I2)-GCO(I2)+GCO2(I2))/(R*T2))
      K51=EXP((-0.25*GFE3O4(I1)-GCO(I1)+GCO2(I1))/(R*T1))
```

```
      DEL=((ALOG(K52)-ALOG(K51))/((1/T2)-(1/T1)))*((1/T)-(1/T1))
      K5=EXP(ALOG(K51)+DEL)
      GO TO 60
   30 T1=(T-100.)/100.
      I1=T1
      I2=I1+1
      T1=I1*100.
      T2=I2*100.
      K41=EXP((-0.25*GFE3O4(I1)+GH2O(I1))/(R*T1))
      K42=EXP((-0.25*GFE3O4(I2)+GH2O(I2))/(R*T2))
      DEL=((ALOG(K42)-ALOG(K41))/((1/T2)-(1/T1)))*((1/T)-(1/T1))
      K4=EXP(ALOG(K41)+DEL)
      K52=EXP((-0.25*GFE3O4(I2)-GCO(I2)+GCO2(I2))/(R*T2))
      K51=EXP((-0.25*GFE3O4(I1)-GCO(I1)+GCO2(I1))/(R*T1))
      DEL=((ALOG(K52)-ALOG(K51))/((1/T2)-(1/T1)))*((1/T)-(1/T1))
      K5=EXP(ALOG(K51)+DEL)
      GO TO 60
   40 T1=(T+100.)/100.
      I1=T1
      I2=I1+1
      T1=I1*100.
      T2=I2*100.
      K41=EXP((-GFEO(I1)+GH2O(I1))/(R*T1))
      K42=EXP((-GFEO(I2)+GH2O(I2))/(R*T2))
      DEL=((ALOG(K42)-ALOG(K41))/((1/T2)-(1/T1)))*((1/T)-(1/T1))
      K4=EXP(ALOG(K41)+DEL)
      K52=EXP((-GFEO(I2)-GCO(I2)+GCO2(I2))/(R*T2))
      K51=EXP((-GFEO(I1)-GCO(I1)+GCO2(I1))/(R*T1))
      DEL=((ALOG(K52)-ALOG(K51))/((1/T2)-(1/T1)))*((1/T)-(1/T1))
      K5=EXP(ALOG(K51)+DEL)
      GO TO 60
   50 T1=T/100.
      I1=T1
      I2=I1+1
      T1=I1*100.
      T2=I2*100.
      K41=EXP((-GFEO(I1)+GH2O(I1))/(R*T1))
      K42=EXP((-GFEO(I2)+GH2O(I2))/(R*T2))
      DEL=((ALOG(K42)-ALOG(K41))/((1/T2)-(1/T1)))*((1/T)-(1/T1))
      K4=EXP(ALOG(K41)+DEL)
      K52=EXP((-GFEO(I2)-GCO(I2)+GCO2(I2))/(R*T2))
      K51=EXP((-GFEO(I1)-GCO(I1)+GCO2(I1))/(R*T1))
      DEL=((ALOG(K52)-ALOG(K51))/((1/T2)-(1/T1)))*((1/T)-(1/T1))
      K5=EXP(ALOG(K51)+DEL)
   60 RETURN
      END
```

8.3.2 Bosch Process Calculations

8.3.2.1 Bosch Recycle Reactor. All calculations in this and other sections are performed on the calculational basis of one mole of carbon dioxide fed to the process. Consider the Bosch process as shown in Fig. 41. Assume the process is operating at steady state. An overall mass balance on the process and the process stoichiometry as written in reaction (A)

$$CO_2 + 2H_2 \rightarrow C(s) + 2H_2O \qquad (A)$$

shows that the water removal and solid carbon accumulation rates must be 2 and 1 moles per mole inlet CO_2, respectively. The O/H ratio in the feed mixture and in the water product is 0.5. As the carbon deposition process in the Bosch reactor does not change the overall O/H ratio, the O/H ratio at all points in the gaseous recycle loop is 0.5.

Let the number of moles of material passing through the recycle stream compressor per mole of inlet CO_2 be r. A material balance around the heat exchanger/water separator at steady state gives

$$\text{moles in} = \text{moles out} = r + 2$$

Assuming that the water separator is 100% efficient, a component mass balance for water around the water separator gives

$$(r + 2)\left(\frac{P_{H_2O}}{P}\right) = 2$$

or

$$r = \frac{2P}{P_{H_2O}} - 2$$

where (P_{H_2O}/P) is the mole fraction of water in the exit stream of the Bosch reactor.

The Bosch process was assumed to be sufficiently rapid so that the exit stream represented an equilibrium mixture corresponding to the system $Fe-Fe_3O_4$(or FeO)-H_2-CO-CH_4-CO_2-H_2O. Under conditions where iron and iron oxide could not simultaneously coexist, the C-H_2-CO-CH_4-CO_2-H_2O equilibrium boundary was taken as limiting conversion. The component concentrations for both of these mixtures were calculated numerically by the subroutines OXEQ and CEQ described previously.

8.3.2.2 Bosch Recycle Reactor with Water-Gas Shift Prereactor. Consider the Bosch process as shown in Fig. 44. Assume that the water-gas shift reactor is designed so equilibrium may be achieved at the specified reactor operating temperature and that no methane is formed in the shift reactor. For a feed mixture containing n moles of H_2 per mole of CO_2, a mass balance at any point in the reaction satisfies the constraints

Component	Inlet (moles/mole inlet CO_2)	Outlet (moles/mole inlet CO_2)
H_2	n	n - x
CO	0	x
CO_2	1	1 - x
H_2O	0	x

At equilibrium,

$$K_3 = \frac{P_{CO}P_{H_2O}}{P_{H_2}P_{CO_2}} = \frac{x^2}{(n - x)(1 - x)}$$

which may be solved for x to give

$$x = \frac{-K_3(n + 1) + \sqrt{K_3^2(n + 1)^2 + 4(1 - K_3)K_3n}}{2(1 - K_3)}$$

If (n - 2) moles of hydrogen are then removed from the water-gas shift reactor effluent and recycled to the reactor, the remainder of the stream contains (2 - x) moles of hydrogen, x moles carbon monoxide, (1 - x) moles carbon dioxide and x moles of water. This mixture has an O/H ratio of 0.5 and thus the gas phase O/H ratio at all points in the recycle loop is again constrained to be 0.5. Thus, the calculation of r, the number of moles of gaseous material passing through the compressor in the Bosch recycle loop, is as presented in the previous section.

8.4 Experimental Data

8.4.1 Summary of Experiments

A summary of the operating conditions for all experiments is contained in Table 8.

8.4.2 Experimental Data

The data obtained during reactor operation follow:

Table 8 . Summary of Experiments

Run No.	Temperature (°K)	Fresh Catalyst	Inlet Flow Rate (cc/sec) (STP)	Nominal Inlet Composition, mole %					
				H_2	CO	CH_4	CO_2	H_2O	He
4	823	yes	20	50	50	0	0	0	0
				100	0	0	0	0	0
				50	0	50	0	0	0
5	823	no	20	100	0	0	0	0	0
				25	0	75	0	0	0
				60	0	40	0	0	0
				75	0	25	0	0	0
6	823	no	20	0	100	0	0	0	0
				0	75	0	25	0	0
				0	0	0	100	0	0
7	823	no	20	0	50	0	50	0	0
				0	55	0	45	0	0
				0	60	0	40	0	0
				0	70	0	30	0	0
9	823	yes	20	50	50	0	0	0	0
10	823	yes	20	50	50	0	0	0	0
				50	0	0	50	0	0
11	823	no	20	100	0	0	0	0	0
				50	0	0	50	0	0
12	823	no	20	50	5	0	45	0	0
				50	10	0	40	0	0
				50	15	0	35	0	0
13	823	yes	20	50	50	0	0	0	0
14	823	yes	20	50	0	0	50	0	0
15	823	no	20	0	0	0	100	0	0
				50	50	0	0	0	0
				50	0	0	50	0	0
			32	45	0	0	55	0	0
			20	50	0	0	50	0	0
16	823	yes	20	0	0	0	100	0	0
				0	0	0	0	0	100
				50	50	0	0	0	0
17	823	no	20	50	0	0	50	0	0
			10	50	0	0	50	0	0
			2	50	0	0	50	0	0
18	833	yes	20	50	50	0	0	0	0
	823			50	0	0	50	0	0
19	823	no	20	50	0	0	50	0	0
				50	25	0	25	0	0
				100	0	0	0	0	0
	673			100	0	0	0	0	0
20	823	yes	20	50	50	0	0	0	0
				50	0	0	50	0	0
21	823	no	20	45	0	0	55	0	0
				95	5	0	0	0	0
				98	2	0	0	0	0
22	823	yes	20	50	50	0	0	0	0
25	823	yes	20	50	50	0	0	0	0
26	673	no	20	50	0	0	50	0	0
				95	5	0	0	0	0
				50	50	0	0	0	0

Table 8 . Summary of Experiments (Continued)

Run No.	Temperature (°K)	Fresh Catalyst	Inlet Flow Rate (cc/sec) (STP)	Nominal Inlet Composition, mole %					
				H_2	CO	CH_4	CO_2	H_2O	He
27	748	no	20	50	0	0	50	0	0
				50	50	0	0	0	0
				100	0	0	0	0	0
28	823	yes	20	50	50	0	0	0	0
29	823	no	20	97	0	0	0	3	0
				48	0	0	48	4	0
				95	2	0	0	3	0
				92	5	0	0	3	0
30	823	no	20	97	0	0	0	3	0
				87	5	0	5	3	0
				77	10	0	10	3	0
31	823	yes	20	75	25	0	0	0	0
33	823	yes	20	75	25	0	0	0	0
				50	0	0	50	0	0
34	823	no	20	50	0	0	50	0	0
	798								
	773								
	748								
35	723	no	20	50	0	0	50	0	0
	698								
	673								
36	823	no	20	75	5	0	20	0	0
37	823	yes	20	75	25	0	0	0	0
				75	10	0	15	0	0
38	823	yes	20	75	25	0	0	0	0
				75	15	0	10	0	0
39	773	yes	20	75	25	0	0	0	0
40	773	no	20	75	25	0	0	0	0
				75	10	0	15	0	0
41	823	yes	20	75	25	0	0	0	0
42	823	no	20	98	0	0	0	2	0
				73	25	0	0	2	0
43	823	yes	20	75	25	0	0	0	0
44	823	no	20	0	0	0	100	0	0
				0	0	0	98	2	0
45	823	yes	20	95	5	0	0	0	0
46	823	yes	20	90	10	0	0	0	0
48	823	**	20	100	0	0	0	0	0
				75	25	0	0	0	0
				50	0	0	50	0	0
49	823	yes	20	0	0	0	100	0	0
				0	0	0	0	0	100
				75	25	0	0	0	0

**Activated carbon (Nuchar 190-C) used as catalyst.

```
                              DATA TAKEN DURING RUN   4 ON 11 JUN 74

TIME SAMP         DELP IGAS         H2         CO        CH4        CO2        H2O          C
   0    1         3.00    1     3837.0   201729.0   166773.0   228473.0        0.0
   0    3         3.00    1     4712.0   233761.0   193902.0   264823.0        0.0
   0    4         4.00    1     4735.0   234336.0   194009.0   263940.0        0.0
   0    5         0.00    1     4403.0   223638.0   185131.0   253124.0        0.0
   0    6         5.00    1     4729.0   235493.0   195014.0   265760.0        0.0
   0    7         3.00    1     4642.0   232682.0   192962.0   262782.0        0.0
   0    8         1.00    1     4773.0   237187.0   196618.0   267790.0        0.0
   0    9         3.00    1     4354.0   221869.0   183878.0   251508.0        0.0
   0   10         4.00    1     4766.0   236991.0   196246.0   266981.0        0.0
   0   12         0.00    2    25654.0        0.0        0.0        0.0        0.0

 915                      8      550.0

 915                      6       48.0        0.0        0.0        0.0        0.0
1000                      7                                                             31.945
1030                      7                                                             31.946
1047   11         2.00    4    25487.0        0.0        0.0        0.0        0.0
1054   12         0.00    4    25654.0        0.0        0.0        0.0        0.0
1058   13         0.00    4    25689.0        0.0        0.0        0.0        0.0
1100                      7                                                             31.942

1100                      6       16.0       34.0        0.0        0.0        0.0
1107   14         0.00    4    10175.0   477808.0        0.0        0.0        0.0
1112   15         0.00    4     9289.0   449561.0        0.0        0.0        0.0
1117   16         0.00    4     8269.0   411085.0        0.0        0.0        0.0
1126   17         0.00    5    10111.0   485548.0        0.0        0.0        0.0
1133                      7                                                             32.000
1136   18        -1.00    5     5056.0   285876.0        0.0     2605.0     3231.0
1200                      7                                                             32.039
1200   20         0.00    5     2315.0   136841.0        0.0     1591.0     1289.0
1218   21         0.00    5    10419.0   497794.0        0.0     1182.0     9193.0
1235   22         0.00    5    10420.0   498382.0        0.0      860.0     5756.0
1235                      7                                                             32.118
1250   23         0.00    5    10510.0   498315.0        0.0      524.0     9888.0
1257                      7                                                             32.175
1307   24         0.00    5    10569.0   501014.0        0.0      593.0     7298.0
1322   25         0.00    5    10355.0   493284.0        0.0      655.0    14511.0
1326                      7                                                             32.259
1340   26         0.00    5    10415.0   496523.0        0.0     1047.0    13700.0
1359   27         0.00    5    10163.0   487298.0      104.0     1976.0     2145.0

1400                      6       32.2        0.0        0.0        0.0        0.0
1400                      7                                                             32.300
1410                      7                                                             32.480
1415   28         0.00    5    28414.0        0.0     1020.0        0.0     1659.0
1427   29         0.00    5    27890.0        0.0     2178.0        0.0     2967.0
1430                      7                                                             32.465
1443   30         0.00    5    27729.0        0.0     2382.0        0.0     1482.0
1454                      7                                                             32.448
1458   31         0.00    5    26676.0        0.0     2954.0        0.0     1301.0
1512   32         0.00    5    27913.0        0.0     3316.0        0.0      894.0
1520                      7                                                             32.412
```

```
1528    33       0.00     4   27269.0        0.0     899.0       0.0       0.0
1537    34       0.00     5   26718.0        0.0    6950.0       0.0     907.0
1543                      7                                                        32.378

1545                      6      16.0        0.0      43.0       0.0       0.0
1555    35       0.00     4   10434.0        0.0  384203.0    1879.0       0.0
1611    36       0.00     5   10707.0        0.0  390596.0       0.0     464.0
1613                      7                                                        32.378
1626    37       0.00     5   10529.0        0.0  385213.0       0.0     657.0
1641    38       0.00     4   10687.0        0.0  385776.0      33.0       2.0
1647                      7                                                        32.378
1700                      7                                                        32.378
```

```
                                  DATA TAKEN DURING RUN   4 ON 11 JUN 74



THE CALIBRATION GASES ARE KNOWN TO BE
                     IGAS        H2        CO        CH4        CO2        H2O
                        1     25.17     24.94     24.97      24.94       0.00
                        2    100.00      0.00      0.00       0.00       0.00
                        3      0.00      0.00      0.00     100.00       0.00

CALIBRATION GAS SAMPLES FOR THIS RUN WERE ANALYSED AS

TIME SAMP       DELP IGAS        H2        CO        CH4        CO2        H2O        C
THE SUM OF THE FOLLOWING DATA DIFFERED FROM 100 PERCENT BY MORE THAN 10 PERCENT BEFORE JUSTIFICATION
   0    1       3.00    1     24.98     24.97     24.98      25.06       0.00
   0    3       3.00    1     25.26     24.85     24.94      24.94       0.00
   0    4       4.00    1     25.34     24.88     24.93      24.83       0.00
   0    5       0.00    1     25.08     24.93     24.97      25.00       0.00
   0    6       5.00    1     25.22     24.90     24.96      24.90       0.00
   0    7       3.00    1     25.14     24.91     25.00      24.93       0.00
   0    8       1.00    1     25.19     24.90     24.98      24.91       0.00
   0    9       3.00    1     25.06     24.91     24.99      25.02       0.00
   0   10       4.00    1     25.22     24.92     24.97      24.87       0.00
   0   12       0.00    2    100.00      0.00      0.00       0.00       0.00

THE RELATIVE CALIBRATION
AREA COEFFICENTS ARE      0.017443  0.886021  0.732193  1.000000  0.689999  0.024859

 ATMOSPHERIC PRESSURF WAS  759.96 .

 THE WEIGHT OF CATALYST INITIALLY CHARGED TO THE REACTOR IS  0.240 GRAMS.

 THE GROSS WEIGHT OF THE CATALYST CARRIER AND SUSPENSION MECHANISM IS  31.945 GRAMS.
```

```
                                  DATA TAKEN DURING RUN   4 ON 11 JUN 74

TIME SAMP        DELP IGAS          H2          CO         CH4         CO2         H2O          C

 915 REACTOR TEMPERATURE 550. DEGREES CENTIGRADE


 915 CHANGED INLET GAS TO      100.00        0.00        0.00        0.00        0.00             TOTAL FLOW 29.7 CC/SEC (STP)
1000                                                                                         0.000 GRAMS CARBON DEPOSITED
1030                                                                                         0.000 GRAMS CARBON DEPOSITED
1047      11       2.00    4   100.00        0.00        0.00        0.00        0.00
1054      12       0.00    4   100.00        0.00        0.00        0.00        0.00
1059      13       0.00    4   100.00        0.00        0.00        0.00        0.00
1100                                                                                        -0.003 GRAMS CARBON DEPOSITED

1100 CHANGED INLET GAS TO       49.98       50.01        0.00        0.00        0.00             TOTAL FLOW 19.8 CC/SEC (STP)
1107      14       0.00    4    47.83       52.16        0.00        0.00        0.00
1112      15       0.00    4    47.54       52.45        0.00        0.00        0.00
THE SUM OF THE FOLLOWING DATA DIFFERED FROM 100 PERCENT BY MORE THAN 10 PERCENT BEFORE JUSTIFICATION
1117      16       0.00    4    47.46       52.53        0.00        0.00        0.00
1126      17       0.00    5    47.30       52.69        0.00        0.00        0.00
1133                                                                                         0.055 GRAMS CARBON DEPOSITED
THE SUM OF THE FOLLOWING DATA DIFFERED FROM 100 PERCENT BY MORE THAN 10 PERCENT BEFORE JUSTIFICATION
1136      18      -1.00    5    46.20       52.60        0.00        0.42        0.76
1200                                                                                         0.093 GRAMS CARBON DEPOSITED
THE SUM OF THE FOLLOWING DATA DIFFERED FROM 100 PERCENT BY MORE THAN 10 PERCENT BEFORE JUSTIFICATION
1200      20       0.00    5    49.08       49.79        0.00        0.51        0.60
1218      21       0.00    5    46.64       52.01        0.00        0.10        1.23
1235      22       0.00    5    46.84       52.29        0.00        0.07        0.77
1235                                                                                         0.172 GRAMS CARBON DEPOSITED
   0      23       0.00    5    46.77       51.85        0.00        0.04        1.32
.2 7                                                                                         0.229 GRAMS CARBON DEPOSITED
1307      24       0.00    5    46.91       52.05        0.00        0.05        0.97
1322      25       0.00    5    46.43       51.55        0.00        0.06        1.94
1326                                                                                         0.313 GRAMS CARBON DEPOSITED
1340      26       0.00    5    46.42       51.64        0.00        0.09        1.82
1359      27       0.00    5    47.08       52.41        0.01        0.18        0.29

1400 CHANGED INLET GAS TO      100.00        0.00        0.00        0.00        0.00             TOTAL FLOW 19.9 CC/SEC (STP)
1400                                                                                         0.354 GRAMS CARBON DEPOSITED
1410                                                                                         0.534 GRAMS CARBON DEPOSITED
1415      28       0.00    5    99.66        0.00        0.12        0.00        0.21
1427      29       0.00    5    99.34        0.00        0.26        0.00        0.38
1430                                                                                         0.519 GRAMS CARBON DEPOSITED
1443      30       0.00    5    99.51        0.00        0.29        0.00        0.19
1454                                                                                         0.502 GRAMS CARBON DEPOSITED
1458      31       0.00    5    99.44        0.00        0.37        0.00        0.17
1512      32       0.00    5    99.47        0.00        0.40        0.00        0.11
1520                                                                                         0.466 GRAMS CARBON DEPOSITED
1528      33       0.00    4    99.88        0.00        0.11        0.00        0.00
1537      34       0.00    5    98.99        0.00        0.88        0.00        0.12
1543                                                                                         0.432 GRAMS CARBON DEPOSITED

1545 CHANGED INLET GAS TO       49.87        0.00       50.12        0.00        0.00             TOTAL FLOW 19.8 CC/SEC (STP)
1555      35       0.00    4    48.92        0.00       50.89        0.18        0.00
```

```
1611   36     0.00    5     49.08     0.00     50.85     0.00     0.06
1613                                                                        0.432 GRAMS CARBON DEPOSITED
1626   37     0.00    5     49.08     0.00     50.82     0.00     0.09
1641   38     0.00    4     49.38     0.00     50.60     0.00     0.00
1647                                                                        0.432 GRAMS CARBON DEPOSITED
1700                                                                        0.432 GRAMS CARBON DEPOSITED
```

```
                                 DATA TAKEN DURING RUN   5 ON 12 JUN 74

TIME  SAMP         DELP IGAS         H2         CO        CH4        CO2        H2O          C

 830                       8      550.0

 830                       6       32.0        0.0        0.0        0.0        0.0
   0     1         2.00    1     4775.0   237003.0   196510.0   266926.0        0.0
   0     2         1.00    1     4744.0   235584.0   195708.0   267054.0        0.0
   0     3         2.00    1     4927.0   241388.0   200764.0   274042.0        0.0
   0     4         0.00    1     4813.0   237568.0   197718.0   270299.0        0.0
   0     5         0.00    1     4887.0   239727.0   199671.0   272539.0        0.0
   0     8         0.00    2    28332.0        0.0     1698.0        0.0      780.0
 915                       7                                                                32.370
 917     6         0.00    5    27970.0        0.0     1413.0        0.0     1571.0
 932     7         0.00    5    28545.0        0.0     2162.0        0.0      883.0
 947     8         0.00    5    28332.0        0.0     1698.0        0.0      780.0
 945                       7                                                                32.330
1003     9         0.00    5    28613.0        0.0     1845.0        0.0      993.0
1017    10         0.00    5    27957.0        0.0     1623.0        0.0      954.0
1018                       7                                                                32.280

1020                       6        7.9        0.0       64.7        0.0        0.0
1032    11         0.00    5     4590.0        0.0   589061.1        0.0        0.0
1049                       7                                                                32.287
1049    12         0.00    5     4482.0        0.0   580928.1        0.0      437.0
1103    13         0.00    5     4506.0        0.0   584716.1       57.0      329.0
1118    14         0.00    5     4495.0        0.0   580100.1        0.0      530.0
1120                       7                                                                32.280
11                         7                                                                32.280
1152    16         0.00    5     4540.0        0.0   582486.1        0.0     1295.0
1207    17         0.00    5     4495.0        0.0   581843.1        0.0      569.0
1215                       7                                                                32.280

1219                       6       19.0        0.0       34.0        0.0        0.0
1222    18         0.00    5    13810.0        0.0   314872.0        0.0      823.0
1237    19         0.00    4    13806.0        0.0   311804.0        0.0      475.0
1253    20         0.00    4    13344.0        0.0   303851.0        0.0        0.0
1307                       7                                                                32.280
1310    21         0.00    5    13846.0        0.0   314031.0        0.0      331.0
1325    22         0.00    5    13432.0        0.0   306902.0        0.0     1264.0
1326                       7                                                                32.279

1330                       6       23.9        0.0       21.5        0.0        0.0
1340    23         0.00    4    18842.0        0.0   199238.0        0.0      704.0
1355    24         0.00    4    17849.0        0.0   190226.0        0.0        0.0
1400                       7                                                                32.273
1412    25         0.00    5    18881.0        0.0   201090.0        0.0      456.0
1427    26         0.00    5    18704.0        0.0   199646.0        0.0     1014.0
1430                       7                                                                32.269
1443    27         0.00    4    18827.0        0.0   200325.0        0.0        0.0
1458    28         0.00    4    19010.0        0.0   201829.0      392.0        0.0
1514    29         0.00    5    18499.0        0.0   202091.0        0.0      692.0
1515                       7                                                                32.253
1528    30         0.00    5    18548.0        0.0   201150.0        0.0     1048.0
```

```
1544   31      0.00    4   19296.0       0.0  201973.0      0.0      330.0
1558   32      0.00    4   19155.0       0.0  201170.0      0.0        0.0
1600                   7                                                     32.243
1614   33      0.00    5   18705.0       0.0  201465.0      0.0        0.0
1633                   7                                                     32.236
```

```
                              DATA TAKEN DURING RUN   5 ON 12 JUN 74



THE CALIBRATION GASES ARE KNOWN TO BE
                     IGAS         H2         CO        CH4        CO2        H2O
                        1      25.17      24.94      24.97      24.94       0.00
                        2     100.00       0.00       0.00       0.00       0.00
                        3       0.00       0.00       0.00     100.00       0.00

CALIBRATION GAS SAMPLES FOR THIS RUN WERE ANALYSED AS

TIME SAMP      DELP IGAS         H2         CO        CH4        CO2        H2O          C
   0    1      2.00    1      25.17      24.98      24.98      24.84       0.00
   0    2      1.00    1      25.13      24.93      24.97      24.95       0.00
   0    3      2.00    1      25.22      24.88      24.95      24.94       0.00
   0    4      0.00    1      25.15      24.88      24.96      24.99       0.00
   0    5      0.00    1      25.20      24.86      24.97      24.95       0.00
   0    8      0.00    2      99.68       0.00       0.21       0.00       0.10

THE RELATIVE CALIBRATION
AREA COEFFICENTS ARE      0.017704  0.882920  0.732259  1.000000  0.689999  0.026188

 ATMOSPHERIC PRESSURE WAS  759.45 .

 THE WEIGHT OF CATALYST INITIALLY CHARGED TO THE REACTOR IS  0.240 GRAMS.

 THE GROSS WEIGHT OF THE CATALYST CARRIER AND SUSPENSION MECHANISM IS  31.945 GRAMS.
```

```
                               DATA TAKEN DURING RUN   5 ON 12 JUN 74

TIME SAMP     DELP IGAS        H2         CO         CH4        CO2        H2O        C

 930 REACTOR TEMPERATURE 550. DEGREES CENTIGRADE

 930 CHANGED INLET GAS TO    100.00       0.00       0.00       0.00       0.00             TOTAL FLOW 19.8 CC/SEC (STP)
 915                                                                                  0.424 GRAMS CARBON DEPOSITED
 917    6     0.00    5       99.60       0.00       0.17       0.00       0.21
 932    7     0.00    5       99.61       0.00       0.27       0.00       0.11
 947    8     0.00    5       99.68       0.00       0.21       0.00       0.10
 945                                                                                  0.384 GRAMS CARBON DEPOSITED
1003    9     0.00    5       99.63       0.00       0.23       0.00       0.13
1017   10     0.00    5       99.66       0.00       0.20       0.00       0.12
1018                                                                                  0.334 GRAMS CARBON DEPOSITED

1020 CHANGED INLET GAS TO     24.61       0.00      75.38       0.00       0.00             TOTAL FLOW 19.9 CC/SEC (STP)
1032   11     0.00    5       24.57       0.00      75.42       0.00       0.00
1049                                                                                  0.341 GRAMS CARBON DEPOSITED
1049   12     0.00    5       24.47       0.00      75.46       0.00       0.06
1103   13     0.00    5       24.43       0.00      75.51       0.00       0.04
1118   14     0.00    5       24.53       0.00      75.38       0.00       0.07
1120                                                                                  0.334 GRAMS CARBON DEPOSITED
1140                                                                                  0.334 GRAMS CARBON DEPOSITED
1152   16     0.00    5       24.58       0.00      75.24       0.00       0.17
1207   17     0.00    5       24.48       0.00      75.43       0.00       0.07
1215                                                                                  0.334 GRAMS CARBON DEPOSITED

1219 CHANGED INLET GAS TO     59.91       0.00      40.08       0.00       0.00             TOTAL FLOW 19.6 CC/SEC (STP)
1222   18     0.00    5       58.90       0.00      40.97       0.00       0.11
1237   19     0.00    4       59.16       0.00      40.76       0.00       0.06
1253   20     0.00    4       59.19       0.00      40.80       0.00       0.00
1307                                                                                  0.334 GRAMS CARBON DEPOSITED
1310   21     0.00    5       59.06       0.00      40.89       0.00       0.04
1325   22     0.00    5       58.96       0.00      40.85       0.00       0.17
1326                                                                                  0.333 GRAMS CARBON DEPOSITED

1330 CHANGED INLET GAS TO     74.82       0.00      25.17       0.00       0.00             TOTAL FLOW 19.8 CC/SEC (STP)
1340   23     0.00    4       74.24       0.00      25.65       0.00       0.09
1355   24     0.00    4       74.39       0.00      25.60       0.00       0.00
1400                                                                                  0.327 GRAMS CARBON DEPOSITED
1412   25     0.00    5       74.12       0.00      25.81       0.00       0.06
1427   26     0.00    5       74.06       0.00      25.79       0.00       0.13
1430                                                                                  0.323 GRAMS CARBON DEPOSITED
1443   27     0.00    4       74.20       0.00      25.79       0.00       0.00
1458   28     0.00    4       74.17       0.00      25.78       0.03       0.00
1514   29     0.00    5       73.70       0.00      26.20       0.00       0.09
1515                                                                                  0.307 GRAMS CARBON DEPOSITED
1528   30     0.00    5       73.79       0.00      26.06       0.00       0.14
1544   31     0.00    4       74.37       0.00      25.57       0.00       0.04
1558   32     0.00    4       74.37       0.00      25.62       0.00       0.00
1600                                                                                  0.297 GRAMS CARBON DEPOSITED
1614   33     0.00    5       73.99       0.00      26.00       0.00       0.00
1630                                                                                  0.290 GRAMS CARBON DEPOSITED
```

```
                                    DATA TAKEN DURING RUN   6 ON 13 JUN 74

TIME SAMP          DELP IGAS          H2          CO        CH4         CO2         H2O          C

 835                       8       550.0

 835                       6        32.0         0.0        0.0         0.0         0.0
 835                       7                                                                 32.236
 900                       7                                                                 32.236

 903                       6         0.0        68.0        0.0         0.0         0.0
 910     1         0.00    4       382.0    974613.1        0.0       855.0       845.0
 926     2         0.00    4       405.0    983450.1        0.0        66.0         0.0
 930                       7                                                                 32.270
 942     3         0.00    5         0.0    937246.1        0.0      2805.0         0.0
 958     4         0.00    5       395.0    980186.1        0.0      4188.0         0.0
1002                       7                                                                 32.311
1006     5         0.00    4       387.0    973850.1        0.0        71.0         0.0
1021     6         0.00    4       419.0    984307.1        0.0       101.0         0.0
1028     7         0.00    5       378.0    955706.1        0.0      2677.0         0.0
1030                       7                                                                 32.350
1035     8         0.00    5       406.0    963240.1        0.0      2812.0         0.0
1043     9         0.00    5       393.0    954177.1        0.0      2612.0         0.0
1052    10         0.00    5       394.0    955937.1        0.0      2494.0         0.0
1058    11         0.00    5       394.0    955856.1        0.0      2411.0         0.0

1100                       6         0.0        51.7        0.0        15.0         0.0
1100                       7                                                                 32.391
1109    12         0.00    4       289.0    722139.1        0.0    285183.0       857.0
[illegible]    13         0.00    4       280.0    710160.1        0.0    286246.0         0.0
1130                       7                                                                 32.411
1140    14         0.00    5       289.0    706298.1        0.0    291324.0         0.0
1153    15         0.00    5       274.0    700422.1        0.0    289178.0         0.0
1200                       7                                                                 32.469
1203    16         0.00    4       283.0    717305.1        0.0    289859.0         0.0
1211    17         0.00    4       274.0    706375.1        0.0    286901.0         0.0
1218    18         0.00    5       288.0    708701.1        0.0    292644.0         0.0
1227    19         0.00    5       279.0    701556.1        0.0    289581.0         0.0
1239    20         0.00    4       273.0    695472.1        0.0    282180.0         0.0
1249    21         0.00    4       262.0    705345.1        0.0    288039.0         0.0
1258    22         0.00    5       284.0    712596.1        0.0    295655.0         0.0
1300                       7                                                                 32.540
1312    23         0.00    5       274.0    703637.1        0.0    291660.0         0.0
1320    24         0.00    5         0.0    704279.1        0.0    291405.0         0.0
1328    25         0.00    5       277.0    699038.1        0.0    288054.0         0.0
1330                       7                                                                 32.573
1336    26         0.00    4       291.0    712426.1        0.0    290057.0         0.0
1346    27         0.00    4       277.0    720611.1        0.0    290280.0         0.0
1354    28         0.00    5       276.0    713670.1        0.0    291 41.0         0.0

1400                       6         0.0         0.0        0.0        45.0         0.0
1400                       7                                                                 32.595
1406    29         0.00    5         0.0      6849.0        0.0 1054218.2      1022.0
1418    30         0.00    4         0.0        82.0        0.0 1100446.2         0.0
1430                       7                                                                 32.600
```

```
1434   31      0.00    4       0.0       0.0       0.0 1087599.2       0.0
1443   32      0.00    5       0.0       0.0       0.0 1091062.2     401.0
1458   33      0.00    5       0.0       0.0       0.0 1078357.2       0.0
1500                   7                                                       32.604
1514   34      0.00    4       0.0       0.0       0.0 1097515.2       0.0
1523   35      0.00    4       0.0       0.0       0.0 1094995.2       0.0
1530                   7                                                       32.600
1532   36      0.00    5       0.0       0.0       0.0 1097144.2       0.0
1542   37      0.00    5       0.0       0.0       0.0 1062718.2       0.0
1553   38      0.00    4       0.0       0.0       0.0 1086840.2       0.0
1600                   7                                                       32.606
1603   39      0.00    5       0.0       0.0       0.0 1085348.2     285.0
   0   40     -3.00    1    4884.0  237745.0  198015.0  267485.0       0.0
   0   41      4.00    1    4888.0  239827.0  199226.0  272012.0       0.0
   0   42      3.00    1    4932.0  241894.0  201178.0  274180.0       0.0
   0   43      8.00    1    4810.0  238956.0  198493.0  271325.0       0.0
   0   44     -2.00    1    4841.0  239653.0  198856.0  271339.0       0.0
   0   45      1.00    1    4756.0  236681.0  196514.0  268513.0       0.0
 947    7      1.00    2   27422.0       0.0       0.0     248.0     487.0
```

```
                         DATA TAKEN DURING RUN   6 ON 13 JUN 74


THE CALIBRATION GASES ARE KNOWN TO BE
                        IGAS          H2         CO        CH4        CO2        H2O
                           1       25.17      24.94      24.97      24.94       0.00
                           2      100.00       0.00       0.00       0.00       0.00
                           3        0.00       0.00       0.00     100.00       0.00

CALIBRATION GAS SAMPLES FOR THIS RUN WERE ANALYSED AS

TIME SAMP       DELP IGAS         H2         CO        CH4        CO2        H2O          C
   0   40      -3.00    1      25.39      24.87      24.99      24.74       0.00
   0   41       4.00    1      25.23      24.88      24.93      24.94       0.00
   0   42       3.00    1      25.20      24.88      24.96      24.93       0.00
   0   43       8.00    1      25.08      24.92      24.97      25.02       0.00
   0   44      -2.00    1      25.09      24.95      24.97      24.97       0.00
   0   45       1.00    1      25.06      24.94      24.97      25.01       0.00
 947    7       1.00    2      99.91       0.00       0.00       0.02       0.06

THE RELATIVE CALIBRATION
AREA COEFFICENTS ARE       0.017745   0.884079   0.732905   1.000000   0.689999   0.025281

 ATMOSPHERIC PRESSURE WAS  763.52 .

 THE WEIGHT OF CATALYST INITIALLY CHARGED TO THE REACTOR IS  0.240 GRAMS.

 THE GROSS WEIGHT OF THE CATALYST CARRIER AND SUSPENSION MECHANISM IS  31.945 GRAMS.
```

```
                                         DATA TAKEN DURING RUN   6 ON 13 JUN 74

TIME SAMP      DELP IGAS        H2          CO         CH4         CO2         H2O         C

 935 REACTOR TEMPERATURE 550. DEGREES CENTIGRADE


 935 CHANGED INLET GAS TO   100.00        0.00        0.00        0.00        0.00            TOTAL FLOW 19.8 CC/SEC (STP)
 935                                                                                    0.290 GRAMS CARBON DEPOSITED
 900                                                                                    0.290 GRAMS CARBON DEPOSITED

 903 CHANGED INLET GAS TO     0.00      100.00        0.00        0.00        0.00            TOTAL FLOW 19.8 CC/SEC (STP)
 910    1      0.00    4      3.16       96.64        0.00        0.07        0.10
 926    2      0.00    4      3.29       96.70        0.00        0.00        0.00
 930                                                                                    0.324 GRAMS CARBON DEPOSITED
 942    3      0.00    5      0.00       99.73        0.00        0.26        0.00
 958    4      0.00    5      3.22       96.40        0.00        0.36        0.00
1002                                                                                    0.365 GRAMS CARBON DEPOSITED
1006    5      0.00    4      3.20       96.78        0.00        0.00        0.00
1021    6      0.00    4      3.37       96.61        0.00        0.00        0.00
1028    7      0.00    5      3.20       96.55        0.00        0.23        0.00
1030                                                                                    0.404 GRAMS CARBON DEPOSITED
1035    8      0.00    5      3.35       96.39        0.00        0.24        0.00
1043    9      0.00    5      3.30       96.46        0.00        0.23        0.00
1052   10      0.00    5      3.30       96.47        0.00        0.22        0.00
1059   11      0.00    5      3.30       96.47        0.00        0.21        0.00

1100 CHANGED INLET GAS TO     0.00       75.11        0.00       24.88        0.00            TOTAL FLOW 20.0 CC/SEC (STP)
1100                                                                                    0.445 GRAMS CARBON DEPOSITED
1109   12      0.00    4      2.55       72.14        0.00       25.18        0.10
1124   13      0.00    4      2.52       71.86        0.00       25.60        0.00
1130                                                                                    0.465 GRAMS CARBON DEPOSITED
1140   14      0.00    5      2.58       71.38        0.00       26.02        0.00
1153   15      0.00    5      2.50       71.42        0.00       26.07        0.00
1200                                                                                    0.523 GRAMS CARBON DEPOSITED
1203   16      0.00    4      2.52       71.82        0.00       25.65        0.00
1211   17      0.00    4      2.49       71.74        0.00       25.76        0.00
1219   18      0.00    5      2.57       71.37        0.00       26.05        0.00
1227   19      0.00    5      2.53       71.40        0.00       26.05        0.00
1239   20      0.00    4      2.52       71.74        0.00       25.73        0.00
1249   21      0.00    4      2.40       71.70        0.00       25.88        0.00
1259   22      0.00    5      2.52       71.31        0.00       26.15        0.00
1300                                                                                    0.594 GRAMS CARBON DEPOSITED
1312   23      0.00    5      2.48       71.36        0.00       26.15        0.00
1320   24      0.00    5      0.00       73.21        0.00       26.78        0.00
1328   25      0.00    5      2.52       71.44        0.00       26.02        0.00
1330                                                                                    0.627 GRAMS CARBON DEPOSITED
1336   26      0.00    4      2.58       71.62        0.00       25.78        0.00
1346   27      0.00    4      2.47       71.91        0.00       25.61        0.00
1354   28      0.00    5      2.47       71.64        0.00       25.87        0.00

1400 CHANGED INLET GAS TO     0.00        0.00        0.00      100.00        0.00            TOTAL FLOW 15.0 CC/SEC (STP)
1400                                                                                    0.649 GRAMS CARBON DEPOSITED
1406   29      0.00    5      0.00        0.72        0.00       99.13        0.13
1419   30      0.00    4      0.00        0.00        0.00       99.99        0.00
```

```
1430                                                                          0.654 GRAMS CARBON DEPOSITED
1434   31     0.00    4     0.00      0.00      0.00    100.00      0.00
1443   32     0.00    5     0.00      0.00      0.00     99.94      0.05
1458   33     0.00    5     0.00      0.00      0.00    100.00      0.00
1500                                                                          0.658 GRAMS CARBON DEPOSITED
1514   34     0.00    4     0.00      0.00      0.00    100.00      0.00
1523   35     0.00    4     0.00      0.00      0.00    100.00      0.00
1530                                                                          0.654 GRAMS CARBON DEPOSITED
1532   36     0.00    5     0.00      0.00      0.00    100.00      0.00
1542   37     0.00    5     0.00      0.00      0.00    100.00      0.00
1553   38     0.00    4     0.00      0.00      0.00    100.00      0.00
1600                                                                          0.660 GRAMS CARBON DEPOSITED
1603   39     0.00    5     0.00      0.00      0.00     99.96      0.03
```

```
                              DATA TAKEN DURING RUN   7 ON 14 JUN 74

TIME SAMP    DELP IGAS         H2         CO        CH4        CO2        H2O          C

 845                    8      550.0

 845                    6        0.0        0.0        0.0       45.0        0.0
 845                    7                                                                32.617
 854    1   -1.00    1     4820.0   249046.0   204938.0   269858.0        0.0
 904    2   -2.00    1     4815.0   246081.0   203740.0   268493.0        0.0
 910                    7                                                                32.627
 915                    7                                                                32.624

 915                    6        0.0       34.5        0.0       30.0        0.0
 918    4   -2.00    1     4779.0   243889.0   201315.0   267798.0        0.0
 928    5    1.00    4      178.0   456627.0        0.0   542324.1        0.0
 945    6   -1.00    4      189.0   473690.0        0.0   552230.1        0.0
 948                    7                                                                32.627
1010    8    0.00    5      183.0   471695.0        0.0   547792.1        0.0
1015                    7                                                                32.627
1024    9   -1.00    4      195.0   479901.0        0.0   556699.1        0.0
1035   10   -1.00    4      174.0   469290.0        0.0   534096.1        0.0
1045   11    0.00    5      188.0   476775.0        0.0   549153.1        0.0
1045                    7                                                                32.627

1045                    6        0.0       38.0        0.0       27.0        0.0
1054   12    0.00    5      204.0   509353.0        0.0   482986.0        0.0
1104   13    1.00    4      213.0   531843.1        0.0   503455.0        0.0
1107                    7                                                                32.627
1112   14    1.00    4      203.0   527177.1        0.0   498352.0        0.0
1120   15    0.00    5      206.0   526630.1        0.0   499576.0        0.0
1129   16    0.00    5      203.0   520282.0        0.0   493628.0        0.0
1130                    7                                                                32.610
1137   17    1.00    4      218.0   532848.1        0.0   504809.0        0.0
1147   18    0.00    4      200.0   526716.1        0.0   497416.0        0.0
1150                    7                                                                32.620
1157   19    0.00    5      216.0   530468.1        0.0   502396.0        0.0
1200                    7                                                                32.617

1203                    6        0.0       41.4        0.0       24.2        0.0
1207   20   -1.00    5      208.0   547915.1        0.0   457951.0        0.0
1215   21    1.00    4      222.0   575905.1        0.0   454982.0        0.0
1224   22    1.00    4      205.0   564665.1        0.0   445254.0        0.0
1230                    7                                                                32.625
1235   23   -1.00    5      253.0   569538.1        0.0   450381.0        0.0
1254   24    0.00    5      222.0   563713.1        0.0   445914.0        0.0
1254   25    0.00    4      235.0   575864.1        0.0   454529.0        0.0
1300                    7                                                                32.617
1304   26    0.00    4      213.0   569973.1        0.0   448496.0        0.0

1305                    6        0.0       47.9        0.0       17.8        0.0
1311   27    0.00    5      270.0   660815.1        0.0   342300.0        0.0
1319   28   -1.00    5      249.0   659180.1        0.0   341058.0        0.0
1325   29    0.00    4      264.0   674456.1        0.0   346845.0        0.0
1330                    7                                                                32.623
```

```
1335   30     0.00   4     249.0  661673.1       0.0  339622.0       0.0
1344   31     0.00   5     272.0  662192.1       0.0  340615.0       0.0
1353   32    -1.00   5     267.0  649887.1       0.0  335637.0       0.0
1355                 7                                                     32.642
1404   33     2.00   4     255.0  646960.1       0.0  330919.0       0.0
1411   34     0.00   4     245.0  654428.1       0.0  333958.0       0.0
1419   35     0.00   5     250.0  660985.1       0.0  342688.0       0.0
1420                 7                                                     32.665
1427   36     0.00   5     266.0  646490.1       0.0  334739.0       0.0
1439   37     0.00   4     255.0  671445.1       0.0  343845.0       0.0
1440                 7                                                     32.686
1449   38     0.00   4     242.0  665400.1       0.0  341414.0       0.0
1456   39     0.00   5     252.0  659224.1       0.0  342136.0       0.0
1500                 7                                                     32.700
1506   40     0.00   5     244.0  623433.1       0.0  321929.0       0.0
1515   41     2.00   4     266.0  663594.1       0.0  338915.0       0.0
1524   42     0.00   4     245.0  656850.1       0.0  336057.0       0.0
1530                 7                                                     32.740
1533   43     3.00   1    4983.0  239637.0  199141.0  271586.0       0.0
1541   44     0.00   1    4764.0  235777.0  195842.0  267692.0       0.0
1549   45     0.00   1    4885.0  239745.0  199460.0  272555.0       0.0
1552   46     4.00   1    4840.0  238364.0  198026.0  270478.0       0.0
 947    7     1.00   2   27422.0       0.0       0.0     248.0     487.0
```

```
                              DATA TAKEN DURING RUN   7 ON 14 JUN 74



THE CALIBRATION GASES ARE KNOWN TO BE
                         IGAS         H2         CO        CH4        CO2         H2O
                            1      25.17      24.94      24.97      24.94        0.00
                            2     100.00       0.00       0.00       0.00        0.00
                            3       0.00       0.00       0.00     100.00        0.00

CALIBRATION GAS SAMPLES FOR THIS RUN WERE ANALYSED AS

TIME SAMP      DELP IGAS         H2         CO        CH4        CO2        H2O          C
 854    1     -1.00    1      24.82      25.33      25.21      24.62       0.00
 904    2     -2.00    1      24.94      25.17      25.21      24.65       0.00
 918    4     -2.00    1      24.98      25.14      25.10      24.77       0.00
1533   43      3.00    1      25.42      24.67      24.80      25.09       0.00
1541   44      0.00    1      25.33      24.69      24.81      25.15       0.00
1549   45      0.00    1      25.37      24.65      24.81      25.15       0.00
1552   46      4.00    1      25.38      24.67      24.80      25.13       0.00
 947    7      1.00    2      99.91       0.00       0.00       0.02       0.06

THE RELATIVE CALIBRATION
AREA COEFFICENTS ARE      0.017720  0.897369  0.741782  1.000000  0.689999  0.025326

 ATMOSPHERIC PRESSURE WAS  765.80 .

 THE WEIGHT OF CATALYST INITIALLY CHARGED TO THE REACTOR IS  0.240 GRAMS.

 THE GROSS WEIGHT OF THE CATALYST CARRIER AND SUSPENSION MECHANISM IS  31.945 GRAMS.
```

```
                              DATA TAKEN DURING RUN   7 ON 14 JUN 74

TIME SAMP     DELP IGAS        H2         CO        CH4        CO2        H2O           C

 845 REACTOR TEMPERATURE 550. DEGREES CENTIGRADE


 845 CHANGED INLET GAS TO     0.00       0.00       0.00     100.00       0.00           TOTAL FLOW 15.0 CC/SEC (STP)
 845                                                                               0.671 GRAMS CARBON DEPOSITED
 910                                                                               0.681 GRAMS CARBON DEPOSITED
 915                                                                               0.678 GRAMS CARBON DEPOSITED

 915 CHANGED INLET GAS TO     0.00      50.18       0.00      49.81       0.00           TOTAL FLOW 20.0 CC/SEC (STP)
 929    5      1.00    4      1.84      47.51       0.00      50.63       0.00
 945    6     -1.00    4      1.88      47.95       0.00      50.16       0.00
 949                                                                               0.681 GRAMS CARBON DEPOSITED
1010    8      0.00    5      1.85      48.06       0.00      50.08       0.00
1015                                                                               0.681 GRAMS CARBON DEPOSITED
1024    9     -1.00    4      1.91      48.05       0.00      50.02       0.00
1035   10     -1.00    4      1.80      48.57       0.00      49.61       0.00
1045   11      0.00    5      1.87      48.25       0.00      49.87       0.00
1045                                                                               0.681 GRAMS CARBON DEPOSITED

1048 CHANGED INLET GAS TO     0.00      55.21       0.00      44.78       0.00           TOTAL FLOW 20.0 CC/SEC (STP)
1054   12      0.00    5      2.05      52.91       0.00      45.02       0.00
1104   13      1.00    4      2.04      52.96       0.00      44.99       0.00
1107                                                                               0.681 GRAMS CARBON DEPOSITED
1112   14      1.00    4      1.98      53.02       0.00      44.98       0.00
1120   15      0.00    5      2.00      52.93       0.00      45.06       0.00
1129   16      0.00    5      2.00      52.92       0.00      45.06       0.00
1130                                                                               0.664 GRAMS CARBON DEPOSITED
1137   17      1.00    4      2.07      52.92       0.00      44.99       0.00
1147   18      0.00    4      1.96      53.06       0.00      44.97       0.00
1150                                                                               0.674 GRAMS CARBON DEPOSITED
1157   19      0.00    5      2.06      52.93       0.00      44.99       0.00
1200                                                                               0.671 GRAMS CARBON DEPOSITED

1203 CHANGED INLET GAS TO     0.00      59.97       0.00      40.02       0.00           TOTAL FLOW 20.1 CC/SEC (STP)
1207   20     -1.00    5      2.05      55.96       0.00      41.97       0.00
1215   21      1.00    4      2.10      57.28       0.00      40.61       0.00
1224   22      1.00    4      2.02      57.37       0.00      40.60       0.00
1230                                                                               0.680 GRAMS CARBON DEPOSITED
1235   23     -1.00    5      2.35      57.11       0.00      40.52       0.00
1254   24      0.00    5      2.15      57.22       0.00      40.62       0.00
1254   25      0.00    4      2.20      57.24       0.00      40.54       0.00
1300                                                                               0.671 GRAMS CARBON DEPOSITED
1304   26      0.00    4      2.06      57.40       0.00      40.53       0.00

1305 CHANGED INLET GAS TO     0.00      70.21       0.00      29.78       0.00           TOTAL FLOW 19.9 CC/SEC (STP)
1311   27      0.00    5      2.49      66.56       0.00      30.94       0.00
1319   28     -1.00    5      2.34      66.68       0.00      30.96       0.00
1325   29      0.00    4      2.40      66.77       0.00      30.81       0.00
1330                                                                               0.677 GRAMS CARBON DEPOSITED
1335   30      0.00    4      2.34      66.85       0.00      30.79       0.00
1344   31      0.00    5      2.50      66.70       0.00      30.78       0.00
```

```
1353   32    -1.00   5    2.51   66.61    0.00   30.87    0.00
1355                                                            0.696 GRAMS CARBON DEPOSITED
1404   33     2.00   4    2.44   66.86    0.00   30.69    0.00
1411   34     0.00   4    2.34   66.98    0.00   30.67    0.00
1419   35     0.00   5    2.34   66.64    0.00   31.00    0.00
1420                                                            0.719 GRAMS CARBON DEPOSITED
1427   36     0.00   5    2.51   66.55    0.00   30.92    0.00
1439   37     0.00   4    2.35   66.90    0.00   30.74    0.00
1440                                                            0.740 GRAMS CARBON DEPOSITED
1449   38     0.00   4    2.28   66.91    0.00   30.80    0.00
1456   39     0.00   5    2.36   66.61    0.00   31.02    0.00
1500                                                            0.754 GRAMS CARBON DEPOSITED
1506   40     0.00   5    2.44   66.66    0.00   30.89    0.00
1515   41     2.00   4    2.46   66.88    0.00   30.65    0.00
1524   42     0.00   4    2.33   66.93    0.00   30.73    0.00
1530                                                            0.794 GRAMS CARBON DEPOSITED
```

```
                              DATA TAKEN DURING RUN:   9 ON 20 JUN 74

TIME SAMP        DELP IGAS        H2        CO       CH4       CO2         H2O          C
1026    1       -1.00    1    4535.0  226267.0  187228.0  253939.0         0.0
1035    2        2.00    1    4701.0  232955.0  193083.0  263345.0         0.0
1043    3       -1.00    1    4580.0  225998.0  187713.0  255123.0         0.0
1051    4        2.00    1    4667.0  228888.0  190506.0  259614.0         0.0
1106    6        3.00    1    4708.0  229698.0  190941.0  260380.0         0.0
1111    7       -1.00    1    4582.0  225401.0  187443.0  255758.0         0.0
1120    8        2.00    1    4685.0  229515.0  191060.0  260853.0         0.0
1126    9        0.00    2   26993.0       0.0       0.0       0.0       353.0
1142   10        0.00    2   27431.0       0.0       0.0       0.0         0.0

1030                     8     550.0

1030                     6      32.0       0.0       0.0       0.0         0.0
1030                     7                                                          32.083
1120                     7                                                          32.116
1126    9        0.00    4   26993.0       0.0       0.0       0.0       353.0
1142   10        0.00    4   27431.0       0.0       0.0       0.0         0.0
1142                     7                                                          32.107
1157   11        0.00    5   26392.0       0.0       0.0       0.0       594.0
1200                     7                                                          32.100

1200                     6      16.0      34.0       0.0       0.0         0.0
1211   12        0.00    5   10597.0  465801.0       0.0       0.0      4030.0
1226   13        0.00    5   10591.0  463770.0       0.0     387.0      6167.0
1242   14        0.00    4   11066.0  473886.0       0.0      17.0         0.0
1257   15        0.00    4   10957.0  467510.0       0.0      38.0         0.0
1300                     7                                                          32.215
1304   16        0.00    5   10946.0  471417.0       0.0     534.0      5193.0
1319   17        0.00    4   10931.0  470129.0       0.0      39.0         0.0
1324   18        0.00    5   10547.0  467966.0       0.0     630.0      6861.0
1330                     7                                                          32.295
1341   19        0.00    5   10552.0  466170.0       0.0     662.0     10409.0
1359   20        0.00    4   10947.0  474512.0       0.0      28.0         0.0
1400                     7                                                          32.413
```

```
                        DATA TAKEN DURING RUN    9 ON 20 JUN 74



THE CALIBRATION GASES ARE KNOWN TO BE
                        IGAS        H2         CO        CH4        CO2        H2O
                           1     25.17      24.94      24.97      24.94       0.00
                           2    100.00       0.00       0.00       0.00       0.00
                           3      0.00       0.00       0.00     100.00       0.00

CALIBRATION GAS SAMPLES FOR THIS RUN WERE ANALYSED AS

TIME SAMP        DELP IGAS         H2         CO        CH4        CO2        H2O          C
1026    1       -1.00    1      25.09      25.03      25.00      24.86       0.00
1035    2        2.00    1      25.03      24.98      24.99      24.99       0.00
1043    3       -1.00    1      25.20      24.92      24.98      24.89       0.00
1051    4        2.00    1      25.21      24.86      24.97      24.95       0.00
1106    6        3.00    1      25.29      24.85      24.93      24.92       0.00
1111    7       -1.00    1      25.21      24.86      24.95      24.96       0.00
1120    8        2.00    1      25.20      24.84      24.96      24.98       0.00
1126    9        0.00    2      99.95       0.00       0.00       0.00       0.04
1142   10        0.00    2     100.00       0.00       0.00       0.00       0.00

THE RELATIVE CALIBRATION
AREA COEFFICENTS ARE       0.017771   0.884822   0.733208   1.000000   0.689999   0.026242

 ATMOSPHERIC PRESSURE WAS  759.45 .

 THE WEIGHT OF CATALYST INITIALLY CHARGED TO THE REACTOR IS  0.250 GRAMS.

 THE GROSS WEIGHT OF THE CATALYST CARRIER AND SUSPENSION MECHANISM IS  32.083 GRAMS.
```

```
                                     DATA TAKEN DURING RUN   9 ON 20 JUN 74

TIME SAMP      DELP IGAS        H2         CO         CH4        CO2        H2O         C

1030 REACTOR TEMPERATURE 550. DEGREES CENTIGRADE


1030 CHANGED INLET GAS TO    100.00       0.00       0.00       0.00       0.00         TOTAL FLOW 19.8 CC/SEC (STP)
1030                                                                                0.000 GRAMS CARBON DEPOSITED
1120                                                                                0.033 GRAMS CARBON DEPOSITED
1126    9        0.00    4    99.95       0.00       0.00       0.00       0.04
1142   10        0.00    4   100.00       0.00       0.00       0.00       0.00
1142                                                                                0.024 GRAMS CARBON DEPOSITED
1157   11        0.00    5    99.91       0.00       0.00       0.00       0.08
1200                                                                                0.017 GRAMS CARBON DEPOSITED

1200 CHANGED INLET GAS TO     49.98      50.01       0.00       0.00       0.00         TOTAL FLOW 19.8 CC/SEC (STP)
1211   12        0.00    5    48.28      51.15       0.00       0.00       0.56
1226   13        0.00    5    48.21      50.88       0.00       0.03       0.86
1242   14        0.00    4    48.96      51.02       0.00       0.00       0.00
1257   15        0.00    4    48.93      51.06       0.00       0.00       0.00
1300                                                                                0.132 GRAMS CARBON DEPOSITED
1304   16        0.00    5    48.33      50.89       0.00       0.05       0.71
1319   17        0.00    4    48.92      51.06       0.00       0.00       0.00
1324   18        0.00    5    47.85      51.12       0.00       0.06       0.96
1330                                                                                0.[illegible]12 GRAMS CARBON DEPOSITED
1341   19        0.00    5    47.71      50.76       0.00       0.06       1.45
1359   20        0.00    4    48.54      51.45       0.00       0.00       0.00
1400                                                                                0.330 GRAMS CARBON DEPOSITED
```

```
                              DATA TAKEN DURING RUN  10 ON 21 JUN 74

TIME  SAMP      DELP IGAS         H2        CO       CH4       CO2       H2O          C
1043     1      1.00    1     4501.0  230127.0  188565.0  251333.0       0.0
1051     2      1.00    1     4666.0  235717.0  194611.0  260414.0       0.0
1102     3      2.00    1     4746.0  232163.0  192952.0  263436.0       0.0
1124     5      3.00    1     4795.0  233736.0  194473.0  265298.0       0.0
1131     6      2.00    1     4704.0  230658.0  192117.0  262505.0       0.0
1139     7      2.00    1     4761.0  232259.0  193346.0  264174.0       0.0
1147     8      1.00    1     4739.0  230873.0  192031.0  263012.0       0.0

1045                    8      550.0

1045                    6       32.0       0.0       0.0       0.0       0.0
1045                    7                                                        32.014
1115                    7                                                        32.032
1130                    7                                                        32.020
1145                    7                                                        32.039
1154     9      0.00    4    26958.0       0.0       0.0     180.0     674.0
1200                    7                                                        32.039
1209    10      0.00    4    27775.0       0.0       0.0      67.0      32.0
1232                    7                                                        32.028
1235    12      0.00    5    27445.0       0.0       0.0      44.0    1121.0
1250    13      0.00    5    27889.0       0.0       0.0      66.0       0.0
1303                    7                                                        32.024
1307    14      0.00    4    27169.0       0.0       0.0       0.0       0.0
1319    15      0.00    4    27962.0       0.0       0.0       0.0       0.0
1330                    7                                                        32.024

1330                    6       16.0      34.0       0.0       0.0       0.0
1334    16      0.00    4    10786.0  471958.0       0.0     608.0    5253.0
1352    17      0.00    5    10838.0  477037.0       0.0     798.0    7863.0
1400                    7                                                        32.109
1408    18      0.00    4    11054.0  477554.0       0.0      20.0       0.0
1413    19      0.00    4    11173.0  481472.0       0.0      41.0       0.0
1419    20      0.00    5    10735.0  474027.0       0.0     862.0   12276.0
1429                    7                                                        32.227
1435    21      0.00    5    10811.0  476958.0       0.0    1035.0    9615.0
1453    22      0.00    5    10695.0  471332.0       0.0    1409.0   17004.0
1501                    7                                                        32.393

1501                    6       16.0       0.0       0.0      30.0       0.0
1509    23      0.00    4    10693.0     212.0       0.0  547021.1     971.0
1515                    7                                                        32.388
1524    24      0.00    4    10440.0       0.0       0.0  546223.1    1037.0
1530                    7                                                        32.393
1534    25      0.00    5     9025.0   49645.0       0.0  500609.0   50543.0
1551    26      0.00    5     8831.0   52760.0       0.0  494642.0   80758.0
1600                    7                                                        32.399
1630                    7                                                        32.399
1633    28      0.00    5     8662.0   55689.0       0.0  487918.0   84457.0
1653    29      0.00    5     8614.0   59598.0       0.0  485159.0   61788.0
1707                    7                                                        32.403
1711    30      0.00    5     8558.0   57645.0       0.0  484835.0   83793.0
1307    14      0.00    2    27169.0       0.0       0.0       0.0       0.0
```

```
1319    15       0.00    2   27962.0       0.0       0.0       0.0       0.0
```

```
                         DATA TAKEN DURING RUN  10 ON 21 JUN 74



THE CALIBRATION GASES ARE KNOWN TO BE
                    IGAS          H2          CO         CH4         CO2         H2O
                       1       25.17       24.94       24.97       24.94        0.00
                       2      100.00        0.00        0.00        0.00        0.00
                       3        0.00        0.00        0.00      100.00        0.00

CALIBRATION GAS SAMPLES FOR THIS RUN WERE ANALYSED AS

TIME SAMP      DELP IGAS         H2          CO         CH4         CO2         H2O          C
1043    1      1.00    1      24.97       25.33       25.09       24.60        0.00
1051    2      1.00    1      24.92       25.18       25.13       24.74        0.00
1102    3      2.00    1      25.26       24.80       24.91       25.02        0.00
1124    5      3.00    1      25.28       24.78       24.92       25.01        0.00
1131    6      2.00    1      25.22       24.77       24.93       25.06        0.00
1139    7      2.00    1      25.27       24.76       24.91       25.04        0.00
1147    8      1.00    1      25.30       24.74       24.87       25.06        0.00
1307   14      0.00    2     100.00        0.00        0.00        0.00        0.00
1319   15      0.00    2     100.00        0.00        0.00        0.00        0.00

THE RELATIVE CALIBRATION
AREA COEFFICENTS ARE      0.017811    0.889263    0.735713    1.000000    0.689999    0.026354

 ATMOSPHERIC PRESSURE WAS  759.45 .

 THE WEIGHT OF CATALYST INITIALLY CHARGED TO THE REACTOR IS  0.252 GRAMS.

 THE GROSS WEIGHT OF THE CATALYST CARRIER AND SUSPENSION MECHANISM IS  32.014 GRAMS.
```

```
                                   DATA TAKEN DURING RUN  10 ON 21 JUN 74

TIME SAMP       DELP IGAS         H2         CO         CH4         CO2         H2O          C

1045 REACTOR TEMPERATURE 550. DEGREES CENTIGRADE


1045 CHANGED INLET GAS TO   100.00       0.00       0.00        0.00        0.00             TOTAL FLOW 19.8 CC/SEC (STP)
1045                                                                                   0.000 GRAMS CARBON DEPOSITED
1115                                                                                   0.017 GRAMS CARBON DEPOSITED
1130                                                                                   0.005 GRAMS CARBON DEPOSITED
1145                                                                                   0.024 GRAMS CARBON DEPOSITED
1154     9      0.00    4      99.88       0.00       0.00        0.01        0.09
1200                                                                                   0.024 GRAMS CARBON DEPOSITED
1209    10      0.00    4      99.98       0.00       0.00        0.00        0.00
1232                                                                                   0.013 GRAMS CARBON DEPOSITED
1235    12      0.00    5      99.84       0.00       0.00        0.00        0.15
1250    13      0.00    5      99.99       0.00       0.00        0.00        0.00
1303                                                                                   0.009 GRAMS CARBON DEPOSITED
1307    14      0.00    4     100.00       0.00       0.00        0.00        0.00
1319    15      0.00    4     100.00       0.00       0.00        0.00        0.00
1330                                                                                   0.009 GRAMS CARBON DEPOSITED

1330 CHANGED INLET GAS TO    49.98      50.01       0.00        0.00        0.00             TOTAL FLOW 19.8 CC/SEC (STP)
1334    16      0.00    4      48.30      50.90       0.00        0.05        0.73
1352    17      0.00    5      47.95      50.88       0.00        0.07        1.08
1400                                                                                   0.094 GRAMS CARBON DEPOSITED
1409    18      0.00    4      49.87      51.12       0.00        0.00        0.00
1413    19      0.00    4      48.87      51.11       0.00        0.00        0.00
1419    20      0.00    5      47.63      50.59       0.00        0.08        1.68
1429                                                                                   0.212 GRAMS CARBON DEPOSITED
1435    21      0.00    5      47.78      50.79       0.00        0.09        1.31
1453    22      0.00    5      47.36      50.17       0.00        0.13        2.33
1501                                                                                   0.378 GRAMS CARBON DEPOSITED

1501 CHANGED INLET GAS TO    49.80       0.00       0.00       50.19        0.00             TOTAL FLOW 19.9 CC/SEC (STP)
1509    23      0.00    4      47.69       0.02       0.00       52.14        0.13
1515                                                                                   0.373 GRAMS CARBON DEPOSITED
1524    24      0.00    4      47.27       0.00       0.00       52.58        0.14
1530                                                                                   0.378 GRAMS CARBON DEPOSITED
1539    25      0.00    5      41.04       5.22       0.00       46.86        6.85
1551    26      0.00    5      39.11       5.38       0.00       44.88       10.62
1600                                                                                   0.384 GRAMS CARBON DEPOSITED
1630                                                                                   0.384 GRAMS CARBON DEPOSITED
1633    28      0.00    5      38.68       5.70       0.00       44.45       11.15
1653    29      0.00    5      39.71       6.29       0.00       45.57        8.41
1707                                                                                   0.388 GRAMS CARBON DEPOSITED
1711    30      0.00    5      38.52       5.93       0.00       44.40       11.12
```

```
                                   DATA TAKEN DURING RUN  11 ON 24 JUN 74

TIME SAMP       DELP IGAS        H2         CO        CH4        CO2        H2O          C
 902    1       0.00    1    4434.0   221765.0   184487.0   251644.0        0.0
 909    2       1.00    1    4542.0   226785.0   189010.0   258834.0        0.0
 906    3      -1.00    1    4453.0   221810.0   184964.0   252801.0        0.0
 925    4       0.00    1    4525.0   225733.0   188273.0   257836.0        0.0
 943    6      -4.00    1    4481.0   224806.0   187357.0   256402.0        0.0
 950    7       1.00    1    4479.0   222362.0   185579.0   253730.0        0.0
 958    8       0.00    1    4544.0   226368.0   188890.0   258372.0        0.0

1145                    8     550.0

1145                    6      32.0        0.0        0.0        0.0        0.0
1200                    7                                                          32.414
1235                    7                                                          32.396
1243   17       0.00    4   25862.0        0.0        0.0        0.0     1656.0
1300   18       0.00    4   26509.0        0.0        0.0      431.0        0.0
1305                    7                                                          32.382
1313   19       0.00    5   25772.0        0.0      665.0      407.0     1243.0
1330                    7                                                          32.363
1330   20       0.00    5   26289.0        0.0      578.0        0.0      820.0

1333                    6      16.0        0.0        0.0       30.0        0.0
1348                    7                                                          32.357
1359   22       0.00    4    9807.0        0.0        0.0   524843.1      894.0
1400                    7                                                          32.362
1414   23       0.00    5    8613.0    41115.0       42.0   488286.0    46327.0
1433   24      -4.00    5    8425.0    42181.0      834.0   480058.0    47153.0
1440                    7                                                          32.355
1453   25      -2.00    5    8598.0    43747.0        0.0   497326.0    42931.0
1504                    7                                                          32.355
1525   27       0.00    4    9758.0        0.0        0.0   529119.1        0.0
1525                    7                                                          32.355
1525                    7                                                          32.355
1543   28       0.00    4    9441.0        0.0        0.0   516638.0        0.0
1558   29      -1.00    5    8265.0    49676.0      316.0   479720.0    48937.0
1616   30      -1.00    5    8021.0    50714.0      562.0   465490.0    55330.0
1635                    7                                                          32.355
1300   18       0.00    2   26509.0        0.0        0.0      431.0        0.0
```

```
                              DATA TAKEN DURING RUN  11 ON 24 JUN 74


THE CALIBRATION GASES ARE KNOWN TO BE
                         IGAS        H2         CO        CH4        CO2        H2O
                            1     25.17      24.94      24.97      24.94       0.00
                            2    100.00       0.00       0.00       0.00       0.00
                            3      0.00       0.00       0.00     100.00       0.00

CALIBRATION GAS SAMPLES FOR THIS RUN WERE ANALYSED AS

TIME SAMP        DELP IGAS        H2         CO        CH4        CO2        H2O           C
 902    1        0.00    1     25.23      24.94      24.95      24.85       0.00
 909    2        1.00    1     25.12      24.92      24.97      24.97       0.00
 906    3       -1.00    1     25.24      24.88      24.95      24.90       0.00
 925    4        0.00    1     25.14      24.90      24.97      24.97       0.00
 943    6       -4.00    1     25.06      24.94      24.99      24.98       0.00
 950    7        1.00    1     25.28      24.85      24.94      24.90       0.00
 958    8        0.00    1     25.15      24.90      24.98      24.95       0.00
1300   18        0.00    2     99.95       0.00       0.00       0.04       0.00

THE RELATIVE CALIBRATION
AREA COEFFICENTS ARE      0.017410  0.878130  0.730316  1.000000  0.689999  0.025845

 ATMOSPHERIC PRESSURE WAS  759.45 .

 THE WEIGHT OF CATALYST INITIALLY CHARGED TO THE REACTOR IS  0.252 GRAMS.

 THE GROSS WEIGHT OF THE CATALYST CARRIER AND SUSPENSION MECHANISM IS  32.014 GRAMS.
```

```
                                DATA TAKEN DURING RUN  11 ON 24 JUN 74

TIME SAMP       DELP IGAS        H2         CO         CH4         CO2         H2O         C

1145 REACTOR TEMPERATURE 550. DEGREES CENTIGRADE

1145 CHANGED INLET GAS TO   100.00       0.00       0.00        0.00        0.00          TOTAL FLOW 19.8 CC/SEC (STP)
1200                                                                                 0.399 GRAMS CARBON DEPOSITED
1235                                                                                 0.381 GRAMS CARBON DEPOSITED
1243    17      0.00    4    99.76       0.00       0.00        0.00        0.23
1300    18      0.00    4    99.95       0.00       0.00        0.04        0.00
1305                                                                                 0.367 GRAMS CARBON DEPOSITED
1313    19      0.00    5    99.69       0.00       0.09        0.04        0.17
1330                                                                                 0.348 GRAMS CARBON DEPOSITED
1330-   20      0.00    5    99.80       0.00       0.07        0.00        0.11

1333 CHANGED INLET GAS TO    49.80       0.00       0.00       50.19        0.00          TOTAL FLOW 19.9 CC/SEC (STP)
1348                                                                                 0.342 GRAMS CARBON DEPOSITED
1359    22      0.00    4    47.36       0.00       0.00       52.50        0.12
1400                                                                                 0.347 GRAMS CARBON DEPOSITED
1414    23      0.00    5    41.54       4.54       0.00       47.39        6.51
1433    24     -4.00    5    41.29       4.71       0.11       47.16        6.71
1440                                                                                 0.340 GRAMS CARBON DEPOSITED
1453    25     -2.00    5    41.21       4.80       0.00       47.97        6.00
1504                                                                                 0.340 GRAMS CARBON DEPOSITED
1525    27      0.00    4    47.12       0.00       0.00       52.87        0.00
1525                                                                                 0.340 GRAMS CARBON DEPOSITED
1525                                                                                 0.340 GRAMS CARBON DEPOSITED
1543    28      0.00    4    47.08       0.00       0.00       52.91        0.00
1558    29     -1.00    5    40.54       5.53       0.04       46.93        6.93
1616    30     -1.00    5    40.12       5.72       0.07       46.13        7.94
1635                                                                                 0.340 GRAMS CARBON DEPOSITED
```

```
                              DATA TAKEN DURING RUN  12 ON 25 JUN 74

TIME SAMP     DELP IGAS        H2        CO       CH4       CO2       H2O          C
 825    1     1.00    1    4446.0  223547.0  185664.0  252925.0       0.0
 830    2     4.00    1    4372.0  219284.0  192586.0  249191.0       0.0
 833    3    -1.00    1    4463.0  222611.0  185591.0  253473.0       0.0
 840    4    -1.00    1    4372.0  218417.0  182163.0  248666.0       0.0
 846    5    -2.00    1    4439.0  221187.0  184376.0  251780.0       0.0
 850    6     0.00    1    4330.0  217643.0  181175.0  247348.0       0.0
 853    7    -5.00    1    4365.0  218784.0  182110.0  248189.0       0.0
 859    8     0.00    2   25089.0       0.0       0.0       0.0       0.0
 835                  7                                                     32.355

 835                  8     550.0

 835                  6      32.0       0.0       0.0       0.0       0.0

 900                  6      16.0       0.0       0.0      30.0       0.0
 900                  7                                                     32.360
 906    9     0.00    4    9333.0       0.0      67.0  476151.0       0.0
 915                  7                                                     32.360
 917   10     0.00    4    8644.0       0.0      75.0  477383.0       0.0
 923   11     0.00    5    8170.0   48226.0      42.0  467486.0   35945.0

 930                  6      16.0       3.5       0.0      27.0       0.0
 930                  7                                                     32.360
 944   12    -2.00    5    7065.0   96649.0      80.0  369161.0   55761.0
 956   13     1.00    4    8916.0   47603.0       0.0  443848.0    1070.0
1003                  7                                                     32.369
1010   14    -1.00    4    8544.0   44544.0       0.0  430900.0       0.0
1020   15     0.00    5    7406.0  112010.0     145.0  387006.0   51406.0
1034   16    -1.00    5    6696.0  104840.0     145.0  356230.0   61819.0
1032                  7                                                     32.379
1049   17     0.00    4    8575.0   47775.0       0.0  430969.0     983.0
1103                  7                                                     32.386
1106   18     0.00    4    8926.0   45508.0       0.0  443089.0       0.0
1113   19     0.00    5    7669.0  117471.0     127.0  395368.0   60569.0
1122   20     0.00    5    6542.0  107892.0     259.0  350170.0   64353.0
1134                  7                                                     32.393
1137   21     0.00    4    8980.0   49427.0       0.0  447692.0    1111.0
1151   22     0.00    4    8082.0   43927.0       0.0  412112.0     558.0
1200                  7                                                     32.400

1200                  6      16.0       7.0       0.0      24.0       0.0
1209   23     0.00    5    7427.0  159049.0     361.0  340008.0   60273.0
1218   24     0.00    5    6578.0  148060.0    1725.0  310410.0   66036.0
1231                  7                                                     32.421
1239   25     1.00    4    9575.0   96136.0       0.0  415686.0       0.0
1245   26     0.00    4    9564.0   93213.0       0.0  410756.0       0.0
1256   27     0.00    5    7718.0  164735.0     428.0  347932.0   65386.0
1303                  7                                                     32.440
1313   28     0.00    5    7557.0  163785.0     451.0  342756.0   78714.0
1331   29     0.00    4    9522.0   96538.0       0.0  425278.0       0.0
1344   30     0.00    4    7599.0   94750.0       0.0  417413.0       0.0
1353   31     0.00    5    7599.0  165732.0     424.0  346938.0   66661.0
```

1334			7						32.460
1405			7						32.481
1410	32	-1.00	5	7558.0	163118.0	489.0	342048.0	76895.0	
1426	33	0.00	4	9669.0	97459.0	0.0	425629.0	0.0	
1431			7						32.492
1440	34	0.00	4	9528.0	95168.0	0.0	419386.0	0.0	
1450	35	0.00	5	7643.0	163894.0	471.0	348683.0	70540.0	
1500			7						32.515
1504	36	-1.00	5	7432.0	164080.0	1685.0	340112.0	75002.0	
1505			6	16.0	10.5	0.0	21.0	0.0	
1523	37	0.00	4	9674.0	144743.0	0.0	377266.0	0.0	
1529	38	0.00	4	9526.0	140571.0	0.0	372469.0	0.0	
1534			7						32.552
1536	39	0.00	5	7673.0	202433.0	937.0	304372.0	64912.0	
1551	40	0.00	5	7548.0	201837.0	2425.0	302666.0	70321.0	
1604			7						32.590
1606	41	0.00	5	7886.0	201939.0	3106.0	312497.0	58352.0	
1622	42	0.00	5	7730.0	199078.0	1955.0	310194.0	67239.0	
1631			7						32.628
1639	43	0.00	4	9508.0	142481.0	0.0	371776.0	0.0	
1648	44	0.00	4	9442.0	140582.0	0.0	368674.0	0.0	
1656	45	0.00	5	8395.0	177673.0	575.0	332982.0	40131.0	
1703			7						32.651

```
                        DATA TAKEN DURING RUN  12 ON 25 JUN 74



THE CALIBRATION GASES ARE KNOWN TO BE
                         IGAS          H2         CO        CH4        CO2        H2O
                            1       25.17      24.94      24.97      24.94       0.00
                            2      100.00       0.00       0.00       0.00       0.00
                            3        0.00       0.00       0.00     100.00       0.00

CALIBRATION GAS SAMPLES FOR THIS RUN WERE ANALYSED AS

TIME SAMP       DELP IGAS          H2         CO        CH4        CO2        H2O          C
 825    1       1.00    1       25.11      24.99      24.98      24.91       0.00
 830    2       4.00    1       25.19      24.90      24.96      24.93       0.00
 833    3      -1.00    1       25.17      24.88      24.97      24.96       0.00
 840    4      -1.00    1       25.22      24.86      24.96      24.94       0.00
 846    5      -2.00    1       25.20      24.87      24.96      24.95       0.00
 850    6       0.00    1       25.17      24.91      24.96      24.94       0.00
 853    7      -5.00    1       25.17      24.92      24.97      24.91       0.00
 858    8       0.00    2      100.00       0.00       0.00       0.00       0.00

THE RELATIVE CALIBRATION
AREA COEFFICENTS ARE      0.017409   0.881110   0.731984   1.000000   0.689999   0.024987

 ATMOSPHERIC PRESSURE WAS  761.23 .

 THE WEIGHT OF CATALYST INITIALLY CHARGED TO THE REACTOR IS  0.252 GRAMS.

 THE GROSS WEIGHT OF THE CATALYST CARRIER AND SUSPENSION MECHANISM IS  32.014 GRAMS.
```

```
                               DATA TAKEN DURING RUN  12 ON 25 JUN 74

TIME SAMP       DELP IGAS          H2          CO          CH4         CO2         H2O           C
 835                                                                                        0.340 GRAMS CARBON DEPOSITED

 835 REACTOR TEMPERATURE 550. DEGREES CENTIGRADE


 835 CHANGED INLET GAS TO      100.00        0.00        0.00        0.00        0.00              TOTAL FLOW 19.8 CC/SEC (STP)

 900 CHANGED INLET GAS TO       49.80        0.00        0.00       50.19        0.00              TOTAL FLOW 19.9 CC/SEC (STP)
 900                                                                                        0.345 GRAMS CARBON DEPOSITED
 906     9       0.00     4     49.05        0.00        0.00       50.93        0.00
 915                                                                                        0.345 GRAMS CARBON DEPOSITED
 917    10       0.00     4     47.47        0.00        0.01       52.51        0.00
 923    11       0.00     5     41.81        5.54        0.00       47.35        5.27

 930 CHANGED INLET GAS TO       49.75        5.12        0.00       45.12        0.00              TOTAL FLOW 19.9 CC/SEC (STP)
 930                                                                                        0.345 GRAMS CARBON DEPOSITED
 944    12      -2.00     5     39.64       11.82        0.01       39.80        8.71
 956    13       1.00     4     46.97        5.73        0.00       47.12        0.16
1003                                                                                        0.354 GRAMS CARBON DEPOSITED
1010    14      -1.00     4     47.03        5.56        0.00       47.40        0.00
1020    15       0.00     5     39.33       13.09        0.02       39.86        7.67
1034    16      -1.00     5     38.41       12.96        0.02       38.82        9.76
1032                                                                                        0.364 GRAMS CARBON DEPOSITED
1049    17       0.00     4     46.84        5.92        0.00       47.07        0.15
1103                                                                                        0.371 GRAMS CARBON DEPOSITED
1106    18       0.00     4     47.22        5.50        0.00       47.26        0.00
1113    19       0.00     5     38.89       13.21        0.01       39.17        8.69
1122    20       0.00     5     37.93       13.42        0.03       38.38       10.22
1134                                                                                        0.378 GRAMS CARBON DEPOSITED
1137    21       0.00     4     46.81        5.90        0.00       47.11        0.16
THE SUM OF THE FOLLOWING DATA DIFFERED FROM 100 PERCENT BY MORE THAN 10 PERCENT BEFORE JUSTIFICATION
1151    22       0.00     4     46.92        5.71        0.00       47.26        0.09
1200                                                                                        0.385 GRAMS CARBON DEPOSITED

1200 CHANGED INLET GAS TO       49.69       10.23        0.00       40.06        0.00              TOTAL FLOW 19.9 CC/SEC (STP)
1209    23       0.00     5     38.61       18.21        0.04       34.30        8.81
1219    24       0.00     5     37.61       18.18        0.25       33.59       10.35
1231                                                                                        0.406 GRAMS CARBON DEPOSITED
1239    25       1.00     4     47.14       10.98        0.00       41.86        0.00
1245    26       0.00     4     47.51       10.74        0.00       41.73        0.00
1256    27       0.00     5     38.49       18.24        0.05       33.95        9.24
1303                                                                                        0.425 GRAMS CARBON DEPOSITED
1313    28       0.00     5     37.62       18.02        0.05       33.23       11.06
1331    29       0.00     4     46.55       10.94        0.00       42.49        0.00
1344    30       0.00     4     42.60       11.75        0.00       45.63        0.00
1353    31       0.00     5     39.13       18.40        0.05       33.94        9.45
1334                                                                                        0.445 GRAMS CARBON DEPOSITED
1405                                                                                        0.466 GRAMS CARBON DEPOSITED
1410    32      -1.00     5     37.76       18.02        0.06       33.29       10.84
1426    33       0.00     4     46.79       10.97        0.00       42.22        0.00
1431                                                                                        0.477 GRAMS CARBON DEPOSITED
1440    34       0.00     4     46.92       10.87        0.00       42.20        0.00
```

```
1450   35     0.00   5   38.04   18.07   0.06   33.88    9.93
1500                                                          0.500 GRAMS CARBON DEPOSITED
1504   36    -1.00   5   37.52   18.25   0.22   33.34   10.65

1505 CHANGED INLET GAS TO 49.64  15.33   0.00   35.02    0.00       TOTAL FLOW 19.9 CC/SEC (STP)
1523   37     0.00   4   46.56   16.21   0.00   37.22    0.00
1529   38     0.00   4   46.70   15.98   0.00   37.31    0.00
1534                                                          0.537 GRAMS CARBON DEPOSITED
1536   39     0.00   5   38.41   22.47   0.12   29.77    9.20
1551   40     0.00   5   37.83   22.35   0.32   29.54    9.94
1604                                                          0.575 GRAMS CARBON DEPOSITED
1606   41     0.00   5   38.89   22.71   0.41   30.28    8.19
1622   42     0.00   5   38.30   21.90   0.25   30.07    9.44
1631                                                          0.613 GRAMS CARBON DEPOSITED
1639   43     0.00   4   46.59   16.18   0.00   37.21    0.00
1649   44     0.00   4   46.70   16.09   0.00   37.19    0.00
1656   45     0.00   5   41.53   19.86   0.07   32.79    5.72
1703                                                          0.636 GRAMS CARBON DEPOSITED
```

```
                                DATA TAKEN DURING RUN  13 ON 26 JUN 74

 TIME  SAMP       DELP IGAS        H2         CO        CH4        CO2        H2O          C
  859     1       0.00    1    4427.0   223233.0   185127.0   252380.0        0.0
  903     2      -1.00    1    4287.0   217152.0   180534.0   246381.0        0.0
  906     3       0.00    1    4343.0   219267.0   182468.0   249176.0        0.0
  910     4       1.00    1    4243.0   215802.0   179125.0   244447.0        0.0
  913     5       0.00    1    4336.0   218998.0   181932.0   248143.0        0.0
  917     6       0.00    1    4239.0   214715.0   178332.0   243617.0        0.0
  921     7       1.00    1    4372.0   220049.0   182932.0   249547.0        0.0
  925     8       0.00    1    4242.0   214965.0   178784.0   244339.0        0.0
  949     9       0.00    2   25682.0       55.0        0.0        0.0        0.0
 1005    10       0.00    2   25425.0        0.0        0.0        0.0        0.0
  930                     7                                                           32.050

  930                     8     550.0

  930                     6      32.0        0.0        0.0        0.0        0.0
 1011    11      -1.00    5   25568.0       54.0        0.0        0.0        0.0
 1013                     7                                                           32.050
 1025    12      -1.00    5   25304.0        0.0        0.0        0.0        0.0
 1030                     7                                                           32.050

 1030                     6      16.0       34.0        0.0        0.0        0.0
 1033    13       0.00    4   10283.0   453963.0        0.0      247.0        0.0
 1039    14       0.00    4   10116.0   449633.0        0.0       53.0        0.0
 1046    15       0.00    5   10191.0   460052.0        0.0      371.0     2812.0
 1101    16       0.00    5   10049.0   456348.0        0.0      460.0     5264.0
 1102                     7                                                           32.090
 1115    17       0.00    4   10326.0   459685.0        0.0       73.0        0.0
 1120    18       0.00    4   10313.0   458028.0        0.0       80.0        0.0
 1127    19      -1.00    5   10192.0   461432.0        0.0      590.0     3792.0
 1132                     7                                                           32.155
 1142    20       0.00    5    9656.0   443455.0       50.0      564.0     6642.0
 1158    21       0.00    4   10449.0   463597.0        0.0       53.0        0.0
 1203                     7                                                           32.246
 1205    22       0.00    4   10285.0   457217.0        0.0      132.0        0.0
 1210    23       0.00    5   10162.0   460637.0       71.0      813.0     6157.0
 1219    24       0.00    5    9995.0   455337.0      145.0     1164.0    12084.0
 1233                     7                                                           32.387
 1240    25       0.00    4   10491.0   463866.0        0.0       39.0        0.0
 1247    26       0.00    4   10300.0   458323.0        0.0       39.0        0.0
 1252    27      -1.00    5    9978.0   434102.0      315.0    14741.0    21157.0
 1302    28       0.00    5    9872.0   408876.0      536.0    30973.0    32974.0
 1303                     7                                                           32.887
```

```
                             DATA TAKEN DURING RUN  13 ON 26 JUN 74



THE CALIBRATION GASES ARE KNOWN TO BE
                         IGAS       H2         CO         CH4        CO2        H2O
                            1     25.17      24.94      24.97      24.94       0.00
                            2    100.00       0.00       0.00       0.00       0.00
                            3      0.00       0.00       0.00     100.00       0.00

CALIBRATION GAS SAMPLES FOR THIS RUN WERE ANALYSED AS

TIME SAMP       DELP IGAS       H2         CO         CH4        CO2        H2O         C
 959    1       0.00    1     25.15      24.96      24.97      24.91       0.00
 903    2      -1.00    1     25.16      24.90      24.98      24.94       0.00
 906    3       0.00    1     25.15      24.88      24.98      24.96       0.00
 910    4       1.00    1     25.15      24.93      24.96      24.93       0.00
 913    5       0.00    1     25.19      24.91      24.97      24.92       0.00
 917    6       0.00    1     25.22      24.89      24.94      24.93       0.00
 921    7       1.00    1     25.21      24.89      24.96      24.92       0.00
 925    8       0.00    1     25.18      24.88      24.96      24.96       0.00
 949    9       0.00    2     99.99       0.00       0.00       0.00       0.00
1005   10       0.00    2    100.00       0.00       0.00       0.00       0.00

THE RELATIVE CALIBRATION
AREA COEFFICENTS ARE      0.017269   0.882838   0.731784   1.000000   0.689999   0.025779

 ATMOSPHERIC PRESSURE WAS  759.45 .

 THE WEIGHT OF CATALYST INITIALLY CHARGED TO THE REACTOR IS  0.236 GRAMS.

 THE GROSS WEIGHT OF THE CATALYST CARRIER AND SUSPENSION MECHANISM IS  32.050 GRAMS.
```

```
                                     DATA TAKEN DURING RUN  13 ON 26 JUN 74

TIME SAMP       DELP IGAS        H2          CO         CH4         CO2         H2O          C
 930                                                                                     0.000 GRAMS CARBON DEPOSITED

 930 REACTOR TEMPERATURE 550. DEGREES CENTIGRADE


 930 CHANGED INLET GAS TO    100.00        0.00        0.00        0.00        0.00            TOTAL FLOW 19.8 CC/SEC (STP)
1011   11      -1.00    5     99.99        0.00        0.00        0.00        0.00
1013                                                                                     0.000 GRAMS CARBON DEPOSITED
1025   12      -1.00    5    100.00        0.00        0.00        0.00        0.00
1030                                                                                     0.000 GRAMS CARBON DEPOSITED

1030 CHANGED INLET GAS TO     49.98       50.01        0.00        0.00        0.00            TOTAL FLOW 19.8 CC/SEC (STP)
1033   13       0.00    4     48.76       51.21        0.00        0.02        0.00
1039   14       0.00    4     48.69       51.30        0.00        0.00        0.00
1046   15       0.00    5     48.05       51.50        0.00        0.03        0.40
1101   16       0.00    5     47.80       51.38        0.00        0.04        0.75
1102                                                                                     0.040 GRAMS CARBON DEPOSITED
1115   17       0.00    4     48.53       51.45        0.00        0.00        0.00
1120   18       0.00    4     48.60       51.38        0.00        0.00        0.00
1127   19      -1.00    5     47.89       51.50        0.00        0.05        0.54
1132                                                                                     0.105 GRAMS CARBON DEPOSITED
1142   20       0.00    5     47.63       51.31        0.00        0.05        0.98
1153   21       0.00    4     48.55       51.43        0.00        0.00        0.00
1203                                                                                     0.195 GRAMS CARBON DEPOSITED
1205   22       0.00    4     48.59       51.39        0.00        0.01        0.00
1210   23       0.00    5     47.71       51.31        0.00        0.07        0.87
1219   24       0.00    5     47.25       50.88        0.01        0.11        1.72
1233                                                                                     0.336 GRAMS CARBON DEPOSITED
1240   25       0.00    4     48.62       51.37        0.00        0.00        0.00
1247   26       0.00    4     48.56       51.43        0.00        0.00        0.00
1252   27      -1.00    5     47.07       48.41        0.04        1.45        3.01
1302   28       0.00    5     46.64       45.54        0.07        3.04        4.69
1303                                                                                     0.836 GRAMS CARBON DEPOSITED
```

```
                                        DATA TAKEN DURING RUN  14 ON  8 JUL 74

TIME  SAMP        DELP IGAS          H2         CO         CH4       CO2        H2O           C
1015     1        0.00    1      4476.0   223234.0    178926.0  260818.0        0.0
1131     2        2.00    1      5057.0   235756.0    194937.0  269496.0        0.0
1139     3        0.00    1      4701.0   220734.0    183143.0  251147.0        0.0
1145     4        0.00    1      5067.0   234707.0    194920.0  267117.0        0.0
1152     5        0.00    1      4706.0   220251.0    183056.0  250907.0        0.0
1159     6        2.00    1      5097.0   235364.0    195547.0  268056.0        0.0
1206     7        1.00    1      4737.0   220786.0    183674.0  251676.0        0.0
1214     8        0.00    2     29202.0        0.0         0.0       0.0        0.0
1219     9        0.00    2     26812.0        0.0         0.0       0.0        0.0
1234    10        0.00    2     29282.0        0.0         0.0       0.0        0.0
1247    11        0.00    2     26866.0        0.0         0.0       0.0        0.0
1303    12       -1.00    2     28908.0        0.0         0.0       0.0        0.0
1315    13       -1.00    2     26682.0        0.0         0.0       0.0        0.0
1330    14       -1.00    2     29092.0        0.0         0.0       0.0        0.0

1130                      8       550.0

1130                      6        32.0        0.0         0.0       0.0        0.0
1330                      7                                                               32.092

1330                      6        16.0        0.0         0.0      30.0        0.0
1404    16       -1.00    4     11152.0      175.0         0.0  557566.1      650.0
1410                      7                                                               32.092
1417    17        1.00    4     10377.0      175.0         0.0  525616.1      650.0
1431    18       -1.00    5     10908.0      210.0         0.0  563012.1      650.0
1446    19       -1.00    5     10002.0      212.0         0.0  530514.1     1300.0
1500    20        0.00    4     11078.0      158.0         0.0  556904.1       60.0
1507                      7                                                               32.092
1514    21        0.00    4     10213.0      158.0         0.0  524512.1       60.0
1527    22       -1.00    5     10817.0      210.0         0.0  565613.1      640.0
1543    23       -1.00    5      9986.0      240.0         0.0  531436.1     1088.0
1557    24        0.00    4     11000.0        0.0         0.0  560180.1     1129.0
1608                      7                                                               32.092
1619    25        0.00    3         0.0        0.0         0.0  976358.1    21959.0
1634    26        0.00    3         0.0        0.0         0.0 1037732.1    20301.0
1652    27        0.00    3         0.0        0.0         0.0  978935.1    23553.0
1706    28        0.00    3         0.0        0.0         0.0 1045277.1    22827.0
```

```
                              DATA TAKEN DURING RUN  14 ON  8 JUL 74


THE CALIBRATION GASES ARE KNOWN TO BE
                    IGAS        H2        CO        CH4        CO2        H2O
                       1     25.17     24.94      24.97      24.94       0.00
                       2    100.00      0.00       0.00       0.00       0.00
                       3      0.00      0.00       0.00      96.87       3.12

CALIBRATION GAS SAMPLES FOR THIS RUN WERE ANALYSED AS

TIME SAMP      DELP IGAS        H2        CO        CH4        CO2        H2O         C
1015    1      0.00    1     24.43     25.22      24.53      25.80       0.00
1131    2      2.00    1     25.15     24.91      24.99      24.93       0.00
1138    3      0.00    1     25.31     24.87      25.03      24.77       0.00
1145    4      0.00    1     25.25     24.87      25.07      24.79       0.00
1152    5      0.00    1     25.35     24.83      25.04      24.76       0.00
1159    6      2.00    1     25.29     24.85      25.05      24.78       0.00
1206    7      1.00    1     25.40     24.80      25.03      24.75       0.00
1214    8      0.00    2    100.00      0.00       0.00       0.00       0.00
1219    9      0.00    2    100.00      0.00       0.00       0.00       0.00
1234   10      0.00    2    100.00      0.00       0.00       0.00       0.00
1247   11      0.00    2    100.00      0.00       0.00       0.00       0.00
1303   12     -1.00    2    100.00      0.00       0.00       0.00       0.00
1315   13     -1.00    2    100.00      0.00       0.00       0.00       0.00
1330   14     -1.00    2    100.00      0.00       0.00       0.00       0.00
1619   25      0.00    3      0.00      0.00       0.00      96.80       3.19
1634   26      0.00    3      0.00      0.00       0.00      97.20       2.79
1652   27      0.00    3      0.00      0.00       0.00      96.58       3.41
1706   28      0.00    3      0.00      0.00       0.00      96.89       3.10

THE RELATIVE CALIBRATION
AREA COEFFICENTS ARE      0.018424  0.875510  0.721527  1.000000  0.681181  0.027026

 ATMOSPHERIC PRESSURE WAS  760.22 .

 THE WEIGHT OF CATALYST INITIALLY CHARGED TO THE REACTOR IS  0.252 GRAMS.

 THE GROSS WEIGHT OF THE CATALYST CARRIER AND SUSPENSION MECHANISM IS  32.077 GRAMS.
```

```
                              DATA TAKEN DURING RUN  14 ON  8 JUL 74

TIME SAMP      DELP IGAS        H2         CO         CH4        CO2        H2O        C

1130 REACTOR TEMPERATURE 550. DEGREES CENTIGRADE

1130 CHANGED INLET GAS TO   100.00       0.00       0.00       0.00       0.00          TOTAL FLOW 19.8 CC/SEC (STP)
1330                                                                              0.014 GRAMS CARBON DEPOSITED

1330 CHANGED INLET GAS TO    49.80       0.00       0.00      50.19       0.00          TOTAL FLOW 19.9 CC/SEC (STP)
1404   16     -1.00    4     47.44       0.01       0.00      52.44       0.08
1410                                                                              0.014 GRAMS CARBON DEPOSITED
1417   17      1.00    4     47.52       0.01       0.00      52.36       0.09
1431   18     -1.00    5     46.77       0.02       0.00      53.11       0.09
1446   19     -1.00    5     46.51       0.02       0.00      53.26       0.19
1500   20      0.00    4     47.39       0.01       0.00      52.58       0.00
1507                                                                              0.014 GRAMS CARBON DEPOSITED
1514   21      0.00    4     47.30       0.01       0.00      52.67       0.00
1527   22     -1.00    5     46.49       0.02       0.00      53.39       0.08
1543   23     -1.00    5     46.45       0.02       0.00      53.35       0.16
1557   24      0.00    4     47.04       0.00       0.00      52.79       0.15
1608                                                                              0.014 GRAMS CARBON DEPOSITED
```

```
                                 DATA TAKEN DURING RUN  15 ON  9 JUL 74

TIME    SAMP          DELP IGAS          H2         CO        CH4        CO2        H2O          C
 837       1          1.00    1      4588.0   220628.0   181978.0   247423.0        0.0
 845       2          1.00    1      4996.0   233429.0   193319.0   264316.0        0.0
 852       3          0.00    1      4643.0   219447.0   182172.0   248681.0        0.0
 859       4          1.00    1      5017.0   233069.0   193725.0   264917.0        0.0
 906       5          0.00    1      4663.0   218751.0   181995.0   249132.0        0.0
 913       6          2.00    1      5013.0   233533.0   194054.0   265887.0        0.0
 919       7          0.00    1      4686.0   219120.0   182048.0   249312.0        0.0
 926       8          1.00    1      5039.0   233898.0   194329.0   265859.0        0.0

 845                          8       550.0

 845                          6         0.0        0.0        0.0       30.0        0.0
 845                          7                                                               32.064
 915                          7                                                               32.080
1000                          7                                                               32.083

1000                          6        16.0       34.0        0.0        0.0        0.0
1019      12          0.00    5     11262.0   444422.0      302.0    21898.0    21759.0
1020                          7                                                               32.637
1036      13          0.00    4     10621.0   452637.0        0.0      891.0      625.0
1040                          7                                                               32.934

1040                          6        16.0        0.0        0.0       30.0        0.0
1050      14          0.00    4     11133.0      326.0        0.0   548399.1        0.0
1106      15          0.00    4     10267.0        0.0        0.0   518786.0      383.0
1120                          7                                                               32.937
1121      16         -2.00    5      9287.0    58307.0        0.0   502123.0    40403.0
1138      17         -2.00    5      8561.0    54242.0        0.0   470619.0    44413.0
1155      18          1.00    4     11278.0        0.0        0.0   563567.1      635.0
1209      19          0.00    4     10388.0        0.0        0.0   528210.1      197.0
1223      20         -2.00    5      9245.0    61742.0        0.0   500591.0    42908.0
1235                          7                                                               32.944
1249      21         -2.00    5      8483.0    57889.0        0.0   470583.0    46194.0
1255      22          0.00    4     11258.0        0.0        0.0   565654.1        0.0
1300      23          0.00    4     10326.0        0.0        0.0   529385.1        0.0
1300                          7                                                               32.945

1305                          6        24.0        0.0        0.0       51.5        0.0
1315      24          0.00    5      9036.0    53844.0        0.0   526929.1    39792.0
1331      25         -2.00    5      8300.0    51499.0        0.0   494763.0    43310.0
1348      26          0.00    4     10910.0        0.0        0.0   577494.1        0.0
1355                          7                                                               32.950
1403      27          0.00    4      9939.0        0.0        0.0   537680.1        0.0
1412      28          0.00    5      8935.0    55414.0        0.0   520469.0    40735.0
1429      29         -2.00    5      8204.0    52183.0        0.0   488409.0    44420.0
1445      30          0.00    4     10826.0        0.0        0.0   575724.1        0.0
1500      31          0.00    4      9921.0        0.0        0.0   537784.1        0.0
1509      32         -2.00    5      8844.0    56157.0        0.0   518785.0    41982.0
1527      33         -2.00    5      8141.0    53364.0        0.0   488551.0    45009.0
1530                          7                                                               32.957

1530                          6        16.0        0.0        0.0       30.0        0.0
```

```
1545    34      0.00    4   11257.0       0.0         0.0  561829.1     512.0
1600    35      0.00    4   10314.0       0.0         0.0  524858.1     376.0
1613    36     -2.00    5    8896.0   72237.0         0.0  485092.0   50272.0
1630    37     -2.00    5    8219.0   68670.0         0.0  456742.0   50385.0
1630                    7                                                         32.957
1644    38      0.00    2   29489.0       0.0         0.0    8685.0       0.0
1651    39      0.00    2   27403.0       0.0         0.0       0.0       0.0
1703    41      0.00    2   27438.0       0.0         0.0       0.0       0.0
1707    42      0.00    2   29986.0       0.0         0.0       0.0       0.0
1711    43      0.00    3       0.0       0.0         0.0  985436.1   26254.0
1727    44      0.00    3       0.0       0.0         0.0 1048313.1   24940.0
1750    46      0.00    3       0.0       0.0         0.0 1051998.2   25003.0
1603    47      0.00    3       0.0       0.0         0.0  990080.1   24874.0
```

```
                    DATA TAKEN DURING RUN  15 ON  9 JUL 74



THE CALIBRATION GASES ARE KNOWN TO BE
                          IGAS        H2         CO         CH4        CO2        H2O
                            1      25.17      24.94      24.97      24.94       0.00
                            2     100.00       0.00       0.00       0.00       0.00
                            3       0.00       0.00       0.00      96.42       3.57

CALIBRATION GAS SAMPLES FOR THIS RUN WERE ANALYSED AS

TIME SAMP         DELP IGAS        H2         CO         CH4        CO2        H2O         C
 837    1         1.00   1      25.03      25.10      25.01      24.84      0.00
 845    2         1.00   1      25.12      24.95      24.96      24.94      0.00
 952    3         0.00   1      25.19      24.91      24.97      24.91      0.00
 959    4         1.00   1      25.17      24.88      24.98      24.96      0.00
 906    5         0.00   1      25.27      24.82      24.94      24.95      0.00
 913    6         2.00   1      25.12      24.88      24.99      25.00      0.00
 919    7         0.00   1      25.32      24.82      24.91      24.92      0.00
 926    8         1.00   1      25.17      24.88      24.97      24.96      0.00
1644   38         0.00   2      99.18       0.00       0.00       0.81      0.00
1651   39         0.00   2     100.00       0.00       0.00       0.00      0.00
1703   41         0.00   2     100.00       0.00       0.00       0.00      0.00
1707   42         0.00   2     100.00       0.00       0.00       0.00      0.00
1711   43         0.00   3       0.00       0.00       0.00      96.26      3.73
1727   44         0.00   3       0.00       0.00       0.00      96.65      3.34
1750   46         0.00   3       0.00       0.00       0.00      96.65      3.34
1603   47         0.00   3       0.00       0.00       0.00      96.47      3.52

THE RELATIVE CALIBRATION
AREA COEFFICENTS ARE      0.018621  0.882526  0.730622  1.000000  0.686864  0.027768

 ATMOSPHERIC PRESSURE WAS  756.91 .

 THE WEIGHT OF CATALYST INITIALLY CHARGED TO THE REACTOR IS  0.252 GRAMS.

 THE GROSS WEIGHT OF THE CATALYST CARRIER AND SUSPENSION MECHANISM IS  32.077 GRAMS.
```

```
                         DATA TAKEN DURING RUN  15 ON  9 JUL 74

TIME SAMP      DELP IGAS          H2        CO        CH4        CO2        H2O         C

 845 REACTOR TEMPERATURE 550. DEGREES CENTIGRADE


 845 CHANGED INLET GAS TO        0.00      0.00      0.00     100.00       0.00               TOTAL FLOW 10.0 CC/SEC (STP)
 845                                                                                  -0.013 GRAMS CARBON DEPOSITED
 915                                                                                   0.002 GRAMS CARBON DEPOSITED
1000                                                                                   0.005 GRAMS CARBON DEPOSITED

1000 CHANGED INLET GAS TO       49.98     50.01      0.00       0.00       0.00               TOTAL FLOW 19.8 CC/SEC (STP)
1019    12      0.00     5      47.27     47.61      0.03       2.07       2.99
1020                                                                                   0.559 GRAMS CARBON DEPOSITED
1036    13      0.00     4      48.13     51.68      0.00       0.08       0.09
1040                                                                                   0.857 GRAMS CARBON DEPOSITED

1040 CHANGED INLET GAS TO       49.80      0.00      0.00      50.19       0.00               TOTAL FLOW 19.9 CC/SEC (STP)
1050    14      0.00     4      47.44      0.03      0.00      52.51       0.00
1106    15      0.00     4      47.25      0.00      0.00      52.68       0.05
1120                                                                                   0.860 GRAMS CARBON DEPOSITED
1121    16     -2.00     5      40.69      6.24      0.00      47.49       5.56
1138    17     -2.00     5      40.36      6.14      0.00      47.02       6.46
1155    18      1.00     4      47.00      0.00      0.00      52.91       0.08
1209    19      0.00     4      47.04      0.00      0.00      52.92       0.02
1223    20     -2.00     5      40.38      6.58      0.00      47.14       5.88
1235                                                                                   0.866 GRAMS CARBON DEPOSITED
1249    21     -2.00     5      39.92      6.52      0.00      46.84       6.69
1255    22      0.00     4      46.90      0.00      0.00      53.09       0.00
1300    23      0.00     4      46.89      0.00      0.00      53.10       0.00
1300                                                                                   0.868 GRAMS CARBON DEPOSITED

1305 CHANGED INLET GAS TO       46.43      0.00      0.00      53.56       0.00               TOTAL FLOW 32.0 CC/SEC (STP)
1315    24      0.00     5      39.48      5.71      0.00      49.36       5.42
1331    25     -2.00     5      39.02      5.77      0.00      48.96       6.23
1348    26      0.00     4      45.78      0.00      0.00      54.21       0.00
1355                                                                                   0.873 GRAMS CARBON DEPOSITED
1403    27      0.00     4      45.76      0.00      0.00      54.23       0.00
1412    28      0.00     5      39.40      5.92      0.00      49.08       5.59
1429    29     -2.00     5      38.96      5.89      0.00      48.69       6.44
1445    30      0.00     4      45.71      0.00      0.00      54.28       0.00
1500    31      0.00     4      45.72      0.00      0.00      54.27       0.00
1509    32     -2.00     5      39.16      6.01      0.00      49.04       5.77
1527    33     -2.00     5      38.73      6.02      0.00      48.70       6.53
1530                                                                                   0.879 GRAMS CARBON DEPOSITED

1530 CHANGED INLET GAS TO       49.80      0.00      0.00      50.19       0.00               TOTAL FLOW 19.9 CC/SEC (STP)
1545    34      0.00     4      47.04      0.00      0.00      52.88       0.07
1600    35      0.00     4      47.05      0.00      0.00      52.88       0.05
1613    36     -2.00     5      39.39      7.74      0.00      45.92       6.92
1630    37     -2.00     5      39.16      7.78      0.00      45.70       7.34
1630                                                                                   0.879 GRAMS CARBON DEPOSITED
```

```
                              DATA TAKEN DURING RUN  16 ON 10 JUL 74

TIME SAMP      DELP IGAS        H2        CO       CH4       CO2       H2O          C
1118    1      0.00    1    5001.0  238085.0  194672.0  265365.0       0.0
1125    2      1.00    1    4719.0  224265.0  184152.0  251662.0       0.0
1133    3      2.00    1    5112.0  239393.0  196953.0  268641.0       0.0
1141    4      1.00    1    4747.0  222397.0  184249.0  252054.0       0.0
1149    5      0.00    1    5094.0  235099.0  195245.0  267065.0       0.0
1154    6      0.00    1    4753.0  221087.0  183278.0  251327.0       0.0
1203    7      1.00    1    5077.0  236716.0  195453.0  267508.0       0.0
1210    8      0.00    1    4754.0  220848.0  183354.0  251636.0       0.0
1217    9      0.00    2   29468.0       0.0       0.0       0.0       0.0
1224   10      0.00    2   27170.0       0.0       0.0       0.0       0.0
1000                   7                                                       32.068

1130                   8     550.0
1200                   7                                                       32.076
1230                   7                                                       32.083
1230   11      0.00    5   29517.0       0.0       0.0       0.0     373.0
1243   12      0.00    5   27185.0       0.0       0.0       0.0     671.0
1256   13      0.00    4   29660.0       0.0       0.0       0.0     352.0
1300                   7                                                       32.083

1300                   6       0.0       0.0       0.0 .    30.0       0.0
1310   14      0.00    4       0.0       0.0       0.0 1010999.1    1188.0
1325   15      0.00    5       0.0       0.0       0.0 1076277.2     360.0
1335                   7                                                       32.083
1340   16     -1.00    5       0.0       0.0       0.0 1009712.1     372.0
1350                   7                                                       32.075

1350                   6       0.0       0.0       0.0       0.0       0.0
1355   17      0.00    4       0.0       0.0       0.0  281351.0     270.0
1409   18      0.00    4       0.0       0.0       0.0    3251.0       0.0
1416   19     -1.00    5       0.0       0.0       0.0    1372.0       0.0
1420                   7                                                       32.084

1420                   6      16.0      34.0       0.0       0.0       0.0
1425   20     -1.00    5   10753.0  457356.0       0.0    5273.0    8309.0
1439   21      0.00    4   12097.0  485556.0       0.0    1110.0       0.0
1439                   7                                                       32.179
1445   22      0.00    4   11200.0  456225.0       0.0    1237.0       0.0
1450                   7                                                       32.240
1451   23     -1.00    5   11729.0  488012.0       0.0    3017.0    6940.0
1506   24     -1.00    5   10771.0  453103.0       0.0    2263.0    9965.0
1508                   7                                                       32.362
1520   25      0.00    4   11951.0  486384.0       0.0     586.0       0.0
1520                   7                                                       32.519
1526   26      0.00    4   11109.0  457998.0       0.0    1059.0       0.0
1531   27      0.00    5   11614.0  451046.0     571.0   23149.0   18426.0
1535                   7                                                       32.800
1540                   7                                                       32.910

1540                   6      16.0       0.0       0.0      30.0       0.0
1546   28     -1.00    5    9468.0   26980.0       0.0  496897.0   23428.0
1600                   7                                                       32.928
```

```
1605   29      0.00    3       0.0        0.0        0.0 1045417.1    23531.0
1623   30      0.00    3       0.0        0.0        0.0  982459.1    24609.0
1639   31      0.00    3       0.0        0.0        0.0 1044153.1    27284.0
1656   32      0.00    3       0.0        0.0        0.0  983282.1    24792.0
```

```
                         DATA TAKEN DURING RUN  16 ON 10 JUL 74



THE CALIBRATION GASES ARE KNOWN TO BE
                         IGAS        H2         CO        CH4        CO2        H2O
                            1     25.17      24.94      24.97      24.94       0.00
                            2    100.00       0.00       0.00       0.00       0.00
                            3      0.00       0.00       0.00      96.40       3.59

CALIBRATION GAS SAMPLES FOR THIS RUN WERE ANALYSED AS

TIME SAMP        DELP IGAS         H2         CO        CH4        CO2        H2O          C
1118    1        0.00    1      24.92      25.19      25.00      24.88       0.00
1125    2        1.00    1      25.12      25.02      24.94      24.89       0.00
1133    3        2.00    1      25.07      25.02      24.99      24.89       0.00
1141    4        1.00    1      25.25      24.82      24.97      24.94       0.00
1149    5        0.00    1      25.22      24.79      25.00      24.97       0.00
1154    6        0.00    1      25.35      24.76      24.92      24.95       0.00
1203    7        1.00    1      25.11      24.92      24.98      24.97       0.00
1210    8        0.00    1      25.35      24.72      24.92      24.98       0.00
1217    9        0.00    2     100.00       0.00       0.00       0.00       0.00
1224   10        0.00    2     100.00       0.00       0.00       0.00       0.00
1605   29        0.00    3       0.00       0.00       0.00      96.75       3.24
1623   30        0.00    3       0.00       0.00       0.00      96.40       3.59
1639   31        0.00    3       0.00       0.00       0.00      96.25       3.74
1656   32        0.00    3       0.00       0.00       0.00      96.37       3.62

THE RELATIVE CALIBRATION
AREA COEFFICENTS ARE       0.018736  0.886684  0.730285  1.000000  0.671066  0.027249

 ATMOSPHERIC PRESSURE WAS  753.10 .

 THE WEIGHT OF CATALYST INITIALLY CHARGED TO THE REACTOR IS  0.246 GRAMS.

 THE GROSS WEIGHT OF THE CATALYST CARRIER AND SUSPENSION MECHANISM IS  32.068 GRAMS.
```

```
                              DATA TAKEN DURING RUN  16 ON 10 JUL 74

TIME SAMP      DELP IGAS        H2         CO         CH4        CO2        H2O        C
1000                                                                                 0.000 GRAMS CARBON DEPOSITED

1130 REACTOR TEMPERATURE 550. DEGREES CENTIGRADE

1200                                                                                 0.008 GRAMS CARBON DEPOSITED
1230                                                                                 0.014 GRAMS CARBON DEPOSITED
1230    11      0.00    5     99.94       0.00       0.00       0.00       0.05
1243    12      0.00    5     99.90       0.00       0.00       0.00       0.09
1256    13      0.00    4     99.95       0.00       0.00       0.00       0.04
1300                                                                                 0.014 GRAMS CARBON DEPOSITED

1300 CHANGED INLET GAS TO      0.00       0.00       0.00     100.00       0.00             TOTAL FLOW 10.0 CC/SEC (STP)
1310    14      0.00    4      0.00       0.00       0.00      99.82       0.17
1325    15      0.00    5      0.00       0.00       0.00      99.95       0.04
1335                                                                                 0.014 GRAMS CARBON DEPOSITED
1340    16     -1.00    5      0.00       0.00       0.00      99.94       0.05
1350                                                                                 0.007 GRAMS CARBON DEPOSITED

1350 CHANGED INLET GAS TO      0.00       0.00       0.00       0.00       0.00             TOTAL FLOW  0.0 CC/SEC (STP)
THE SUM OF THE FOLLOWING DATA DIFFERED FROM 100 PERCENT BY MORE THAN 10 PERCENT BEFORE JUSTIFICATION
1355    17      0.00    4      0.00       0.00       0.00  .   99.85       0.14
THE SUM OF THE FOLLOWING DATA DIFFERED FROM 100 PERCENT BY MORE THAN 10 PERCENT BEFORE JUSTIFICATION
1409    18      0.00    4      0.00       0.00       0.00     100.00       0.00
THE SUM OF THE FOLLOWING DATA DIFFERED FROM 100 PERCENT BY MORE THAN 10 PERCENT BEFORE JUSTIFICATION
1416    19     -1.00    5      0.00       0.00       0.00     100.00       0.00
1420                                                                                 0.016 GRAMS CARBON DEPOSITED

1420 CHANGED INLET GAS TO     49.98      50.01       0.00       0.00       0.00             TOTAL FLOW 19.8 CC/SEC (STP)
1425    20     -1.00    5     47.62      50.63       0.00       0.51       1.21
1439    21      0.00    4     49.24      50.65       0.00       0.10       0.00
1439                                                                                 0.111 GRAMS CARBON DEPOSITED
1445    22      0.00    4     49.27      50.60       0.00       0.12       0.00
1450                                                                                 0.172 GRAMS CARBON DEPOSITED
1451    23     -1.00    5     47.95      50.81       0.00       0.27       0.95
1506    24     -1.00    5     47.91      50.39       0.00       0.22       1.46
1508                                                                                 0.294 GRAMS CARBON DEPOSITED
1520    25      0.00    4     48.98      50.95       0.00       0.05       0.00
1520                                                                                 0.451 GRAMS CARBON DEPOSITED
1526    26      0.00    4     49.02      50.86       0.00       0.10       0.00
1531    27      0.00    5     47.93      47.29       0.07       2.15       2.55
1535                                                                                 0.732 GRAMS CARBON DEPOSITED
1540                                                                                 0.842 GRAMS CARBON DEPOSITED

1540 CHANGED INLET GAS TO     49.80       0.00       0.00      50.19       0.00             TOTAL FLOW 19.9 CC/SEC (STP)
1546    28     -1.00    5     43.84       3.03       0.00      49.63       3.48
1600                                                                                 0.860 GRAMS CARBON DEPOSITED
```

```
                                       DATA TAKEN DURING RUN  17 ON 11 JUL 74

 TIME SAMP       DELP IGAS        H2        CO       CH4       CO2       H2O         C
  920                    7                                                       32.928
  923    1       2.00    1    5068.0  235550.0  194647.0  265408.0       0.0
  930    2       2.00    1    4678.0  221746.0  183450.0  249507.0       0.0
  935    3       0.00    1    5061.0  236534.0  195353.0  265262.0       0.0
  939    4       3.00    1    4715.0  219373.0  182736.0  250224.0       0.0
  943    5       1.00    1    5042.0  233253.0  193885.0  265212.0       0.0

  945                    8     550.0

  945                    6      16.0       0.0       0.0      30.0       0.0
  952    7       1.00    1    5062.0  233327.0  193940.0  265424.0       0.0
  956    8       0.00    1    4708.0  218679.0  182164.0  249318.0       0.0
 1003    9       0.00    4   10681.0       0.0       0.0  523234.0       0.0
 1010   10       0.00    4   10317.0       0.0       0.0  505848.0       0.0

 1010                    6       8.0       0.0       0.0      15.0       0.0
 1017   11       0.00    5    9318.0   42640.0       0.0  518575.0   33035.0
 1035   12      -2.00    5    8462.0   40693.0       0.0  489362.0   40225.0
 1050   13       0.00    4   10591.0       0.0       0.0  566665.1       0.0
 1050                    7                                                       32.947
 1055   14       0.00    4    9772.0       0.0       0.0 '531573.1       0.0
 1103   15      -2.00    5    9073.0   46048.0     136.0  519956.0   32105.0
 1117   16      -2.00    5    8365.0   45232.0       0.0  488688.0   40937.0
 1122                    7                                                       32.947
 1132   17       0.00    4   10570.0       0.0       0.0  568129.1       0.0
 1140   18       0.00    4    9801.0       0.0       0.0  533098.1       0.0
 1147   19      -2.00    5    9061.0   47614.0       0.0  518513.0   35967.0
 1210   21      -2.00    5    9013.0   50132.0       0.0  519290.0   37805.0
 1227   22       0.00    4    9995.0       0.0       0.0  533237.1       0.0
 1235   23       0.00    4   10580.0       0.0       0.0  570769.1       0.0
 1243   24      -2.00    5    8207.0   49287.0       0.0  484121.0   42700.0
 1300   25      -2.00    5    8923.0   53816.0       0.0  518521.0   40874.0
 1316   26       0.00    4    9848.0       0.0       0.0  542424.1       0.0
 1323   27       1.00    4   10701.0       0.0       0.0  579049.1       0.0
 1332   28      -1.00    5    8992.0   52666.0       0.0  489507.0   35213.0
 1405   30       0.00    4    9913.0       0.0       0.0  543335.1       0.0
 1405                    7                                                       32.947
 1412   31       0.00    4   10632.0       0.0       0.0  578552.1       0.0

 1414                    6       1.6       0.0       0.0       3.0       0.0
 1419   32      -1.00    5    6432.0  111548.0       0.0  466680.0   53887.0
 1437   33      -2.00    5    7561.0  121942.0      16.0  443974.0   68619.0
 1454   34       0.00    4   10231.0       0.0       0.0  528810.1       0.0
 1503   35       0.00    4   11137.0       0.0       0.0  558676.1       0.0
 1511   36      -2.00    5    7319.0  104671.0     572.0  419470.0   68305.0
 1514                    7                                                       32.947
 1545   38       0.00    4   10205.0       0.0       0.0  526952.1       0.0
 1533   39       0.00    4   11163.0       0.0       0.0  556695.1       0.0
 1603   40       0.00    5    7623.0   85801.0       0.0  428961.0   67885.0
 1618   41      -1.00    5    8094.0   91433.0      15.0  452800.0   68479.0
 1620                    7                                                       32.947
 1635   42       0.00    3       0.0       0.0       0.0  986400.1   22127.0
```

```
1651   43      0.00   3       0.0      0.0      0.0 1050738.2   23260.0
1708   44      0.00   3       0.0      0.0      0.0  989695.1   23958.0
1720   45      0.00   3       0.0      0.0      0.0 1056024.2   21691.0
1721   46      0.00   3       0.0      0.0      0.0  993918.1   24238.0
1750   47      0.00   2   29919.0      0.0      0.0     512.0       0.0
1755   48      0.00   2   27487.0      0.0      0.0       0.0       0.0
1800   49      0.00   2   30074.0      0.0      0.0       0.0       0.0
1805   50      0.00   2   27565.0      0.0      0.0       0.0       0.0
```

```
                           DATA TAKEN DURING RUN  17 ON 11 JUL 74



THE CALIBRATION GASES ARE KNOWN TO BE
                         IGAS          H2         CO         CH4        CO2        H2O
                            1       25.17      24.94       24.97      24.94       0.00
                            2      100.00       0.00        0.00       0.00       0.00
                            3        0.00       0.00        0.00      96.80       3.19

CALIBRATION GAS SAMPLES FOR THIS RUN WERE ANALYSED AS

TIME SAMP          DELP IGAS          H2         CO        CH4        CO2        H2O         C
 923    1          2.00    1       25.13      25.00      24.96      24.90       0.00
 930    2          2.00    1       25.10      25.01      25.00      24.88       0.00
 935    3          0.00    1       25.06      25.06      25.01      24.85       0.00
 939    4          3.00    1       25.29      24.77      24.93      24.98       0.00
 943    5          1.00    1       25.14      24.87      24.97      25.00       0.00
 952    7          1.00    1       25.19      24.85      24.95      24.99       0.00
 956    8          0.00    1       25.32      24.77      24.93      24.96       0.00
1635   42          0.00    3        0.00       0.00       0.00      96.88       3.11
1651   43          0.00    3        0.00       0.00       0.00      96.92       3.07
1709   44          0.00    3        0.00       0.00       0.00      96.64       3.35
1720   45          0.00    3        0.00       0.00       0.00      97.13       2.86
1721   46          0.00    3        0.00       0.00       0.00      96.62       3.37
1750   47          0.00    2       99.95       0.00       0.00       0.04       0.00
1755   48          0.00    2      100.00       0.00       0.00       0.00       0.00
1900   49          0.00    2      100.00       0.00       0.00       0.00       0.00
1905   50          0.00    2      100.00       0.00       0.00       0.00       0.00

THE RELATIVE CALIBRATION
AREA COEFFICENTS ARE        0.018784  0.884019  0.731670  1.000000  0.697544  0.027770

 ATMOSPHERIC PRESSURE WAS  757.42 .

 THE WEIGHT OF CATALYST INITIALLY CHARGED TO THE REACTOR IS  0.246 GRAMS.

 THE GROSS WEIGHT OF THE CATALYST CARRIER AND SUSPENSION MECHANISM IS  32.068 GRAMS.
```

```
                                 DATA TAKEN DURING RUN  17 ON 11 JUL 74

TIME SAMP        DELP IGAS         H2         CO        CH4        CO2        H2O         C
 920                                                                                 0.860 GRAMS CARBON DEPOSITED

 945 REACTOR TEMPERATURE 550. DEGREES CENTIGRADE


 945 CHANGED INLET GAS TO       49.80       0.00       0.00      50.19       0.00          TOTAL FLOW 19.9 CC/SEC (STP)
1003     9       0.00    4      47.77       0.00       0.00      52.22       0.00
1010    10       0.00    4      47.94       0.00       0.00      52.05       0.00

1010 CHANGED INLET GAS TO       49.80       0.00       0.00      50.19       0.00          TOTAL FLOW  9.9 CC/SEC (STP)
1017    11       0.00    5      41.19       4.61       0.00      49.64       4.53
1035    12      -2.00    5      40.21       4.64       0.00      49.32       5.81
1050    13       0.00    4      45.60       0.00       0.00      54.39       0.00
1050                                                                                 0.879 GRAMS CARBON DEPOSITED
1055    14       0.00    4      45.65       0.00       0.00      54.34       0.00
1103    15      -2.00    5      40.52       5.01       0.01      50.01       4.42
1117    16      -2.00    5      39.79       5.14       0.00      49.16       5.90
1122                                                                                 0.879 GRAMS CARBON DEPOSITED
1132    17       0.00    4      45.52       0.00       0.00      54.47       0.00
1140    18       0.00    4      45.64       0.00       0.00      54.35       0.00
1147    19      -2.00    5      40.27       5.15       0.00      49.63       4.93
1210    21      -2.00    5      39.93       5.40       0.00      49.49       5.16
1227    22       0.00    4      45.82       0.00       0.00      54.17       0.00
1235    23       0.00    4      45.42       0.00       0.00      54.57       0.00
1243    24      -2.00    5      39.32       5.62       0.00      48.86       6.17
1300    25      -2.00    5      39.45       5.77       0.00      49.20       5.56
1316    26       0.00    4      45.30       0.00       0.00      54.69       0.00
1323    27       1.00    4      45.29       0.00       0.00      54.70       0.00
1332    28      -1.00    5      41.10       5.85       0.00      48.08       4.95
1405    30       0.00    4      45.38       0.00       0.00      54.61       0.00
1405                                                                                 0.879 GRAMS CARBON DEPOSITED
1412    31       0.00    4      45.18       0.00       0.00      54.81       0.00

1414 CHANGED INLET GAS TO       49.80       0.00       0.00      50.19       0.00          TOTAL FLOW  1.9 CC/SEC (STP)
1419    32      -1.00    5      32.47      12.71       0.00      47.02       7.78
1437    33      -2.00    5      34.94      13.19       0.00      42.45       9.40
1454    34       0.00    4      46.67       0.00       0.00      53.32       0.00
1503    35       0.00    4      46.95       0.00       0.00      53.04       0.00
1511    36      -2.00    5      35.88      11.92       0.07      42.24       9.86
1514                                                                                 0.879 GRAMS CARBON DEPOSITED
1545    38       0.00    4      46.71       0.00       0.00      53.28       0.00
1533    39       0.00    4      47.08       0.00       0.00      52.91       0.00
1603    40       0.00    5      37.12       9.79       0.00      43.27       9.81
1618    41      -1.00    5      37.07       9.94       0.00      43.54       9.44
1620                                                                                 0.879 GRAMS CARBON DEPOSITED
```

```
                                  DATA TAKEN DURING RUN  18 ON 15 JUL 74

TIME SAMP        DELP IGAS        H2         CO        CH4        CO2        H2O            C
1022    1        0.00    1    4911.0  233638.0  192983.0  262371.0         0.0
1029    2        0.00    1    4578.0  216395.0  179899.0  245839.0         0.0
1035    3        0.00    1    5010.0  231325.0  193090.0  264177.0         0.0
1044    4       -2.00    1    4631.0  316755.0  181049.0  247870.0         0.0
1051    5        0.00    1    5020.0  230912.0  193968.0  265469.0         0.0
1058    6        0.00    1    4665.0  219265.0  182235.0  249305.0         0.0
1105    7        0.00    2   29243.0       0.0       0.0      10.0       569.0
1118    8        0.00    2   26528.0       0.0       0.0      32.0       487.0
1630   31        0.00    3       0.0       0.0       0.0 1052049.2     23254.0
1646   32        0.00    3       0.0       0.0       0.0 1050000.2     23835.0
1703   33        0.00    3       0.0       0.0       0.0 1058190.2     24167.0
1718   34        0.00    3       0.0       0.0       0.0 1010439.1     24702.0
1028                     7                                                          31.967

1030                     8     560.0

1030                     6      41.0       0.0       0.0       0.0         0.0
1105    7        0.00    4   29243.0       0.0       0.0      10.0       569.0
1118    8        0.00    4   26528.0       0.0       0.0      32.0       487.0
1130    9       -1.00    5   28285.0       0.0       0.0       0.0     21201.0

1130                     6      16.0      34.0       0.0       0.0         0.0
1130                     7                                                          31.980
1146   10       -2.00    5   10610.0  454577.0       0.0     505.0      5120.0
1200                     7                                                          32.031
1201   11        0.00    4   11910.0  487221.0       0.0      54.0         0.0
1214   12        0.00    4   10848.0  454475.0       0.0      44.0         0.0
1222   13       -2.00    5   11572.0  489778.0       0.0     544.0      2812.0
1230                     7                                                          32.100
1236   14       -2.00    5   10554.0  455659.0       0.0     502.0      3269.0
1252   15        0.00    4   11924.0  488049.0       0.0      52.0         0.0
1259   16        0.00    4   10939.0  456578.0       0.0      33.0         0.0
1305   17       -2.00    5   11687.0  493095.0       0.0     581.0      4883.0
1319                     7                                                          32.229
1321   18       -2.00    5   10598.0  459163.0       0.0     590.0      4097.0
1335   19       -2.00    5   11614.0  491267.0      63.0     909.0      6937.0
1349                     7                                                          32.321
1352   20       -1.00    5   10493.0  458204.0    1852.0    2326.0      8570.0
1353                     7                                                          32.377

1353                     8     550.0

1353                     6      16.0       0.0       0.0      30.0         0.0
1409   21       -2.00    5    9791.0   47302.0       0.0  509801.0     33525.0
1422   22        0.00    4   10277.0    3180.0       0.0  534056.1       202.0
1435   23        0.00    4   11284.0    2219.0       0.0  562476.1         0.0
1445   24       -2.00    5    8584.0   53416.0       0.0  481404.0     40853.0
1505   25       -2.00    5    9342.0   59423.0       0.0  502044.0     42896.0
1505                     7                                                          32.393
1531   27        0.00    4   11361.0       0.0       0.0  562746.1         0.0
1541   28       -2.00    5    8348.0   60789.0      56.0  468716.0     47390.0
1559   29       -1.00    5    9168.0   69045.0     372.0  495853.0     48796.0
```

```
1614   30       0.00    4   10269.0        0.0        0.0  536220.1        0.0
1615                    7                                                          32.396
```

```
                         DATA TAKEN DURING RUN  18 ON 15 JUL 74



THE CALIBRATION GASES ARE KNOWN TO BE
                         IGAS          H2         CO        CH4        CO2        H2O
                            1       25.17      24.94      24.97      24.94       0.00
                            2      100.00       0.00       0.00       0.00       0.00
                            3        0.00       0.00       0.00      96.42       3.57

CALIBRATION GAS SAMPLES FOR THIS RUN WERE ANALYSED AS

TIME SAMP      DELP IGAS         H2         CO        CH4        CO2        H2O
1022    1      0.00    1      25.36      23.85      25.47      25.31       0.00
1029    2      0.00    1      25.65      23.61      25.39      25.34       0.00
1035    3      0.00    1      25.67      23.53      25.39      25.39       0.00
1044    4     -2.00    1      23.19      30.99      22.89      22.91       0.00
1051    5      0.00    1      25.64      23.43      25.45      25.45       0.00
1059    6      0.00    1      25.68      23.60      25.35      25.35       0.00
1105    7      0.00    2      99.91       0.00       0.00       0.00       0.08
1118    8      0.00    2      99.92       0.00       0.00       0.00       0.07
1630   31      0.00    3       0.00       0.00       0.00      96.72       3.27
1646   32      0.00    3       0.00       0.00       0.00      96.64       3.35
1703   33      0.00    3       0.00       0.00       0.00      96.62       3.37
1718   34      0.00    3       0.00       0.00       0.00      96.39       3.60

THE RELATIVE CALIBRATION
AREA COEFFICENTS ARE      0.018592   0.944772   0.730847   1.000000   0.653580   0.027172

 ATMOSPHERIC PRESSURE WAS  751.83 .

 THE WEIGHT OF CATALYST INITIALLY CHARGED TO THE REACTOR IS  0.250 GRAMS.

 THE GROSS WEIGHT OF THE CATALYST CARRIER AND SUSPENSION MECHANISM IS  31.967 GRAMS.
```

```
                                       DATA TAKEN DURING RUN  18 ON 15 JUL 74

TIME SAMP        DELP IGAS          H2          CO          CH4          CO2          H2O         C
1029                                                                                              0.000 GRAMS CARBON DEPOSITED

1030 REACTOR TEMPERATURE 560. DEGREES CENTIGRADE


1030 CHANGED INLET GAS TO      100.00        0.00        0.00         0.00         0.00              TOTAL FLOW 25.4 CC/SEC (STP)
1105    7        0.00    4      99.91        0.00        0.00         0.00         0.08
1115    8        0.00    4      99.92        0.00        0.00         0.00         0.07
1130    9       -1.00    5      96.96        0.00        0.00         0.00         3.03

1130 CHANGED INLET GAS TO       49.98       50.01        0.00         0.00         0.00              TOTAL FLOW 19.8 CC/SEC (STP)
1137                                                                                              0.013 GRAMS CARBON DEPOSITED
1146   10       -2.00    5      49.54       49.59        0.00         0.05         0.80
1200                                                                                              0.063 GRAMS CARBON DEPOSITED
1201   11        0.00    4      50.52       49.47        0.00         0.00         0.00
1214   12        0.00    4      50.43       49.56        0.00         0.00         0.00
1222   13       -2.00    5      49.59       49.95        0.00         0.05         0.41
1230                                                                                              0.132 GRAMS CARBON DEPOSITED
1236   14       -2.00    5      49.53       49.89        0.00         0.05         0.51
1252   15        0.00    4      50.50       49.49        0.00         0.00         0.00
1259   16        0.00    4      50.47       49.51        0.00         0.00         0.00
1305   17       -2.00    5      49.45       49.77        0.00         0.05         0.71
1318                                                                                              0.261 GRAMS CARBON DEPOSITED
1321   18       -2.00    5      49.35       49.94        0.00         0.06         0.64
1335   19       -2.00    5      49.25       49.63        0.00         0.08         1.01
1340                                                                                              0.354 GRAMS CARBON DEPOSITED
1352   20       -1.00    5      48.65       49.50        0.25         0.23         1.33
1353                                                                                              0.409 GRAMS CARBON DEPOSITED

1353 REACTOR TEMPERATURE 550. DEGREES CENTIGRADE


1353 CHANGED INLET GAS TO       49.80        0.00        0.00        50.19         0.00              TOTAL FLOW 19.9 CC/SEC (STP)
1409   21       -2.00    5      42.48        4.71        0.00        47.97         4.82
1422   22        0.00    4      46.59        0.33        0.00        53.04         0.03
1435   23        0.00    4      47.19        0.21        0.00        52.58         0.00
1445   24       -2.00    5      40.40        5.61        0.00        47.77         6.20
1505   25       -2.00    5      40.82        5.90        0.00        47.11         6.15
1505                                                                                              0.425 GRAMS CARBON DEPOSITED
1531   27        0.00    4      47.41        0.00        0.00        52.58         0.00
1541   28       -2.00    5      39.67        6.40        0.00        46.68         7.22
1559   29       -1.00    5      39.96        6.81        0.04        46.21         6.95
1614   30        0.00    4      46.64        0.00        0.00        53.35         0.00
1615                                                                                              0.428 GRAMS CARBON DEPOSITED
```

```
                         DATA TAKEN DURING RUN  19 ON 16 JUL 74

TIME SAMP       DELP IGAS         H2         CO        CH4        CO2         H2O           C
1010    1       2.00    1     5129.0   238535.0   196320.0   263374.0         0.0
1017    2       2.00    1     4680.0   221755.0   183821.0   250177.0         0.0
1024    3       0.00    1     5117.0   235140.0   195575.0   268261.0         0.0
1031    4       0.00    1     4668.0   219385.0   182441.0   249490.0         0.0
1425   22       0.00    2    26742.0        0.0        0.0        0.0         0.0
1449   25       0.00    2    29865.0        0.0        0.0        0.0         0.0
1454   26       0.00    2    26926.0        0.0        0.0        0.0         0.0
1619   34       0.00    3        0.0        0.0        0.0   999108.1     24677.0
1642   36       0.00    3        0.0        0.0        0.0  1002733.1     22771.0
1657   37       0.00    3        0.0        0.0        0.0  1056520.2     29424.0
1715   38       0.00    3        0.0        0.0        0.0  1003746.1     22356.0

1030 -                  8      550.0

1030                    6       16.0        0.0        0.0       30.0         0.0
1038    5       0.00    4    11056.0        0.0        0.0   559448.1         0.0
1050    6       0.00    4    10085.0        0.0        0.0   522506.0         0.0
1058    7       0.00    5     8918.0    73273.0       19.0   491123.0     57981.0
1116    8      -1.00    5     8039.0    68497.0        0.0   463850.0     47939.0
1131                    7                                                             32.413
1135    9       0.00    4    11114.0        0.0        0.0   564447.1         0.0
1144   10       0.00    4    10118.0        0.0        0.0   526056.1         0.0
1154   11      -1.00    5     8721.0    74457.0       17.0   485819.0     81413.0
1200                    7                                                             32.415
1214   12      -1.00    5     7850.0    70888.0      120.0   455820.0     59926.0

1231                    6       16.0       17.0        0.0       15.0         0.0
1233                    7                                                             32.420
1235   13       0.00    4    11498.0   243691.0        0.0   296971.0         0.0
1244   14       0.00    4    10352.0   229889.0        0.0   281396.0         0.0
1254   15       0.00    5     9238.0   283586.0     4531.0   245270.0     67324.0
1301                    7                                                             32.633
1311   16      -1.00    5     8627.0   254409.0     4949.0   237291.0     50350.0
1321                    7                                                             32.747
1326   17       0.00    4    11342.0   240736.0        0.0   289626.0         0.0
1334   18       0.00    4    10304.0   225545.0        0.0   270932.0         0.0

1400                    6       32.0        0.0        0.0        0.0         0.0
1413   21       0.00    4    29413.0        0.0        0.0     6656.0         0.0
1425   22       0.00    4    26742.0        0.0        0.0        0.0         0.0
1432   23       0.00    5    29012.0        0.0    13306.0        0.0         0.0
1439   24       0.00    5    26209.0        0.0    10715.0        0.0         0.0

1439                    8      400.0

1439                    6       32.0        0.0        0.0        0.0         0.0
1444                    7                                                             32.612
1449   25       0.00    4    29865.0        0.0        0.0        0.0         0.0
1454   26       0.00    4    26926.0        0.0        0.0        0.0         0.0
1501   27       0.00    5    29393.0        0.0     7542.0        0.0         0.0
1509   28       0.00    5    26595.0        0.0     5726.0        0.0         0.0
1514                    7                                                             32.450
```

```
1516   29     0.00   4   29859.0     0.0      0.0     0.0     0.0
1525   30     0.00   4   27105.0     0.0      0.0     0.0     0.0
1535   31     0.00   5   29645.0     0.0   4342.0     0.0     0.0
1542                 7                                             32.362
1545   32     0.00   5   26849.0     0.0   3175.0     0.0     0.0
16[illegible]                 7                                             32.300
```

```
                         DATA TAKEN DURING RUN  19 ON 16 JUL 74



THE CALIBRATION GASES ARE KNOWN TO BE
                    IGAS         H2         CO        CH4        CO2        H2O
                       1      25.17      24.94      24.97      24.94       0.00
                       2     100.00       0.00       0.00       0.00       0.00
                       3       0.00       0.00       0.00      96.88       3.11

CALIBRATION GAS SAMPLES FOR THIS RUN WERE ANALYSED AS

TIME SAMP       DELP IGAS        H2         CO        CH4        CO2        H2O          C
1010    1       2.00    1     25.24      25.13      24.99      24.62       0.00
1017    2       2.00    1     25.07      24.95      24.99      24.97       0.00
1024    3       0.00    1     25.19      24.79      24.91      25.09       0.00
1031    4       0.00    1     25.18      24.75      24.98      25.08       0.00
1425   22       0.00    2    100.00       0.00       0.00       0.00       0.00
1448   25       0.00    2    100.00       0.00       0.00       0.00       0.00
1454   26       0.00    2    100.00       0.00       0.00       0.00       0.00
1619   34       0.00    3      0.00       0.00       0.00      96.89       3.10
1642   36       0.00    3      0.00       0.00       0.00      97.13       2.86
1657   37       0.00    3      0.00       0.00       0.00      96.51       3.48
1715   38       0.00    3      0.00       0.00       0.00      97.19       2.80

THE RELATIVE CALIBRATION
AREA COEFFICENTS ARE      0.018918   0.887132   0.734255   1.000000   0.770713   0.026969

 ATMOSPHERIC PRESSURE WAS  762.00 .

 THE WEIGHT OF CATALYST INITIALLY CHARGED TO THE REACTOR IS  0.250 GRAMS.

 THE GROSS WEIGHT OF THE CATALYST CARRIER AND SUSPENSION MECHANISM IS  31.967 GRAMS.
```

```
                                 DATA TAKEN DURING RUN  19 ON 16 JUL 74

TIME SAMP      DELP IGAS        H2          CO          CH4         CO2          H2O          C

1030 REACTOR TEMPERATURE 550. DEGREES CENTIGRADE


1030 CHANGED INLET GAS TO      49.80        0.00        0.00       50.19         0.00            TOTAL FLOW 19.9 CC/SEC (STP)
1038    5       0.00    4      47.00        0.00        0.00       52.99         0.00
1050    6       0.00    4      46.89        0.00        0.00       53.10         0.00
1058    7       0.00    5      39.20        7.73        0.00       46.00         7.04
1116    8      -1.00    5      39.97        7.81        0.00       46.91         6.29
1131                                                                                   0.445 GRAMS CARBON DEPOSITED
1135    9       0.00    4      46.89        0.00        0.00       53.10         0.00
1144   10       0.00    4      46.79        0.00        0.00       53.20         0.00
1154   11      -1.00    5      37.83        7.72        0.00       44.71         9.72
1200                                                                                   0.447 GRAMS CARBON DEPOSITED
1214   12      -1.00    5      38.12        8.05        0.01       45.95         7.83

1231 CHANGED INLET GAS TO      49.89       24.95        0.00       25.14         0.00            TOTAL FLOW 19.8 CC/SEC (STP)
1233                                                                                   0.452 GRAMS CARBON DEPOSITED
1236   13       0.00    4      47.24       25.34        0.00       27.40         0.00
1244   14       0.00    4      46.56       25.61        0.00       27.81         0.00
1254   15       0.00    5      39.52       29.35        0.56       22.52         8.02
1301                                                                                   0.665 GRAMS CARBON DEPOSITED
1311   16      -1.00    5      40.60       28.57        0.67       23.64         6.50
1321                                                                                   0.779 GRAMS CARBON DEPOSITED
1326   17       0.00    4      47.44       25.42        0.00       27.13         0.00
1334   18       0.00    4      47.19       25.56        0.00       27.24         0.00

1400 CHANGED INLET GAS TO     100.00        0.00        0.00        0.00         0.00            TOTAL FLOW 19.8 CC/SEC (STP)
1413   21       0.00    4      99.38        0.00        0.00        0.61         0.00
1425   22       0.00    4     100.00        0.00        0.00        0.00         0.00
1432   23       0.00    5      99.32        0.00        1.67        0.00         0.00
1439   24       0.00    5      98.53        0.00        1.46        0.00         0.00

1439 REACTOR TEMPERATURE 400. DEGREES CENTIGRADE


1439 CHANGED INLET GAS TO     100.00        0.00        0.00        0.00         0.00            TOTAL FLOW 19.8 CC/SEC (STP)
1444                                                                                   0.645 GRAMS CARBON DEPOSITED
1449   25       0.00    4     100.00        0.00        0.00        0.00         0.00
1454   26       0.00    4     100.00        0.00        0.00        0.00         0.00
1501   27       0.00    5      99.05        0.00        0.94        0.00         0.00
1509   28       0.00    5      99.22        0.00        0.77        0.00         0.00
1514                                                                                   0.482 GRAMS CARBON DEPOSITED
1516   29       0.00    4     100.00        0.00        0.00        0.00         0.00
1525   30       0.00    4     100.00        0.00        0.00        0.00         0.00
1535   31       0.00    5      99.45        0.00        0.54        0.00         0.00
1542                                                                                   0.395 GRAMS CARBON DEPOSITED
1545   32       0.00    5      99.57        0.00        0.42        0.00         0.00
1608                                                                                   0.332 GRAMS CARBON DEPOSITED
```

```
                                        DATA TAKEN DURING RUN  20 ON 18 JUL 74

TIME SAMP          DELP IGAS         H2         CO        CH4        CO2         H2O          C
 921    1          1.00    1     5047.0   241234.0   196032.0   266043.0         0.0
 928    2          1.00    1     4639.0   221724.0   183329.0   248465.0         0.0
 935    3          0.00    1     5085.0   239036.0   197283.0   267333.0         0.0
 941    4          1.00    1     4687.0   223009.0   186894.0   250005.0         0.0
 958    5          0.00    2    29594.0        0.0        0.0        0.0         0.0
1010    6          0.00    2    26612.0        0.0        0.0        0.0         0.0
1653   33          0.00    3        0.0        0.0        0.0  1062723.2     27311.0
1726   35         -1.00    3        0.0        0.0        0.0  1059382.2     26360.0

 948                       6       48.0        0.0        0.0        0.0         0.0

 949                       8      550.0
 958    5          0.00    4    29594.0        0.0        0.0        0.0         0.0
1010    6          0.00    4    26612.0        0.0        0.0        0.0         0.0
1030                       7                                                               31.860
1034    7          0.00    5    29639.0        0.0        0.0        0.0         0.0
1041    8          0.00    5    26698.0        0.0        0.0        0.0         0.0
1058                       7                                                               31.862

1103                       6       16.0       34.0        0.0        0.0         0.0
1105    9          0.00    4    11892.0   489823.0        0.0       57.0         0.0
1111   10          0.00    4    10809.0   466730.0        0.0        0.0         0.0
1118   11          0.00    4    11888.0   490473.0        0.0        0.0         0.0
1127   12         -1.00    5    10462.0   470067.0        0.0      153.0      7508.0
1131                       7                                                               31.907
1141   13          0.00    5    11628.0   496561.0        0.0      357.0      2443.0
1149                       7                                                               31.930
1155   14         -1.00    5    10732.0   471768.0        0.0     4191.0      2059.0
1210   15         -2.00    5    11778.0   493446.0        0.0      570.0      3297.0
1214                       7                                                               31.966
1224   16         -2.00    5    10733.0   466865.0        0.0      314.0      2115.0
1246                       7                                                               32.024
1254   18         -2.00    5    10700.0   470590.0        0.0     1327.0      2826.0
1309   19         -2.00    5    11748.0   494290.0      140.0      604.0      3269.0
1312                       7                                                               32.077
1321                       7                                                               32.161
1323   20         -2.00    5    10708.0   467203.0        0.0      472.0      4647.0
1337   21         -1.00    5    11705.0   493655.0       52.0      716.0      4849.0
1353   22         -1.00    5    10648.0   464616.0        0.0      656.0      5078.0
1408   23         -2.00    5    11632.0   493374.0        0.0     1127.0      7245.0
1412                       7                                                               32.280
1424   24         -1.00    5    10733.0   467852.0        0.0     1190.0      7683.0
1429                       7                                                               32.374

1429                       6       32.0        0.0        0.0        0.0         0.0

1439                       6       16.0        0.0        0.0       30.0         0.0
1443   25          0.00    4    11208.0     1384.0        0.0   566316.1         0.0
1457   26          0.00    4    10391.0      323.0        0.0   543034.1         0.0
1500                       7                                                               32.371
1504   27          0.00    5     9409.0    52267.0       18.0   519333.0     42078.0
1525   28         -1.00    5     8543.0    53948.0        0.0   491666.0     42720.0
```

```
1532                   7                                                      32.374
1544   29     -2.00    5    9212.0   60363.0       0.0  512440.0   50514.0
1603   30     -1.00    5    8402.0   58903.0       0.0  486825.0   46806.0
1607                   7                                                      32.377
1618   31     -2.00    5    9027.0   65527.0       0.0  508153.0   58745.0
1631                   7                                                      32.380
```

```
                         DATA TAKEN DURING RUN  20 ON 18 JUL 74



THE CALIBRATION GASES ARE KNOWN TO BE
                    IGAS         H2         CO        CH4        CO2        H2O
                       1      25.17      24.94      24.97      24.94       0.00
                       2     100.00       0.00       0.00       0.00       0.00
                       3       0.00       0.00       0.00      96.76       3.23

CALIBRATION GAS SAMPLES FOR THIS RUN WERE ANALYSED AS

TIME SAMP      DELP IGAS         H2         CO        CH4        CO2        H2O          C
 921    1      1.00    1      25.10      25.16      24.83      24.90       0.00
 928    2      1.00    1      25.23      24.84      24.94      24.98       0.00
 935    3      0.00    1      25.19      24.88      24.94      24.97       0.00
 941    4      1.00    1      25.18      24.74      25.17      24.89       0.00
 959    5      0.00    2     100.00       0.00       0.00       0.00       0.00
1010    6      0.00    2     100.00       0.00       0.00       0.00       0.00
1653   33      0.00    3       0.00       0.00       0.00      96.89       3.10
1726   35     -1.00    3       0.00       0.00       0.00      96.99       3.00

THE RELATIVE CALIBRATION
AREA COEFFICENTS ARE      0.018677   0.897533   0.739083   1.000000   0.802260   0.027196

 ATMOSPHERIC PRESSURE WAS  759.96 .

 THE WEIGHT OF CATALYST INITIALLY CHARGED TO THE REACTOR IS  0.252 GRAMS.

 THE GROSS WEIGHT OF THE CATALYST CARRIER AND SUSPENSION MECHANISM IS  31.843 GRAMS.
```

```
                              DATA TAKEN DURING RUN  20 ON 18 JUL 74

TIME SAMP      DELP IGAS       H2          CO         CH4         CO2         H2O           C

 949 CHANGED INLET GAS TO    100.00       0.00       0.00        0.00        0.00              TOTAL FLOW 29.7 CC/SEC (STP)

 949 REACTOR TEMPERATURE 550. DEGREES CENTIGRADE

 958    5       0.00    4    100.00       0.00       0.00        0.00        0.00
1010    6       0.00    4    100.00       0.00       0.00        0.00        0.00
1030                                                                               0.016 GRAMS CARBON DEPOSITED
1034    7       0.00    5    100.00       0.00       0.00        0.00        0.00
1041    8       0.00    5    100.00       0.00       0.00        0.00        0.00
1058                                                                               0.019 GRAMS CARBON DEPOSITED

1103 CHANGED INLET GAS TO     49.98      50.01       0.00        0.00        0.00              TOTAL FLOW 19.8 CC/SEC (STP)
1105    9       0.00    4     49.06      50.93       0.00        0.00        0.00
1111   10       0.00    4     48.39      51.60       0.00        0.00        0.00
1118   11       0.00    4     49.02      50.97       0.00        0.00        0.00
1127   12      -1.00    5     47.12      51.93       0.00        0.01        0.92
1131                                                                               0.063 GRAMS CARBON DEPOSITED
1141   13       0.00    5     48.12      51.55       0.00        0.03        0.28
1149                                                                               0.086 GRAMS CARBON DEPOSITED
1155   14      -1.00    5     47.66      51.67       0.00        0.41        0.25
1210   15      -2.00    5     48.46      51.10       0.00        0.05        0.38
1214                                                                               0.123 GRAMS CARBON DEPOSITED
1224   16      -2.00    5     48.09      51.61       0.00        0.03        0.26
1246                                                                               0.180 GRAMS CARBON DEPOSITED
1254   18      -2.00    5     47.74      51.77       0.00        0.13        0.34
1309   19      -2.00    5     48.36      51.18       0.01        0.05        0.37
1312                                                                               0.233 GRAMS CARBON DEPOSITED
1321                                                                               0.317 GRAMS CARBON DEPOSITED
1323   20      -2.00    5     47.87      51.50       0.00        0.04        0.57
1337   21      -1.00    5     48.24      51.12       0.00        0.06        0.56
1353   22      -1.00    5     47.87      51.43       0.00        0.06        0.62
1409   23      -2.00    5     47.97      51.07       0.00        0.10        0.83
1412                                                                               0.437 GRAMS CARBON DEPOSITED
1424   24      -1.00    5     47.67      51.26       0.00        0.11        0.94
1429                                                                               0.530 GRAMS CARBON DEPOSITED

1429 CHANGED INLET GAS TO    100.00       0.00       0.00        0.00        0.00              TOTAL FLOW 19.8 CC/SEC (STP)

1439 CHANGED INLET GAS TO     49.80       0.00       0.00       50.19        0.00              TOTAL FLOW 19.9 CC/SEC (STP)
1443   25       0.00    4     46.91       0.14       0.00       52.94        0.00
1452   26       0.00    4     46.52       0.03       0.00       53.43        0.00
1500                                                                               0.527 GRAMS CARBON DEPOSITED
1504   27       0.00    5     40.97       5.45       0.00       48.65        4.91
1525   28      -1.00    5     40.11       5.94       0.00       48.66        5.27
1532                                                                               0.530 GRAMS CARBON DEPOSITED
1544   29      -2.00    5     40.07       6.27       0.00       47.77        5.87
1603   30      -1.00    5     39.57       6.49       0.00       48.16        5.77
1607                                                                               0.534 GRAMS CARBON DEPOSITED
1619   31      -2.00    5     39.26       6.77       0.00       47.16        6.79
1631                                                                               0.536 GRAMS CARBON DEPOSITED
```

```
                         DATA TAKEN DURING RUN  21 ON 19 JUL 74

TIME SAMP     DELP IGAS       H2        CO       CH4       CO2        H2O           C
 903    1     1.00    1   4646.0  222489.0  185904.0  249382.0        0.0
 909    2     1.00    1   5076.0  235404.0  195922.0  267707.0        0.0
 916    3     0.00    1   4729.0  222371.0  187271.0  252012.0        0.0
 923    4     0.00    1   5084.0  235924.0  196414.0  268421.0        0.0
   0    0     0.00    2  29000.0       0.0       0.0       0.0        0.0
1643   35     0.00    3      0.0       0.0       0.0 1007438.1    25284.0
1658   36     0.00    3      0.0       0.0       0.0 1053451.2    26263.0
 930                  7                                                        32.387

 933                  8    550.0

 933                  6     16.0       0.0       0.0      34.0        0.0
1000                  7                                                        32.384
1003    5     0.00    4   9511.0       0.0       0.0  559591.1      288.0
1016    6     0.00    4  10319.0       0.0       0.0  591617.1      861.0
1031    7    -2.00    5   7647.0   58660.0       0.0  502050.0    44678.0
1035                  7                                                        32.391
1046    8    -1.00    5   8274.0   62502.0       0.0  528030.1    48341.0
1100                  7                                                        32.400
1104    9     0.00    4   9600.0       0.0       0.0  566188.1      263.0
1117   10     0.00    4  10329.0       0.0       0.0  591508.1      279.0
1130   11    -2.00    5   7592.0   59647.0       0.0  504860.0    44218.0
1134                  7                                                        32.395
1147   12    -1.00    5   8128.0   66853.0       0.0  527832.1    51161.0

1153                  6     30.5       4.0       0.0       0.0        0.0
1159   13     0.00    4  25328.0   54544.0       0.0    1281.0      127.0
1204                  7                                                        32.491
1213   14     0.00    4  27486.0   56775.0       0.0     543.0        0.0
1219   15    -2.00    5  24387.0   27665.0   13252.0    3251.0    19760.0
1224                  7                                                        32.631

1228                  6     30.5       1.0       0.0       0.0        0.0
1234   16    -2.00    5  28599.0    3359.0    9393.0     335.0    13371.0
1243                  7                                                        32.668
1249   17     0.00    4  27129.0   13488.0       0.0     266.0        0.0
1255   18     0.00    4  29327.0   13023.0       0.0     678.0        0.0
1302   19    -1.00    5  26448.0    3733.0    8355.0     344.0    10379.0
1307                  7                                                        32.696
1316   20    -1.00    5  28745.0    4238.0    8618.0     294.0    10705.0
1330   21     0.00    4  27128.0   13185.0       0.0     390.0        0.0
1334                  7                                                        32.722
1337   22     0.00    4  29396.0   13298.0       0.0     237.0        0.0
1344   23     0.00    5  26617.0    4399.0    8059.0     312.0    10031.0
1359   24     0.00    5  28768.0    4493.0    8542.0     287.0    12039.0
1403                  7                                                        32.749
1414   25     0.00    4  27158.0   13351.0       0.0     178.0        0.0
1427   26     0.00    4  29452.0   12924.0       0.0     292.0        0.0
1437                  7                                                        32.779
1443   27     0.00    5  26739.0    4081.0    8470.0     265.0    11012.0
1457   28    -1.00    5  28951.0    5003.0    9792.0     820.0    13153.0
1511                  7                                                        32.816
```

```
1516    29       0.00     4    27340.0    13672.0        0.0        0.0        0.0
1520    30       0.00     4    29631.0    12974.0        0.0      208.0        0.0
1529    31       0.00     5    26772.0     4962.0     7990.0      277.0    10259.0
1535                      7                                                             32.821
1544                      7                                                             32.837
1547    32       0.00     5    28911.0     6449.0     9028.0      267.0    12113.0
1603                      7                                                             32.856
1605    33       0.00     4    27242.0    18756.0        0.0     1797.0        0.0
```

```
                              DATA TAKEN DURING RUN  21 ON 19 JUL 74



THE CALIBRATION GASES ARE KNOWN TO BE
                      IGAS         H2         CO         CH4        CO2        H2O
                         1      25.17      24.94       24.97      24.94       0.00
                         2     100.00       0.00        0.00       0.00       0.00
                         3       0.00       0.00        0.00      96.72       3.27

CALIBRATION GAS SAMPLES FOR THIS RUN WERE ANALYSED AS

TIME SAMP       DELP IGAS         H2         CO         CH4        CO2        H2O        C
 903    1       1.00    1      25.06      25.03       25.09      24.80       0.00
 909    2       1.00    1      25.22      24.89       24.85      25.02       0.00
 916    3       0.00    1      25.21      24.82       25.08      24.87       0.00
 923    4       0.00    1      25.19      24.89       24.86      25.04       0.00
   0    0       0.00    2     100.00       0.00        0.00       0.00       0.00
1643   35       0.00    3       0.00       0.00        0.00      96.78       3.21
1658   36       0.00    3       0.00       0.00        0.00,     96.80       3.19

THE RELATIVE CALIBRATION
AREA COEFFICENTS ARE       0.018649  0.884115  0.736939  1.000000  0.756490  0.027902

 ATMOSPHERIC PRESSURE WAS  759.96 .

 THE WEIGHT OF CATALYST INITIALLY CHARGED TO THE REACTOR IS  0.252 GRAMS.

 THE GROSS WEIGHT OF THE CATALYST CARRIER AND SUSPENSION MECHANISM IS  31.843 GRAMS.
```

```
                               DATA TAKEN DURING RUN  21 ON 19 JUL 74

TIME SAMP      DELP IGAS       H2        CO       CH4        CO2       H2O        C
 930                                                                               0.543 GRAMS CARBON DEPOSITED

 933 REACTOR TEMPERATURE 550. DEGREES CENTIGRADE

 933 CHANGED INLET GAS TO     46.68      0.00      0.00      53.31      0.00              TOTAL FLOW 21.2 CC/SEC (STP)
1000                                                                               0.540 GRAMS CARBON DEPOSITED
1003    5      0.00    4      43.92      0.00      0.00      56.03      0.03
1016    6      0.00    4      44.07      0.00      0.00      55.81      0.10
1031    7     -2.00    5      37.10      6.65      0.00      50.32      5.91
1035                                                                               0.548 GRAMS CARBON DEPOSITED
1046    8     -1.00    5      37.26      6.69      0.00      49.99      6.04
1100                                                                               0.556 GRAMS CARBON DEPOSITED
1104    9      0.00    4      43.81      0.00      0.00      56.15      0.03
1117   10      0.00    4      44.12      0.00      0.00      55.83      0.03
1130   11     -2.00    5      36.85      6.75      0.00      50.53      5.85
1134                                                                               0.551 GRAMS CARBON DEPOSITED
1147   12     -1.00    5      36.65      7.13      0.00      49.82      6.38

1153 CHANGED INLET GAS TO     94.18      5.81      0.00       0.00      0.00              TOTAL FLOW 20.0 CC/SEC (STP)
1159   13      0.00    4      93.68      6.17      0.00       0.12      0.01
1204                                                                               0.647 GRAMS CARBON DEPOSITED
1213   14      0.00    4      93.90      6.04      0.00       0.05      0.00
1219   15     -2.00    5      92.03      3.17      1.82       0.32      2.64
1224                                                                               0.787 GRAMS CARBON DEPOSITED

1228 CHANGED INLET GAS TO     98.47      1.52      0.00       0.00      0.00              TOTAL FLOW 19.2 CC/SEC (STP)
1234   16     -2.00    5      96.74      0.35      1.20       0.03      1.66
1243                                                                               0.825 GRAMS CARBON DEPOSITED
1249   17      0.00    4      98.45      1.52      0.00       0.02      0.00
1255   18      0.00    4      98.55      1.38      0.00       0.06      0.00
1302   19     -1.00    5      97.02      0.42      1.13       0.03      1.37
1307                                                                               0.853 GRAMS CARBON DEPOSITED
1316   20     -1.00    5      97.09      0.45      1.10       0.02      1.33
1330   21      0.00    4      98.47      1.48      0.00       0.03      0.00
1334                                                                               0.878 GRAMS CARBON DEPOSITED
1337   22      0.00    4      98.56      1.41      0.00       0.02      0.00
1344   23      0.00    5      97.05      0.49      1.09       0.03      1.32
1359   24      0.00    5      96.91      0.47      1.08       0.02      1.49
1403                                                                               0.905 GRAMS CARBON DEPOSITED
1414   25      0.00    4      98.47      1.50      0.00       0.01      0.00
1427   26      0.00    4      98.60      1.37      0.00       0.02      0.00
1437                                                                               0.936 GRAMS CARBON DEPOSITED
1443   27      0.00    5      96.92      0.45      1.14       0.02      1.44
1457   28     -1.00    5      96.53      0.52      1.23       0.07      1.62
1511                                                                               0.972 GRAMS CARBON DEPOSITED
1516   29      0.00    4      98.46      1.53      0.00       0.00      0.00
1520   30      0.00    4      98.61      1.36      0.00       0.01      0.00
1529   31      0.00    5      96.99      0.55      1.07       0.02      1.34
1535                                                                               0.978 GRAMS CARBON DEPOSITED
1544                                                                               0.993 GRAMS CARBON DEPOSITED
1547   32      0.00    5      96.66      0.68      1.14       0.02      1.49
```

```
1603                                                                     1.012 GRAMS CARBON DEPOSITED
1605   33     0.00   4    97.72     2.09     0.00     0.17     0.00
```

```
                                 DATA TAKEN DURING RUN  22 ON  22 JUL 7

TIME SAMP       DELP IGAS       H2         CO        CH4        CO2        H2O          C
1324    1       3.00    1   4999.0  244330.0  195550.0  262495.0        0.0
1333    2       2.00    1   4735.0  225509.0  188639.0  252440.0        0.0
1340    3       0.00    1   5086.0  234441.0  194825.0  266693.0        0.0
1347    4       0.00    1   4749.0  222380.0  185933.0  253162.0        0.0
1359    5       1.00    1   5157.0  235850.0  196185.0  268623.0        0.0
1407    6       0.00    2  27246.0       0.0       0.0       0.0      654.0
1419    7       0.00    2  29698.0       0.0       0.0       0.0        0.0
1425    8       0.00    2  27476.0       0.0       0.0       0.0        0.0
1429    9       0.00    2  29791.0       0.0       0.0       0.0        0.0

1354                    8    550.0

1354                    6     30.0       0.0       0.0       0.0        0.0
1354                    7                                                       31.850

1401                    6     48.0       0.0       0.0       0.0        0.0
1433                    7                                                       31.857

1437                    6     16.0      34.0       0.0       0.0        0.0
1449   11       0.00    4  11170.0  463267.0       0.0      62.0      119.0
1501                    7                                                       31.905
1504   12       0.00    4  12030.0  487695.0       0.0      44.0        0.0
1511   13      -1.00    5  10896.0  468716.0       0.0     486.0     2871.0
1525   14       0.00    5  11811.0  493936.0       0.0     561.0     3640.0
1530                    7                                                       31.974
1540   15       0.00    5  10906.0  471124.0       0.0     593.0     3006.0
1601                    7                                                       32.037
1609   17      -1.00    5  10960.0  473240.0       0.0     733.0     3747.0
1624   18      -1.00    5  11748.0  496529.0      32.0     732.0     5173.0
1629                    7                                                       32.129
1640   19      -1.00    5  10877.0  473431.0       0.0     804.0     4481.0
1654   20      -1.00    5  11754.0  495431.0      52.0    1029.0     6320.0
1700                    7                                                       32.248
```

```
                          DATA TAKEN DURING RUN  22 ON  22 JUL 7



THE CALIBRATION GASES ARE KNOWN TO BE
                    IGAS          H2         CO        CH4        CO2        H2O
                       1       25.17      24.94      24.97      24.94       0.00
                       2      100.00       0.00       0.00       0.00       0.00
                       3        0.00       0.00       0.00     100.00       0.00

CALIBRATION GAS SAMPLES FOR THIS RUN WERE ANALYSED AS

TIME SAMP      DELP IGAS          H2         CO        CH4        CO2        H2O          C
1324    1      3.00    1       24.88      25.63      24.87      24.59       0.00
1333    2      2.00    1       25.05      24.86      25.22      24.85       0.00
1340    3      0.00    1       25.30      24.70      24.89      25.09       0.00
1347    4      0.00    1       25.24      24.66      25.00      25.07       0.00
1359    5      1.00    1       25.39      24.65      24.86      25.07       0.00
1407    6      0.00    2       99.90       0.00       0.00       0.00       0.09
1419    7      0.00    2      100.00       0.00       0.00       0.00       0.00
1425    8      0.00    2      100.00       0.00       0.00       0.00       0.00
1429    9      0.00    2      100.00       0.00       0.00       0.00       0.00

THE RELATIVE CALIBRATION
AREA COEFFICENTS ARE      0.018789   0.892943   0.736501   1.000000   0.689999   0.027359

 ATMOSPHERIC PRESSURE WAS  759.96 .

 THE WEIGHT OF CATALYST INITIALLY CHARGED TO THE REACTOR IS  0.251 GRAMS.

 THE GROSS WEIGHT OF THE CATALYST CARRIER AND SUSPENSION MECHANISM IS  31.850 GRAMS.
```

```
                              DATA TAKEN DURING RUN  22 ON  22 JUL 7

TIME SAMP     DELP IGAS        H2        CO        CH4       CO2       H2O        C

1354 REACTOR TEMPERATURE 550. DEGREES CENTIGRADE


1354 CHANGED INLET GAS TO    100.00      0.00      0.00      0.00      0.00          TOTAL FLOW 18.6 CC/SEC (STP)
1354                                                                          0.000 GRAMS CARBON DEPOSITED

1401 CHANGED INLET GAS TO    100.00      0.00      0.00      0.00      0.00          TOTAL FLOW 29.7 CC/SEC (STP)
1433                                                                          0.006 GRAMS CARBON DEPOSITED

1437 CHANGED INLET GAS TO     49.98     50.01      0.00      0.00      0.00          TOTAL FLOW 19.8 CC/SEC (STP)
1449   11      0.00    4      49.02     50.95      0.00      0.00      0.01
1501                                                                          0.055 GRAMS CARBON DEPOSITED
1504   12      0.00    4      49.20     50.79      0.00      0.00      0.00
1511   13     -1.00    5      48.02     51.51      0.00      0.04      0.40
1525   14      0.00    5      48.26     51.19      0.00      0.05      0.48
1530                                                                          0.124 GRAMS CARBON DEPOSITED
1540   15      0.00    5      47.91     51.60      0.00      0.05      0.42
1601                                                                          0.186 GRAMS CARBON DEPOSITED
1609   17     -1.00    5      47.83     51.56      0.00      0.07      0.52
1624   18     -1.00    5      47.91     51.32      0.00      0.06      0.69
1629                                                                          0.278 GRAMS CARBON DEPOSITED
1640   19     -1.00    5      47.62     51.66      0.00      0.07      0.63
1654   20     -1.00    5      47.89     51.16      0.00      0.09      0.84
1700                                                                          0.397 GRAMS CARBON DEPOSITED
```

```
                             DATA TAKEN DURING RUN  25 ON 25 JUL 74

TIME SAMP      DELP IGAS         H2         CO        CH4        CO2        H2O           C
1226    1      0.00    1     4774.0   226036.0   186882.0   254713.0        0.0
1234    2      0.00    1     5142.0   235772.0   196307.0   268089.0        0.0
1241    3     -1.00    1     4823.0   226030.0   188823.0   255854.0        0.0
1249    4      0.00    1     5167.0   238436.0   197625.0   269628.0        0.0
1703   24      0.00    3        0.0        0.0        0.0  1059528.2    23966.0
1718   25      0.00    3        0.0        0.0        0.0  1015552.1    22910.0
1219                   7                                                           31.878

1220                   8      550.0

1220                   6       48.0        0.0        0.0        0.0        0.0
1255    5      0.00    4    27632.0        0.0        0.0        0.0        0.0
1255    5      0.00    2    27632.0        0.0        0.0        0.0        0.0
1301                   7                                                           31.894
1304    6      0.00    4    29866.0        0.0        0.0        0.0        0.0
1304    6      0.00    2    29866.0        0.0        0.0        0.0        0.0
1310    7      0.00    5    27713.0        0.0        0.0        0.0      169.0
1323    8      0.00    5    29889.0        0.0        0.0      121.0        0.0
1329                   7                                                           31.905

1333                   6       16.0       34.0        0.0        0.0        0.0
1336    9      0.00    4    11185.0   466165.0        0.0      137.0        0.0
1350   10      0.00    4    12027.0   490293.0        0.0      120.0        0.0
1357   11      0.00    4    11238.0   464877.0        0.0      208.0        0.0
1401                   7                                                           31.926
1406   12     -2.00    5    11740.0   495968.0        0.0      424.0     1750.0
1418   13     -2.00    5    10944.0   470130.0        0.0      386.0     1699.0
1430                   7                                                           31.971
1434   14     -2.00    5    11716.0   495180.0        0.0      722.0     2814.0
1449   15     -2.00    5    10931.0   471459.0        0.0      450.0     3344.0
1502                   7                                                           32.029
1506   16     -2.00    5    11733.0   495375.0        0.0      536.0     3713.0
1520   17     -2.00    5    10908.0   470597.0        0.0      625.0     4389.0
1530                   7                                                           32.113
1535   18     -2.00    5    11681.0   494052.0      725.0     1440.0     5484.0
1550   19     -2.00    5    10841.0   469361.0        0.0      982.0     6524.0
1601                   7                                                           32.249
1606   20     -2.00    5    11682.0   493418.0     1688.0     2837.0     9667.0
1618   21     -2.00    5    10810.0   468112.0        0.0     4083.0     9930.0
1628   22     -2.00    5    11618.0   456438.0     1746.0    27499.0    22589.0
1630                   7                                                           32.606
```

```
                              DATA TAKEN DURING RUN  25 ON 25 JUL 74



THE CALIBRATION GASES ARE KNOWN TO BE
                    IGAS       H2          CO         CH4         CO2         H2O
                       1     25.17       24.94       24.97       24.94        0.00
                       2    100.00        0.00        0.00        0.00        0.00
                       3      0.00        0.00        0.00       96.98        3.01

CALIBRATION GAS SAMPLES FOR THIS RUN WERE ANALYSED AS

TIME SAMP      DELP IGAS       H2          CO         CH4         CO2         H2O          C
1226    1      0.00    1     25.07       25.02       24.95       24.94        0.00
1234    2      0.00    1     25.28       24.81       24.93       24.96        0.00
1241    3     -1.00    1     25.13       24.87       25.07       24.91        0.00
1249    4      0.00    1     25.20       24.92       24.92       24.93        0.00
1703   24      0.00    3      0.00        0.00        0.00       97.03        2.96
1719   25      0.00    3      0.00        0.00        0.00       97.03        2.96
1255    5      0.00    2    100.00        0.00        0.00        0.00        0.00
1304    6      0.00    2    100.00        0.00        0.00        0.00        0.00

THE RELATIVE CALIBRATION
AREA COEFFICENTS ARE        0.018808    0.884673    0.733306    1.000000    0.739266    0.027350

 ATMOSPHERIC PRESSURE WAS  759.96 .

 THE WEIGHT OF CATALYST INITIALLY CHARGED TO THE REACTOR IS  0.249 GRAMS.

 THE GROSS WEIGHT OF THE CATALYST CARRIER AND SUSPENSION MECHANISM IS  31.872 GRAMS.
```

```
                                  DATA TAKEN DURING RUN  25 ON 25 JUL 74

TIME SAMP       DELP IGAS        H2         CO        CH4        CO2        H2O         C
1219                                                                                0.006 GRAMS CARBON DEPOSITED

1220 REACTOR TEMPERATURE 550. DEGREES CENTIGRADE


1220 CHANGED INLET GAS TO    100.00       0.00       0.00       0.00       0.00          TOTAL FLOW 29.7 CC/SEC (STP)
1255    5       0.00    4    100.00       0.00       0.00       0.00       0.00
1301                                                                                0.021 GRAMS CARBON DEPOSITED
1304    6       0.00    4    100.00       0.00       0.00       0.00       0.00
1310    7       0.00    5     99.97       0.00       0.00       0.00       0.02
1323    8       0.00    5     99.98       0.00       0.00       0.01       0.00
1329                                                                                0.033 GRAMS CARBON DEPOSITED

1333 CHANGED INLET GAS TO     49.98      50.01       0.00       0.00       0.00          TOTAL FLOW 19.8 CC/SEC (STP)
1336    9       0.00    4     48.69      51.29       0.00       0.01       0.00
1350   10       0.00    4     48.86      51.12       0.00       0.01       0.00
1357   11       0.00    4     48.85      51.12       0.00       0.02       0.00
1401                                                                                0.054 GRAMS CARBON DEPOSITED
1406   12      -2.00    5     47.96      51.77       0.00       0.03       0.21
1418   13      -2.00    5     47.92      51.81       0.00       0.03       0.22
1430                                                                                0.098 GRAMS CARBON DEPOSITED
1434   14      -2.00    5     47.89      51.69       0.00       0.06       0.35
1449   15      -2.00    5     47.72      51.79       0.00       0.04       0.43
1502                                                                                0.157 GRAMS CARBON DEPOSITED
1506   16      -2.00    5     47.86      51.62       0.00       0.04       0.46
1520   17      -2.00    5     47.65      51.70       0.00       0.06       0.57
1530                                                                                0.241 GRAMS CARBON DEPOSITED
1535   18      -2.00    5     47.65      51.43       0.09       0.13       0.68
1550   19      -2.00    5     47.44      51.59       0.00       0.09       0.85
1601                                                                                0.376 GRAMS CARBON DEPOSITED
1606   20      -2.00    5     47.32      51.01       0.21       0.25       1.19
1618   21      -2.00    5     47.10      51.20       0.00       0.39       1.29
1628   22      -2.00    5     47.19      47.26       0.21       2.51       2.79
1630                                                                                0.733 GRAMS CARBON DEPOSITED
```

```
                                   DATA TAKEN DURING RUN  26 ON 26 JUL 74

TIME SAMP       DELP IGAS       H2        CO       CH4       CO2       H2O           C
1025   1        0.00    1   5109.0  237105.0  196164.0  267771.0       0.0
1031   2        0.00    1   4798.0  227107.0  190170.0  256069.0       0.0
1039   3        1.00    1   5174.0  236930.0  197381.0  269599.0       0.0
1045   4        0.00    1   4895.0  224868.0  187475.0  257632.0       0.0
1606  28        0.00    2  28052.0       0.0       0.0     232.0       0.0
1613  29        0.00    2  30209.0       0.0       0.0       0.0       0.0
1625  30        0.00    3      0.0       0.0       0.0 1019568.1   22539.0
1641  31        0.00    3      0.0       0.0       0.0 1067184.2   24167.0
1005                    7                                                     32.601

1009                    6     16.0       0.0       0.0      30.0       0.0

1031                    8    400.0
1053   5        0.00    4  11227.0       0.0       0.0  562948.1     242.0
1100                    7                                                     32.618
1107   6        0.00    4  10570.0       0.0       0.0  538988.1       0.0
1115   7       -2.00    5  10798.0    5062.0      20.0  565585.1    5846.0
1131   8       -2.00    5  10096.0    4507.0       0.0  541436.1    4737.0
1135                    7                                                     32.620
1146   9        0.00    4  11282.0       0.0       0.0  565817.1       0.0
1154  10        0.00    4  10438.0       0.0       0.0  538774.1       0.0
1200                    7                                                     32.620
1204  11       -1.00    5  10863.0    6731.0       0.0  568898.1    4752.0
1217  12       -1.00    5  10125.0    3227.0       0.0  544723.1    3639.0
1232  13       -1.00    5  10907.0    3988.0       0.0  569443.1    5588.0
1235                    7                                                     32.620
1248  14        0.00    4  10475.0       0.0       0.0  540682.1       0.0
1257  15        0.00    4  11298.0       0.0       0.0  566709.1       0.0
1301                    7                                                     32.620
1305  16       -2.00    5  10121.0    4145.0       0.0  544540.1    4355.0
1319  17       -1.00    5  10872.0    3191.0       0.0  571978.1    3423.0
1333                    7                                                     32.617

1334                    6     30.5       0.0       0.0       0.0       0.0

1346                    6     30.5       3.5       0.0       0.0       0.0
1349  18        0.00    4  25876.0   48423.0       0.0     580.0       0.0
1355  19        0.00    4  28002.0   50433.0       0.0     424.0       0.0
1403   2        0.00    5  25797.0   50293.0      62.0     449.0     977.0
1405                    7                                                     32.621
1416  21       -2.00    5  27898.0   53066.0      92.0     315.0     690.0
1430  22        0.00    4  25987.0   49108.0      83.0     213.0       0.0
1433                    7                                                     32.616
1445  23        0.00    4  28119.0   50685.0       0.0     245.0       0.0

1458                    6     16.0      34.0       0.0       0.0       0.0
1507                    7                                                     32.616
1517  25       -1.00    5  11846.0  502223.0       0.0     244.0     304.0
1531  26        0.00    4  11291.0  471559.0       0.0     121.0       0.0
1534                    7                                                     32.621
1543  27       -2.00    5  11837.0  503031.0       0.0     241.0       0.0
1602                    7                                                     32.621
```

```
                         DATA TAKEN DURING RUN  26 ON 26 JUL 74



THE CALIBRATION GASES ARE KNOWN TO BE
                    IGAS        H2        CO       CH4       CO2       H2O
                       1     25.17     24.94     24.97     24.94      0.00
                       2    100.00      0.00      0.00      0.00      0.00
                       3      0.00      0.00      0.00     97.01      2.98

CALIBRATION GAS SAMPLES FOR THIS RUN WERE ANALYSED AS

TIME SAMP        DELP IGAS        H2        CO       CH4       CO2       H2O          C
1025    1        0.00    1     25.13     25.02     24.91     24.92      0.00
1031    2        0.00    1     24.95     24.99     25.19     24.85      0.00
1038    3        1.00    1     25.25     24.86     24.93     24.95      0.00
1045    4        0.00    1     25.36     24.76     24.84     25.02      0.00
1606   28        0.00    2     99.97      0.00      0.00      0.02      0.00
1613   29        0.00    2    100.00      0.00      0.00      0.00      0.00
1625   30        0.00    3      0.00      0.00      0.00     97.11      2.88
1641   31        0.00    3      0.00      0.00      0.00     97.04      2.95

THE RELATIVE CALIBRATION
AREA COEFFICENTS ARE      0.018824  0.862077  0.732837  1.000000  0.744010  0.027657

 ATMOSPHERIC PRESSURE WAS  759.96 .

 THE WEIGHT OF CATALYST INITIALLY CHARGED TO THE REACTOR IS  0.249 GRAMS.

 THE GROSS WEIGHT OF THE CATALYST CARRIER AND SUSPENSION MECHANISM IS  31.872 GRAMS.
```

```
                          DATA TAKEN DURING RUN  26 ON 26 JUL 74

TIME SAMP      DELP IGAS       H2        CO        CH4        CO2        H2O        C
1005                                                                           0.729 GRAMS CARBON DEPOSITED

1008 CHANGED INLET GAS TO     49.80      0.00      0.00      50.19       0.00         TOTAL FLOW 19.9 CC/SEC (STP)

1031 REACTOR TEMPERATURE 400. DEGREES CENTIGRADE

1053   5       0.00    4      47.01      0.00      0.00      52.95       0.03
1100                                                                           0.745 GRAMS CARBON DEPOSITED
1107   6       0.00    4      46.93      0.00      0.00      53.06       0.00
1115   7      -2.00    5      45.54      0.53      0.00      53.17       0.73
1131   8      -2.00    5      45.39      0.50      0.00      53.46       0.62
1135                                                                           0.747 GRAMS CARBON DEPOSITED
1146   9       0.00    4      46.99      0.00      0.00      53.00       0.00
1154  10       0.00    4      46.70      0.00      0.00      53.29       0.00
1200                                                                           0.747 GRAMS CARBON DEPOSITED
1204  11      -1.00    5      45.51      0.71      0.00      53.17       0.59
1217  12      -1.00    5      45.44      0.36      0.00      53.71       0.48
1232  13      -1.00    5      45.65      0.42      0.00      53.22       0.70
1235                                                                           0.747 GRAMS CARBON DEPOSITED
1248  14       0.00    4      46.68      0.00      0.00      53.31       0.00
1257  15       0.00    4      46.98      0.00      0.00      53.01       0.00
1301                                                                           0.747 GRAMS CARBON DEPOSITED
1305  16      -2.00    5      45.34      0.46      0.00      53.61       0.57
1319  17      -1.00    5      45.64      0.33      0.00      53.58       0.43
1333                                                                           0.744 GRAMS CARBON DEPOSITED

1334 CHANGED INLET GAS TO    100.00      0.00      0.00       0.00       0.00         TOTAL FLOW 18.9 CC/SEC (STP)

1346 CHANGED INLET GAS TO     94.87      5.12      0.00       0.00       0.00         TOTAL FLOW 19.9 CC/SEC (STP)
1349  18       0.00    4      94.53      5.40      0.00       0.05       0.00
1355  19       0.00    4      94.66      5.29      0.00       0.03       0.00
1403   2       0.00    5      94.21      5.60      0.00       0.04       0.12
1405                                                                           0.748 GRAMS CARBON DEPOSITED
1416  21      -2.00    5      94.29      5.57      0.01       0.02       0.08
1430  22       0.00    4      94.50      5.46      0.01       0.02       0.00
1433                                                                           0.743 GRAMS CARBON DEPOSITED
1445  23       0.00    4      94.66      5.30      0.00       0.02       0.00

1459 CHANGED INLET GAS TO     49.98     50.01      0.00       0.00       0.00         TOTAL FLOW 19.8 CC/SEC (STP)
1507                                                                           0.743 GRAMS CARBON DEPOSITED
1517  25      -1.00    5      47.75     52.18      0.00       0.02       0.03
1531  26       0.00    4      48.42     51.56      0.00       0.01       0.00
1534                                                                           0.748 GRAMS CARBON DEPOSITED
1549  27      -2.00    5      47.71     52.26      0.00       0.02       0.00
1602                                                                           0.748 GRAMS CARBON DEPOSITED
```

```
                                       DATA TAKEN DURING RUN  27 ON 29 JUL 74

TIME SAMP         DELP IGAS          H2         CO        CH4        CO2        H2O            C
 954    1         1.00    1      4828.0   231231.0   188750.0   255867.0        0.0
 902    2         0.00    1      5175.0   239008.0   197931.0   270452.0        0.0
 909    3         0.00    1      4882.0   227773.0   190070.0   258842.0        0.0
 916    4        -1.00    1      5171.0   237905.0   197655.0   270163.0        0.0
 926    5         0.00    2     27571.0        0.0        0.0        0.0        0.0
 934    6         0.00    2     29816.0        0.0        0.0        0.0        0.0
 940    7         0.00    2     27627.0        0.0        0.0        0.0        0.0
 950    9         0.00    2     27624.0        0.0        0.0        0.0        0.0
 955   10         0.00    2     29932.0        0.0        0.0        0.0        0.0
1527   41         0.00    3         0.0        0.0        0.0  1009338.1    21952.0
1544   42         0.00    3         0.0        0.0        0.0  1054219.2    22910.0
1616   44         0.00    3         0.0        0.0        0.0  1057194.2    22658.0
 923                      7                                                                32.627

 924                      6        32.0        0.0        0.0        0.0        0.0

 924                      8       475.0
1000                      7                                                                32.616

1003                      6        16.0       30.0        0.0        0.0        0.0

1004                      6        16.0        0.0        0.0       30.0        0.0
1008   11         0.00    4     10635.0       75.0        0.0   532805.1       77.0
1020   12         0.00    4     11340.0        0.0        0.0   560190.1        0.0
1029   13        -2.00    5      9501.0    27001.0       74.0   509243.0    23249.0
1031                      7                                                                32.623
1045   14        -2.00    5     10187.0    29814.0       91.0   534001.1    25157.0
1100   15         1.00    4     10642.0        0.0        0.0   538012.1        0.0
1104                      7                                                                32.630
1108   16         0.00    4     11238.0        0.0        0.0   558181.1        0.0
1117   17        -2.00    5      9335.0    32874.0      127.0   504704.0    30359.0
1133   18        -2.00    5      9895.0    36726.0      142.0   526367.1    29198.0
1143                      7                                                                32.631

1145                      6        16.0       34.0        0.0        0.0        0.0
1150   19         0.00    4     11204.0   465104.0        0.0        0.0     1253.0
1157   20         0.00    4     12067.0   490513.0        0.0        0.0      504.0
1203   21        -2.00    5     10891.0   470640.0        0.0     2154.0     4586.0
1217   22        -2.00    5     11701.0   494406.0      163.0     1321.0     4823.0
1230                      7                                                                32.768
1233   23         0.00    4     11170.0   468875.0        0.0        0.0      151.0
1240   24         0.00    4     11999.0   491804.0        0.0        0.0      210.0
1257   25        -2.00    5     10783.0   471611.0        0.0     1459.0     4793.0
1308   26        -2.00    5     11592.0   494485.0      160.0     1689.0     5051.0
1330   28         0.00    4     11971.0   493501.0        0.0        0.0      117.0
1335                      7                                                                32.980

1339                      6        32.0        0.0        0.0        0.0        0.0
1341   29         0.00    5     27726.0      301.0      282.0       85.0      962.0
1358   30         0.00    5     29871.0        0.0      561.0       96.0        0.0
1404   31         0.00    4     27640.0      119.0        0.0        0.0      570.0
1410   32         0.00    4     29843.0      426.0        0.0        0.0        0.0
```

```
1413                      7                                                                32.986
1430    34      0.00      5   29979.0       0.0     596.0     496.0       0.0
1433    35      0.00      5   27795.0     212.0     524.0       0.0       0.0
1436                      7                                                                32.974
1440    36      0.00      4   30023.0       0.0       0.0       0.0       0.0
1445    37      0.00      4   27769.0       0.0       0.0       0.0       0.0
1450    38      0.00      5   29995.0     207.0     630.0       0.0       0.0
1500    40      0.00      5   29969.0       0.0     619.0       0.0       0.0
1503                      7                                                                32.967
```

```
                              DATA TAKEN DURING RUN  27 ON 29 JUL 74


THE CALIBRATION GASES ARE KNOWN TO BE
                    IGAS        H2         CO        CH4        CO2        H2O
                       1     25.17      24.94      24.97      24.94       0.00
                       2    100.00       0.00       0.00       0.00       0.00
                       3      0.00       0.00       0.00      96.98       3.01

CALIBRATION GAS SAMPLES FOR THIS RUN WERE ANALYSED AS

TIME SAMP       DELP IGAS        H2         CO        CH4        CO2        H2O          C
 854    1       1.00    1     25.04      25.22      24.94      24.78       0.00
 902    2       0.00    1     25.22      24.85      24.94      24.97       0.00
 909    3       0.00    1     25.18      24.77      25.04      24.99       0.00
 916    4      -1.00    1     25.25      24.79      24.95      24.99       0.00
 926    5       0.00    2    100.00       0.00       0.00       0.00       0.00
 934    6       0.00    2    100.00       0.00       0.00       0.00       0.00
 940    7       0.00    2    100.00       0.00       0.00       0.00       0.00
 950    9       0.00    2    100.00       0.00       0.00       0.00       0.00
 955   10       0.00    2    100.00       0.00       0.00       0.00       0.00
1527   41       0.00    3      0.00       0.00       0.00      97.00       2.99
1544   42       0.00    3      0.00       0.00       0.00      97.01       2.98
1616   44       0.00    3      0.00       0.00       0.00      97.05       2.94

THE RELATIVE CALIBRATION
AREA COEFFICENTS ARE      0.018823  0.887913  0.732925  1.000000  0.705369  0.026953

 ATMOSPHERIC PRESSURE WAS  759.96 .

 THE WEIGHT OF CATALYST INITIALLY CHARGED TO THE REACTOR IS  0.250 GRAMS.

 THE GROSS WEIGHT OF THE CATALYST CARRIER AND SUSPENSION MECHANISM IS  31.872 GRAMS.
```

```
                                   DATA TAKEN DURING RUN  27 ON 29 JUL 74

TIME SAMP      DELP IGAS        H2         CO        CH4        CO2        H2O        C
 923                                                                                0.755 GRAMS CARBON DEPOSITED

 924 CHANGED INLET GAS TO   100.00       0.00       0.00       0.00       0.00          TOTAL FLOW 19.8 CC/SEC (STP)

 924 REACTOR TEMPERATURE 475. DEGREES CENTIGRADE

1000                                                                                0.743 GRAMS CARBON DEPOSITED

1003 CHANGED INLET GAS TO    53.11      46.88       0.00       0.00       0.00          TOTAL FLOW 18.6 CC/SEC (STP)

1004 CHANGED INLET GAS TO    49.80       0.00       0.00      50.19       0.00          TOTAL FLOW 19.9 CC/SEC (STP)
1008   11      0.00    4     47.57       0.00       0.00      52.40       0.01
1020   12      0.00    4     47.60       0.00       0.00      52.39       0.00
1029   13     -2.00    5     43.56       2.99       0.00      50.18       3.24
1031                                                                                0.750 GRAMS CARBON DEPOSITED
1045   14     -2.00    5     43.64       3.13       0.01      49.87       3.33
1100   15      1.00    4     47.36       0.00       0.00      52.63       0.00
1104                                                                                0.757 GRAMS CARBON DEPOSITED
1108   16      0.00    4     47.51       0.00       0.00      52.48       0.00
1117   17     -2.00    5     42.70       3.62       0.01      49.43       4.21
1133   18     -2.00    5     42.83       3.88       0.01      49.38       3.88
1143                                                                                0.758 GRAMS CARBON DEPOSITED

1145 CHANGED INLET GAS TO    49.98      50.01       0.00       0.00       0.00          TOTAL FLOW 19.8 CC/SEC (STP)
1150   19      0.00    4     48.95      50.86       0.00       0.00       0.17
1157   20      0.00    4     49.15      50.78       0.00       0.00       0.06
1203   21     -2.00    5     47.76      51.39       0.00       0.20       0.63
1217   22     -2.00    5     47.99      51.23       0.02       0.12       0.62
1230                                                                                0.896 GRAMS CARBON DEPOSITED
1233   23      0.00    4     48.77      51.20       0.00       0.00       0.02
1240   24      0.00    4     48.99      50.97       0.00       0.00       0.02
1257   25     -2.00    5     47.53      51.65       0.00       0.14       0.66
1308   26     -2.00    5     47.77      51.39       0.02       0.15       0.66
1330   28      0.00    4     48.86      51.11       0.00       0.00       0.01
1335                                                                                1.107 GRAMS CARBON DEPOSITED

1338 CHANGED INLET GAS TO   100.00       0.00       0.00       0.00       0.00          TOTAL FLOW 19.8 CC/SEC (STP)
1341   29      0.00    5     99.79       0.03       0.03       0.00       0.13
1358   30      0.00    5     99.92       0.00       0.06       0.00       0.00
1404   31      0.00    4     99.90       0.01       0.00       0.00       0.07
1410   32      0.00    4     99.95       0.04       0.00       0.00       0.00
1413                                                                                1.113 GRAMS CARBON DEPOSITED
1430   34      0.00    5     99.88       0.00       0.07       0.04       0.00
1433   35      0.00    5     99.90       0.02       0.06       0.00       0.00
1436                                                                                1.102 GRAMS CARBON DEPOSITED
1440   36      0.00    4    100.00       0.00       0.00       0.00       0.00
1445   37      0.00    4    100.00       0.00       0.00       0.00       0.00
1450   38      0.00    5     99.90       0.02       0.07       0.00       0.00
1500   40      0.00    5     99.92       0.00       0.07       0.00       0.00
1503                                                                                1.094 GRAMS CARBON DEPOSITED
```

```
                         DATA TAKEN DURING RUN  28 ON 30 JUL 74

TIME SAMP      DELP IGAS         H2         CO        CH4        CO2        H2O          C
1230    1     -1.00    1     4805.0   223979.0   185865.0   255204.0        0.0
1235    2      0.00    1     5134.0   235376.0   195880.0   268137.0        0.0
1240    3      0.00    1     4831.0   224022.0   186425.0   256066.0        0.0
1244    4      0.00    1     5151.0   235958.0   196628.0   269274.0        0.0
1250    5      0.00    2    27452.0        0.0        0.0        0.0        0.0
1258    6      0.00    2    29671.0        0.0        0.0        0.0        0.0
1305    7      0.00    2    27654.0        0.0        0.0        0.0        0.0
1309    8      0.00    2    29867.0        0.0        0.0        0.0        0.0
1610   23      0.00    3        0.0        0.0        0.0  1006204.1    18006.0
1624   24      1.00    3        0.0        0.0        0.0  1055619.2    24246.0
1640   25      0.00    3        0.0        0.0        0.0  1008936.1    24474.0
1658   26      1.00    3        0.0        0.0        0.0  1058620.2    22532.0

1225                   6       16.0        0.0        0.0        0.0        0.0

1225                   8      550.0
1300                   7                                                           31.794

1302                   6       30.0        0.0        0.0        0.0        0.0

1313                   6       16.0       34.0        0.0        0.0        0.0
1318    9      0.00    4    11309.0   465112.0        0.0       24.0      751.0
1329   10      0.00    4    12061.0   489027.0        0.0       68.0      273.0
1330                   7                                                           31.827
1340   11     -2.00    5    10784.0   471823.0        0.0      707.0     2490.0
1353   12     -1.00    5    11645.0   496489.0        0.0      421.0     3868.0
1400                   7                                                           31.884
1405   13     -1.00    5    10821.0   473025.0        0.0      643.0     4010.0
1417   14     -1.00    5    11672.0   496145.0        0.0      791.0     4326.0
1431                   7                                                           31.946
1440   16     -2.00    5    11675.0   495891.0        0.0      709.0     4499.0
1453   17     -1.00    5    10821.0   473237.0        0.0      719.0     4598.0
1500                   7                                                           32.026
1506   18     -2.00    5    11629.0   495837.0        0.0      837.0     5061.0
1517   19     -1.00    5    10818.0   471494.0      911.0     5726.0        0.0
1529   20      0.00    5    11611.0   495516.0       52.0      968.0     5868.0
1531                   7                                                           32.148
1540   21     -2.00    5    10770.0   470199.0        0.0     1141.0     7580.0
1545                   7                                                           32.208
1553   22      0.00    5    11578.0   495858.0      886.0     1652.0     8507.0
1603                   7                                                           32.317

1603                   6       30.0        0.0        0.0        0.0        0.0
```

```
                              DATA TAKEN DURING RUN  28 ON 30 JUL 74


THE CALIBRATION GASES ARE KNOWN TO BE
                    IGAS          H2          CO         CH4         CO2         H2O
                       1       25.17       24.94       24.97       24.94        0.00
                       2      100.00        0.00        0.00        0.00        0.00
                       3        0.00        0.00        0.00       96.79        3.20

CALIBRATION GAS SAMPLES FOR THIS RUN WERE ANALYSED AS

TIME SAMP       DELP IGAS         H2          CO         CH4         CO2         H2O           C
1230    1      -1.00    1      25.15       24.94       24.94       24.95        0.00
1235    2       0.00    1      25.18       24.91       24.98       24.91        0.00
1240    3       0.00    1      25.19       24.88       24.95       24.96        0.00
1244    4       0.00    1      25.17       24.89       24.99       24.93        0.00
1250    5       0.00    2     100.00        0.00        0.00        0.00        0.00
1258    6       0.00    2     100.00        0.00        0.00        0.00        0.00
1305    7       0.00    2     100.00        0.00        0.00        0.00        0.00
1309    8       0.00    2     100.00        0.00        0.00        0.00        0.00
1610   23       0.00    3       0.00        0.00        0.00       97.36        2.63
1624   24       1.00    3       0.00        0.00        0.00       96.64        3.35
1640   25       0.00    3       0.00        0.00        0.00       96.46        3.53
1658   26       1.00    3       0.00        0.00        0.00       96.88        3.11

THE RELATIVE CALIBRATION
AREA COEFFICENTS ARE      0.018815    0.877714    0.728418    1.000000    0.662500    0.027256

 ATMOSPHERIC PRESSURE WAS  759.96 .

 THE WEIGHT OF CATALYST INITIALLY CHARGED TO THE REACTOR IS  0.250 GRAMS.

 THE GROSS WEIGHT OF THE CATALYST CARRIER AND SUSPENSION MECHANISM IS  31.785 GRAMS.
```

```
                                   DATA TAKEN DURING RUN  28 ON 30 JUL 74

TIME SAMP      DELP IGAS        H2        CO        CH4        CO2        H2O        C

1225 CHANGED INLET GAS TO   100.00      0.00       0.00       0.00       0.00            TOTAL FLOW  9.9 CC/SEC (STP)

1225 REACTOR TEMPERATURE 550. DEGREES CENTIGRADE

1300                                                                           0.008 GRAMS CARBON DEPOSITED

1302 CHANGED INLET GAS TO   100.00      0.00       0.00       0.00       0.00            TOTAL FLOW 18.6 CC/SEC (STP)

1313 CHANGED INLET GAS TO    49.98     50.01       0.00       0.00       0.00            TOTAL FLOW 19.6 CC/SEC (STP)
1319   9        0.00   4     48.75     51.13       0.00       0.00       0.10
1329  10        0.00   4     48.80     51.15       0.00       0.00       0.03
1330                                                                           0.041 GRAMS CARBON DEPOSITED
1340  11       -2.00   5     47.29     52.27       0.00       0.06       0.36
1353  12       -1.00   5     47.47     51.95       0.00       0.03       0.53
1400                                                                           0.098 GRAMS CARBON DEPOSITED
1405  13       -1.00   5     47.20     52.14       0.00       0.06       0.58
1417  14       -1.00   5     47.48     51.83       0.00       0.07       0.59
1431                                                                           0.160 GRAMS CARBON DEPOSITED
1440  16       -2.00   5     47.49     51.81       0.00       0.06       0.62
1453  17       -1.00   5     47.14     52.11       0.00       0.06       0.67
1500                                                                           0.240 GRAMS CARBON DEPOSITED
1506  18       -2.00   5     47.37     51.84       0.00       0.07       0.70
1517  19       -1.00   5     47.26     52.05       0.12       0.55       0.00
1529  20        0.00   5     47.31     51.77       0.00       0.08       0.81
1531                                                                           0.362 GRAMS CARBON DEPOSITED
1540  21       -2.00   5     46.98     51.79       0.00       0.11       1.10
1545                                                                           0.422 GRAMS CARBON DEPOSITED
1553  22        0.00   5     46.98     51.57       0.11       0.15       1.17
1603                                                                           0.531 GRAMS CARBON DEPOSITED

1603 CHANGED INLET GAS TO   100.00      0.00       0.00       0.00       0.00            TOTAL FLOW 18.6 CC/SEC (STP)
```

```
                                   DATA TAKEN DURING RUN  29 ON 31 JUL 74

TIME SAMP        DELP IGAS          H2         CO        CH4        CO2        H2O          C

5515 F003 ERROR
 949    1        0.00    1      4920.0   226604.0   188024.0   257881.0        0.0
 956    2       -1.00    1      5122.0   238008.0   197331.0   270012.0        0.0
1003    3        0.00    1      4892.0   226678.0   188925.0   258207.0        0.0
1009    4        1.00    1      5224.0   238070.0   198263.0   271522.0        0.0
1705   29        0.00    2     28275.0        0.0        0.0       30.0      760.0
1710   30        0.00    2     30530.0        0.0        0.0       64.0      859.0

1034                     8       550.0

1034                     6        30.0        0.0        0.0        0.0       22.1
1035                     7                                                               32.322
1044    5        0.00    4     26920.0        0.0        0.0        0.0    20345.0
1058    6        0.00    4     28908.0        0.0        0.0      192.0    22566.0
1105                     7                                                               32.321

1114                     6        16.0        0.0        0.0       30.0       21.7
1117    7        0.00    4      9887.0        0.0        0.0   536857.1    21163.0
1133    8        0.00    4     10484.0        0.0        0.0   564560.1    22109.0
1136                     7                                                               32.321
1150    9       -2.00    5      8899.0    20310.0        0.0   526596.1    38056.0
1206   10       -2.00    5      9511.0    22515.0        0.0   551278.1    39691.0

1221                     6        32.0        1.0        0.0        0.0        0.0
1223                     7                                                               32.319
1225   11        0.00    4     26201.0        0.0        0.0     1385.0    21889.0
1240   12        0.00    4     28305.0    16685.0        0.0      435.0    23413.0
1253   13       -2.00    5     26087.0    14337.0      498.0     1991.0    18481.0
1308                     7                                                               32.330
1310   14       -2.00    5     28206.0    15048.0      596.0      606.0    22773.0
1325   15        0.00    4     26343.0    15407.0        0.0      216.0    22207.0
1330                     7                                                               32.327
1339   16        0.00    4     28274.0    17033.0        0.0      222.0    23227.0
1355   17       -2.00    5     26032.0    13675.0      565.0      800.0    22540.0
1400                     7                                                               32.333
1410   18       -2.00    5     28112.0    14395.0      765.0      753.0    23611.0
1425   19       -2.00    4     26277.0    15609.0        0.0      222.0    27322.0
1435                     7                                                               32.334
1441   20        0.00    4     28395.0    21756.0        0.0     1782.0    25667.0
1456   21       -2.00    5     26322.0    14462.0     1383.0     1089.0    24481.0
1503                     7                                                               32.339

1505                     6        32.0        3.4        0.0        0.0        0.0
1517   22       -1.00    5     26926.0    48064.0     3078.0     3449.0    27674.0
1523                     7                                                               32.379
1526   23        0.00    4     25182.0    49798.0        0.0       74.0    24259.0
1541                     7                                                               32.420
1543   24        0.00    4     27229.0    53199.0        0.0       42.0    24283.0
1559   25       -1.00    5     25010.0    42284.0     3489.0     3790.0    28724.0
1603                     7                                                               32.454
1615   26       -2.00    5     26841.0    43332.0     3963.0     4125.0    28333.0
```

```
1620                7                                                             32.497

1620                6      32.0       0.0       0.0       0.0       0.0
1645    27   0.00   4   27258.0       0.0       0.0      63.0   25093.0
1651    28   0.00   4   30462.0       0.0       0.0       0.0    3001.0
```

```
                        DATA TAKEN DURING RUN  29 ON 31 JUL 74



THE CALIBRATION GASES ARE KNOWN TO BE
                     IGAS         H2         CO        CH4        CO2        H2O
                        1      25.17      24.94      24.97      24.94       0.00
                        2     100.00       0.00       0.00       0.00       0.00
                        3       0.00       0.00       0.00     100.00       0.00

CALIBRATION GAS SAMPLES FOR THIS RUN WERE ANALYSED AS

TIME SAMP       DELP IGAS        H2         CO        CH4        CO2        H2O          C
 949     1      0.00    1     25.30      24.88      24.89      24.91       0.00
 956     2     -1.00    1     24.99      25.01      25.01      24.97       0.00
1003     3      0.00    1     25.18      24.87      25.00      24.93       0.00
1009     4      1.00    1     25.23      24.85      24.96      24.94       0.00
1705    29      0.00    2     99.89       0.00       0.00       0.00       0.10
1710    30      0.00    2     99.88       0.00       0.00       0.00       0.11

THE RELATIVE CALIBRATION
AREA COEFFICENTS ARE       0.018877  0.879786  0.729575  1.000000  0.689999  0.027733

 ATMOSPHERIC PRESSURE WAS  759.96 .

 THE WEIGHT OF CATALYST INITIALLY CHARGED TO THE REACTOR IS  0.250 GRAMS.

 THE GROSS WEIGHT OF THE CATALYST CARRIER AND SUSPENSION MECHANISM IS  31.785 GRAMS.
```

```
                              DATA TAKEN DURING RUN  29 ON 31 JUL 74

TIME SAMP       DELP IGAS        H2         CO        CH4        CO2        H2O        C

1034 REACTOR TEMPERATURE 550. DEGREES CENTIGRADE


1034 CHANGED INLET GAS TO      97.17       0.00       0.00       0.00       2.82             TOTAL FLOW 19.1 CC/SEC (STP)
1035                                                                                  0.536 GRAMS CARBON DEPOSITED
1044     5       0.00     4    97.10       0.00       0.00       0.00       2.89
1059     6       0.00     4    96.95       0.00       0.00       0.01       3.03
1105                                                                                  0.535 GRAMS CARBON DEPOSITED

1114 CHANGED INLET GAS TO      48.42       0.00       0.00      48.80       2.77             TOTAL FLOW 20.4 CC/SEC (STP)
1117     7       0.00     4    44.34       0.00       0.00      52.64       3.00
1133     8       0.00     4    44.24       0.00       0.00      52.76       2.99
1136                                                                                  0.535 GRAMS CARBON DEPOSITED
1150     9      -2.00     5    40.76       2.26       0.00      51.57       5.40
1206    10      -2.00     5    40.86       2.38       0.00      51.38       5.36

1221 CHANGED INLET GAS TO      98.55       1.44       0.00       0.00       0.00             TOTAL FLOW 20.1 CC/SEC (STP)
1223                                                                                  0.533 GRAMS CARBON DEPOSITED
1225    11       0.00     4    96.69       0.00       0.00       0.13       3.16
1240    12       0.00     4    95.07       1.75       0.00       0.04       3.13
1253    13      -2.00     5    95.47       1.61       0.06       0.19       2.65
1308                                                                                  0.544 GRAMS CARBON DEPOSITED
1310    14      -2.00     5    95.21       1.58       0.07       0.05       3.06
1325    15       0.00     4    95.12       1.71       0.00       0.02       3.14
1330                                                                                  0.541 GRAMS CARBON DEPOSITED
1339    16       0.00     4    95.07       1.79       0.00       0.02       3.11
1355    17      -2.00     5    95.08       1.53       0.07       0.07       3.22
1400                                                                                  0.547 GRAMS CARBON DEPOSITED
1410    18      -2.00     5    95.12       1.52       0.09       0.07       3.18
1425    19      -2.00     4    94.40       1.72       0.00       0.02       3.85
1435                                                                                  0.548 GRAMS CARBON DEPOSITED
1441    20       0.00     4    94.18       2.25       0.00       0.16       3.39
1456    21      -2.00     5    94.65       1.60       0.18       0.10       3.45
1503                                                                                  0.553 GRAMS CARBON DEPOSITED

1505 CHANGED INLET GAS TO      95.23       4.76       0.00       0.00       0.00             TOTAL FLOW 20.8 CC/SEC (STP)
1512    22      -1.00     5    90.62       5.00       0.38       0.31       3.67
1523                                                                                  0.593 GRAMS CARBON DEPOSITED
1526    23       0.00     4    91.09       5.48       0.00       0.00       3.40
1541                                                                                  0.634 GRAMS CARBON DEPOSITED
1543    24       0.00     4    91.25       5.52       0.00       0.00       3.21
1559    25      -1.00     5    90.47       4.65       0.46       0.36       4.03
1603                                                                                  0.668 GRAMS CARBON DEPOSITED
1615    26      -2.00     5    90.80       4.53       0.49       0.37       3.77
1620                                                                                  0.711 GRAMS CARBON DEPOSITED

1620 CHANGED INLET GAS TO     100.00       0.00       0.00       0.00       0.00             TOTAL FLOW 19.6 CC/SEC (STP)
1645    27       0.00     4    96.48       0.00       0.00       0.00       3.51
1651    28       0.00     4    99.60       0.00       0.00       0.00       0.39
```

```
                                        DATA TAKEN DURING RUN  30 ON 01 AUG 74

TIME SAMP       DELP IGAS        H2        CO       CH4       CO2       H2O         C
 926    1       1.00    1    4929.0  230575.0  190991.0  261174.0       0.0
 931    2       1.00    1    5249.0  240707.0  200166.0  273864.0       0.0
 936    3       0.00    1    4932.0  228740.0  190318.0  261032.0       0.0
 949    4       0.00    1    5219.0  239397.0  198958.0  272209.0       0.0
1646   31       0.00    2   28538.0       0.0       0.0     109.0       0.0
1653   32       0.00    2   30163.0       0.0       0.0     279.0       0.0
 913                    7                                                      32.495

 919                    6      29.8       0.0       0.0       0.0      23.7

 930                    8     550.0
 956    5       0.00    4   27015.0       0.0       0.0      31.0   23040.0
1003                    7                                                      32.494
1009    6       0.00    4   29074.0       0.0       0.0      44.0   22124.0
1022    7       0.00    5   27003.0       0.0       0.0      50.0   24522.0
1036    8       0.00    5   29102.0       0.0      46.0      34.0   23212.0
1040                    7                                                      32.482

1043                    6      29.8       3.4       0.0       3.0      23.7
1049    9       0.00    4   23177.0   45917.0       0.0   60826.0   26249.0
1103   10       0.00    4   24849.0   49589.0       0.0   64986.0   22971.0
1106                    7                                                      32.509
1117   11      -2.00    5   22072.0   61925.0    1861.0   44202.0   42817.0
1135   12      -2.00    5   23849.0   65896.0    2174.0   45095.0   42004.0
1139                    7                                                      32.545
1152   13      -2.00    5   22116.0   64987.0    2410.0   41739.0   47956.0
1206                    7                                                      32.569
1209   14      -2.00    5   23764.0   69869.0    3168.0   42872.0   47109.0
1225   15      -2.00    5   21935.0   71459.0    7105.0   44757.0   46974.0
1236                    7                                                      32.596
1241   16      -2.00    5   23656.0   69727.0    3422.0   42050.0   44513.0
1259   17      -2.00    5   21882.0   67224.0    3333.0   39517.0   47659.0
1310                    7                                                      32.629

1313                    6      26.6       6.8       0.0       6.0      23.7
1317   18       0.00    4   20929.0  101647.0       0.0  122819.0   25084.0
1332   19       0.00    4   19515.0   98068.0       0.0  118275.0   25312.0
1346   20      -2.00    5   19111.0  134263.0    3420.0   89568.0   56036.0
1352                    7                                                      32.712
1405   21      -2.00    5   17695.0  130719.0    3709.0   83043.0   59505.0
1413                    7                                                      32.750
1421   22      -2.00    5   18941.0  138082.0    4627.0   85993.0   57862.0
1426                    7                                                      32.774
1437   23      -2.00    5   17716.0  130070.0    5178.0   85895.0   59819.0
1444                    7                                                      32.807
1456   24      -2.00    5   18953.0  135107.0    7042.0   93523.0   59399.0
1500                    7                                                      32.833

1508                    6      32.0       0.0       0.0       0.0       0.0
```

```
                    DATA TAKEN DURING RUN  30 ON 01 AUG 74



THE CALIBRATION GASES ARE KNOWN TO BE
                    IGAS       H2       CO       CH4       CO2       H2O
                       1     25.17    24.94    24.97     24.94      0.00
                       2    100.00     0.00     0.00      0.00      0.00
                       3      0.00     0.00     0.00    100.00      0.00

CALIBRATION GAS SAMPLES FOR THIS RUN WERE ANALYSED AS

TIME SAMP       DELP IGAS       H2       CO       CH4       CO2       H2O          C
 926    1       1.00    1    25.11    24.98    24.97     24.91      0.00
 931    2       1.00    1    25.18    24.89    24.97     24.93      0.00
 936    3       0.00    1    25.19    24.86    24.95     24.97      0.00
 949    4       0.00    1    25.20    24.89    24.96     24.92      0.00
1646   31       0.00    2    99.98     0.00     0.00      0.01      0.00
1653   32       0.00    2    99.97     0.00     0.00      0.02      0.00

THE RELATIVE CALIBRATION
AREA COEFFICENTS ARE     0.018848  0.880434  0.729673  1.000000  0.689999  0.027426

 ATMOSPHERIC PRESSURE WAS  759.96 .

 THE WEIGHT OF CATALYST INITIALLY CHARGED TO THE REACTOR IS  0.250 GRAMS.

 THE GROSS WEIGHT OF THE CATALYST CARRIER AND SUSPENSION MECHANISM IS  31.785 GRAMS.
```

```
                                  DATA TAKEN DURING RUN  30 ON 01 AUG 74

TIME SAMP       DELP IGAS         H2         CO        CH4        CO2        H2O          C
 913                                                                                   0.709 GRAMS CARBON DEPOSITED

 919 CHANGED INLET GAS TO      96.96       0.00       0.00       0.00       3.03             TOTAL FLOW 19.0 CC/SEC (STP)

 930 REACTOR TEMPERATURE 550. DEGREES CENTIGRADE

 956    5       0.00    4      96.77       0.00       0.00       0.00       3.22
1003                                                                                   0.708 GRAMS CARBON DEPOSITED
1008    6       0.00    4      97.06       0.00       0.00       0.00       2.93
1022    7       0.00    5      96.57       0.00       0.00       0.00       3.42
1036    8       0.00    5      96.92       0.00       0.00       0.00       3.06
1040                                                                                   0.696 GRAMS CARBON DEPOSITED

1043 CHANGED INLET GAS TO      87.53       4.70       0.00       4.73       3.03             TOTAL FLOW 21.1 CC/SEC (STP)
1049    9       0.00    4      85.47       5.01       0.00       5.84       3.65
1103   10       0.00    4      85.86       5.15       0.00       5.94       3.04
1106                                                                                   0.723 GRAMS CARBON DEPOSITED
1117   11      -2.00    5      82.67       6.80       0.24       4.27       6.00
1135   12      -2.00    5      83.17       6.85       0.27       4.12       5.57
1139                                                                                   0.759 GRAMS CARBON DEPOSITED
1152   13      -2.00    5      81.96       7.06       0.31       3.99       6.65
1206                                                                                   0.783 GRAMS CARBON DEPOSITED
1209   14      -2.00    5      82.29       7.20       0.39       3.89       6.20
1225   15      -2.00    5      80.67       7.69       0.92       4.24       6.45
1236                                                                                   0.810 GRAMS CARBON DEPOSITED
1241   16      -2.00    5      82.57       7.24       0.42       3.84       5.90
1258   17      -2.00    5      81.75       7.35       0.43       3.80       6.65
1310                                                                                   0.843 GRAMS CARBON DEPOSITED

1313 CHANGED INLET GAS TO      78.10       9.39       0.00       9.46       3.03             TOTAL FLOW 21.1 CC/SEC (STP)
1317   18       0.00    4      74.84      10.63       0.00      11.20       3.31
1332   19       0.00    4      74.45      10.68       0.00      11.34       3.51
1346   20      -2.00    5      69.94      13.97       0.42       8.20       7.44
1352                                                                                   0.926 GRAMS CARBON DEPOSITED
1405   21      -2.00    5      68.99      14.25       0.48       7.97       8.28
1413                                                                                   0.965 GRAMS CARBON DEPOSITED
1421   22      -2.00    5      69.47      14.37       0.58       7.88       7.68
1426                                                                                   0.988 GRAMS CARBON DEPOSITED
1437   23      -2.00    5      68.71      14.11       0.67       8.20       8.28
1444                                                                                   1.021 GRAMS CARBON DEPOSITED
1456   24      -2.00    5      68.87      13.93       0.87       8.49       7.81
1500                                                                                   1.047 GRAMS CARBON DEPOSITED

1508 CHANGED INLET GAS TO     100.00       0.00       0.00       0.00       0.00             TOTAL FLOW 19.8 CC/SEC (STP)
```

```
                                DATA TAKEN DURING RUN  31 ON 05 AUG 74

TIME SAMP        DELP IGAS        H2        CO       CH4       CO2        H2O           C
 943    1        0.00    1    4759.0  241241.0  190278.0  254752.0        0.0
 951    2        0.00    1    5222.0  242025.0  199424.0  271748.0        0.0
 957    3       -1.00    1    4898.0  228840.0  190080.0  259993.0        0.0
1004    4        0.00    1    5265.0  240726.0  200029.0  273598.0        0.0
1012    5        0.00    2   28198.0       0.0       0.0       0.0      793.0
1026    6        0.00    2   30489.0       0.0       0.0       0.0      447.0
 903                    7                                                         31.889

 930                    8     550.0

 946                    6      48.0       0.0       0.0       0.0        0.0
1039                    7                                                         31.898

1043                    6      24.0      17.0       0.0       0.0        0.0
1046    7        0.00    4   19171.0  243243.0       0.0     548.0      308.0
1100    8        0.00    4   20649.0  255670.0       0.0      91.0      549.0
1114    9       -1.00    5   18915.0  245264.0      36.0     387.0     3308.0
1129   10       -2.00    5   20386.0  257430.0      69.0     386.0     3754.0
1131                    7                                                         31.981
1143   11       -1.00    5   18952.0  245831.0     128.0     354.0     4570.0
1159   12       -1.00    5   20348.0  258018.0     297.0     304.0     3733.0
1202                    7                                                         32.040
1213   13       -2.00    5   18917.0  247483.0     787.0     482.0     4255.0
1228   14       -2.00    5   20302.0  260462.0    2078.0    1769.0     4061.0
1231                    7                                                         32.108
1244   15       -2.00    5   18826.0  245414.0     258.0     418.0     4417.0
1259   16       -2.00    5   20233.0  256464.0     279.0     361.0     7317.0
1301                    7                                                         32.174
1314   17       -2.00    5   18853.0  246063.0     928.0     600.0     5454.0
1325   18       -2.00    5   20309.0  257075.0     897.0     442.0     5242.0
1335                    7                                                         32.271
1342   19       -2.00    5   18842.0  248036.0    3074.0    2574.0     7071.0
1359   20       -2.00    5   20232.0  256051.0     436.0     568.0     6855.0
1402                    7                                                         32.354
1413   21       -2.00    5   18851.0  245117.0    1052.0     639.0     7436.0
1428   22       -2.00    5   20208.0  254422.0     524.0     777.0     8605.0
1430                    7                                                         32.489
1443   23       -2.00    5   18807.0  244441.0    2381.0    1847.0     9544.0
1500   24       -2.00    5   20237.0  253464.0     767.0    1371.0    10338.0
1503                    7                                                         32.675

1503                    6      24.0       0.0       0.0       0.0        0.0

1508                    6      32.0       0.0       0.0       0.0        0.0
```

```
                          DATA TAKEN DURING RUN  31 ON 05 AUG 74



THE CALIBRATION GASES ARE KNOWN TO BE
                      IGAS         H2         CO        CH4        CO2        H2O
                         1      25.17      24.94      24.97      24.94       0.00
                         2     100.00       0.00       0.00       0.00       0.00
                         3       0.00       0.00       0.00     100.00       0.00

CALIBRATION GAS SAMPLES FOR THIS RUN WERE ANALYSED AS

TIME SAMP         DELP IGAS         H2         CO        CH4        CO2        H2O          C
 943    1         0.00    1      24.66      25.83      24.95      24.54       0.00
 951    2         0.00    1      25.31      24.73      24.96      24.99       0.00
 957    3        -1.00    1      25.29      24.57      25.00      25.12       0.00
1004    4         0.00    1      25.40      24.53      24.96      25.09       0.00
1012    5         0.00    2      99.88       0.00       0.00       0.00       0.11
1026    6         0.00    2      99.94       0.00       0.00       0.00       0.05

THE RELATIVE CALIBRATION                                 .
AREA COEFFICENTS ARE       0.018820  0.899897  0.734722  1.000000  0.689999  0.027604

 ATMOSPHERIC PRESSURE WAS  759.96 .

 THE WEIGHT OF CATALYST INITIALLY CHARGED TO THE REACTOR IS  0.250 GRAMS.

 THE GROSS WEIGHT OF THE CATALYST CARRIER AND SUSPENSION MECHANISM IS  31.889 GRAMS.
```

```
                                   DATA TAKEN DURING RUN  31 ON 05 AUG 74

TIME SAMP     DELP IGAS       H2        CO       CH4       CO2       H2O        C
 903                                                                         0.000 GRAMS CARBON DEPOSITED

 930 REACTOR TEMPERATURE 550. DEGREES CENTIGRADE


 946 CHANGED INLET GAS TO  100.00      0.00      0.00      0.00      0.00          TOTAL FLOW 29.7 CC/SEC (STP)
1039                                                                         0.008 GRAMS CARBON DEPOSITED

1043 CHANGED INLET GAS TO   74.99     25.00      0.00      0.00      0.00          TOTAL FLOW 19.8 CC/SEC (STP)
1046    7     0.00    4     73.73     26.16      0.00      0.05      0.04
1100    8     0.00    4     73.91     26.00      0.00      0.00      0.07
1114    9    -1.00    5     73.06     26.42      0.00      0.03      0.46
1129   10    -2.00    5     73.23     26.22      0.00      0.03      0.49
1131                                                                         0.091 GRAMS CARBON DEPOSITED
1143   11    -1.00    5     72.91     26.39      0.01      0.03      0.63
1159   12    -1.00    5     73.15     26.28      0.03      0.02      0.49
1202                                                                         0.150 GRAMS CARBON DEPOSITED
1213   13    -2.00    5     72.71     26.54      0.10      0.04      0.59
1229   14    -2.00    5     72.64     26.40      0.25      0.16      0.53
1231                                                                         0.218 GRAMS CARBON DEPOSITED
1244   15    -2.00    5     72.84     26.46      0.03      0.04      0.62
1258   16    -2.00    5     72.82     26.13      0.03      0.03      0.97
1301                                                                         0.284 GRAMS CARBON DEPOSITED
1314   17    -2.00    5     72.62     26.42      0.12      0.05      0.76
1325   18    -2.00    5     72.97     26.17      0.11      0.04      0.69
1335                                                                         0.381 GRAMS CARBON DEPOSITED
1342   19    -2.00    5     71.96     26.40      0.40      0.24      0.98
1359   20    -2.00    5     72.87     26.10      0.05      0.05      0.91
1402                                                                         0.464 GRAMS CARBON DEPOSITED
1413   21    -2.00    5     72.48     26.27      0.13      0.06      1.03
1429   22    -2.00    5     72.78     25.93      0.06      0.07      1.14
1430                                                                         0.599 GRAMS CARBON DEPOSITED
1443   23    -2.00    5     72.07     26.10      0.31      0.17      1.32
1500   24    -2.00    5     72.64     25.76      0.09      0.12      1.37
1503                                                                         0.785 GRAMS CARBON DEPOSITED

1503 CHANGED INLET GAS TO  100.00      0.00      0.00      0.00      0.00          TOTAL FLOW 14.8 CC/SEC (STP)

1508 CHANGED INLET GAS TO  100.00      0.00      0.00      0.00      0.00          TOTAL FLOW 19.8 CC/SEC (STP)
```

```
                                 DATA TAKEN DURING RUN  33 ON 13 AUG 74

TIME SAMP       DELP IGAS         H2         CO        CH4        CO2        H2O          C
1131                    7                                                                31.938

1131                    8      550.0

1138                    6       32.0        0.0        0.0        0.0        0.0
1134    2       0.00    1     5282.0   242698.0   201307.0   273461.0        0.0
1140    4       0.00    1     5333.0   242276.0   201604.0   276859.0        0.0
1149    5       0.00    1     5042.0   231729.0   192656.0   264302.0        0.0
1156    6       0.00    1     5371.0   244113.0   203067.0   278025.0        0.0
1205    7       0.00    1     5111.0   233146.0   193968.0   265992.0        0.0
1210    8       0.00    2    30982.0        0.0        0.0        0.0        0.0
1218    9      -1.00    2    28664.0        0.0        0.0        0.0        0.0
1225   10       0.00    2    30972.0        0.0        0.0        0.0        0.0
1232   11       0.00    2    29622.0        0.0        0.0        0.0        0.0

1243                    6       24.0       17.0        0.0        0.0        0.0
1248   12       0.00    4    20862.0   253391.0        0.0        0.0      661.0
1305                    7                                                                31.973
1310   14       0.00    4    20785.0   254646.0        0.0       47.0      360.0
1324   15       0.00    5    19121.0   244524.0      357.0      396.0     3773.0
1334                    7                                                                32.028
1339   16       0.00    5    20556.0   255887.0      115.0      363.0     3592.0
1355   17       0.00    5    19067.0   243911.0      130.0      292.0     4237.0
1403                    7                                                                32.078
1410   18       0.00    5    20526.0   256549.0      298.0      360.0     4032.0
1426   19       0.00    5    19082.0   245011.0      760.0      459.0     4141.0
1430                    7                                                                32.136
1441   20       0.00    5    20494.0   257078.0     1663.0     1347.0     4541.0
1459   21       0.00    5    19114.0   244002.0      386.0      374.0     4683.0
1500                    7                                                                32.215
1512   22       0.00    5    20580.0   255052.0      365.0      422.0     4969.0
1528   23       0.00    5    19147.0   243246.0      239.0      660.0     6422.0
1531                    7                                                                32.312
1545   24       0.00    5    20578.0   255209.0      310.0      726.0     7196.0
1549                    7                                                                32.361

1549                    6       16.0        0.0        0.0       30.0        0.0
1602   25       0.00    4    10906.0        0.0        0.0   551504.1      959.0
1616   26       0.00    4    11713.0        0.0        0.0   577255.1      689.0
1613   27       0.00    5     9333.0    47390.0        0.0   506556.0    40947.0
1634                    7                                                                32.361
1649   28      -1.00    5     9823.0    53474.0        0.0   525706.1    41091.0
```

```
                              DATA TAKEN DURING RUN  33 ON 13 AUG 74



THE CALIBRATION GASES ARE KNOWN TO BE
                         IGAS          H2         CO        CH4        CO2        H2O
                            1       25.17      24.94      24.97      24.94       0.00
                            2      100.00       0.00       0.00       0.00       0.00
                            3        0.00       0.00       0.00     100.00       0.00

CALIBRATION GAS SAMPLES FOR THIS RUN WERE ANALYSED AS

TIME SAMP        DELP IGAS          H2         CO        CH4        CO2        H2O          C
1104    2        0.00    1       25.10      25.03      25.03      24.82       0.00
1140    4        0.00    1       25.17      24.86      24.95      25.00       0.00
1149    5        0.00    1       25.19      24.88      24.94      24.97       0.00
1156    6        0.00    1       25.15      24.90      24.97      24.95       0.00
1205    7        0.00    1       25.27      24.85      24.92      24.94       0.00
1210    8        0.00    2      100.00       0.00       0.00       0.00       0.00
1219    9       -1.00    2      100.00       0.00       0.00       0.00       0.00
1225   10        0.00    2      100.00       0.00       0.00       0.00       0.00
1232   11        0.00    2      100.00       0.00       0.00       0.00       0.00

THE RELATIVE CALIBRATION
AREA COEFFICENTS ARE       0.019055   0.879851   0.729708   1.000000   0.689999   0.027369

 ATMOSPHERIC PRESSURE WAS  759.96 .

 THE WEIGHT OF CATALYST INITIALLY CHARGED TO THE REACTOR IS  0.250 GRAMS.

 THE GROSS WEIGHT OF THE CATALYST CARRIER AND SUSPENSION MECHANISM IS  31.938 GRAMS.
```

```
                              DATA TAKEN DURING RUN  33 ON 13 AUG 74

TIME SAMP      DELP IGAS        H2        CO        CH4       CO2       H2O       C
1131                                                                               0.000 GRAMS CARBON DEPOSITED

1131 REACTOR TEMPERATURE 550. DEGREES CENTIGRADE

1139 CHANGED INLET GAS TO     100.00      0.00      0.00      0.00      0.00           TOTAL FLOW 19.8 CC/SEC (STP)

1243 CHANGED INLET GAS TO      74.99     25.00      0.00      0.00      0.00           TOTAL FLOW 19.9 CC/SEC (STP)
1248   12      0.00    4       73.96     25.94      0.00      0.00      0.08
1305                                                                               0.034 GRAMS CARBON DEPOSITED
1310   14      0.00    4       73.84     26.10      0.00      0.00      0.04
1324   15      0.00    5       72.94     26.45      0.04      0.03      0.52
1334                                                                               0.090 GRAMS CARBON DEPOSITED
1339   16      0.00    5       73.23     26.24      0.01      0.03      0.46
1355   17      0.00    5       72.92     26.44      0.01      0.02      0.59
1403                                                                               0.139 GRAMS CARBON DEPOSITED
1410   18      0.00    5       73.10     26.29      0.03      0.03      0.52
1426   19      0.00    5       72.79     26.49      0.09      0.04      0.57
1430                                                                               0.197 GRAMS CARBON DEPOSITED
1441   20      0.00    5       72.80     26.27      0.20      0.12      0.59
1459   21      0.00    5       72.88     26.38      0.05      0.03      0.64
1500                                                                               0.276 GRAMS CARBON DEPOSITED
1512   22      0.00    5       73.15     26.11      0.04      0.03      0.64
1529   23      0.00    5       72.78     26.23      0.03      0.06      0.88
1531                                                                               0.373 GRAMS CARBON DEPOSITED
1545   24      0.00    5       72.91     26.04      0.03      0.06      0.93
1549                                                                               0.422 GRAMS CARBON DEPOSITED

1549 CHANGED INLET GAS TO      49.80      0.00      0.00     50.19      0.00           TOTAL FLOW 19.9 CC/SEC (STP)
1602   25      0.00    4       47.04      0.00      0.00     52.82      0.13
1616   26      0.00    4       47.33      0.00      0.00     52.57      0.09
1613   27      0.00    5       41.19      5.11      0.00     48.06      5.63
1634                                                                               0.422 GRAMS CARBON DEPOSITED
1649   29     -1.00    5       41.16      5.53      0.00     47.87      5.42
```

```
                            DATA TAKEN DURING RUN  34 ON 14 AUG 74

TIME SAMP        DELP IGAS         H2         CO        CH4        CO2        H2O          C
1000                     7                                                            32.379

1007                     8      550.0

1015                     6       16.0        0.0        0.0       30.0        0.0
1023    1        0.00    1     4936.0   230601.0   190980.0   261156.0        0.0
1030    2        0.00    1     5268.0   248349.0   204999.0   274044.0        0.0
1037    3        0.00    1     4996.0   229835.0   191701.0   262505.0        0.0
1046    4        0.00    1     5290.0   241335.0   200682.0   274958.0        0.0
3300    8        0.00    2    30982.0        0.0        0.0        0.0        0.0
3300    9       -1.00    2    29664.0        0.0        0.0        0.0        0.0
3300   10        0.00    2    30972.0        0.0        0.0        0.0        0.0
3300   11        0.00    2    28622.0        0.0        0.0        0.0        0.0
1054    5       -1.00    4    10815.0        0.0        0.0   547477.1      208.0
1108    6        0.00    4    11588.0        0.0        0.0   574817.1        0.0
1123    7       -2.00    5     9070.0    53235.0        0.0   494370.0    45718.0
1139    8       -2.00    5     9691.0    58984.0        0.0   518746.0    46820.0
1156    9        0.00    4    10995.0        0.0        0.0   555791.1        0.0
1205   10        0.00    4    11744.0        0.0        0.0   581621.1        0.0
1213   11       -1.00    5     9029.0    58721.0        0.0   494780.0    52283.0
1217                     7                                                        [illegible]2
1230   12       -1.00    5     9495.0    64186.0       14.0   517635.0    52139.0

1235                     8      525.0
1249   13        0.00    4    10963.0        0.0        0.0   555084.1        0.0
1256   14        0.00    4    11669.0        0.0        0.0   580169.1        0.0
1305   15       -1.00    5     9054.0    56115.0       43.0   495897.0    50980.0
1323   16       -2.00    5     9672.0    60457.0       49.0   519263.0    47753.0
1327                     7                                                            32.388
1340   17        0.00    4    11020.0        0.0        0.0   555684.1        0.0
1349   18        0.00    4    11759.0        0.0        0.0   579494.1        0.0
1355   19       -1.00    5     9021.0    58156.0       27.0   493520.0    48172.0
1413   20       -2.00    5     9649.0    61336.0       24.0   517098.0    50199.0

1413                     8      500.0
1417                     7                                                            32.385
1431   21        0.00    4    11041.0        0.0        0.0   555800.1        0.0
1438   22        0.00    4    11682.0        0.0        0.0   579356.1        0.0
1449   23       -2.00    5     9127.0    52560.0       73.0   500162.0    46064.0
1506   24       -2.00    5     9809.0    55918.0       42.0   524920.1    45118.0
1522   25        0.00    4    10964.0        0.0        0.0   553018.1        0.0
1529   26        0.00    4    11692.0        0.0        0.0   578890.1        0.0
1538   27       -1.00    5     9136.0    54540.0       81.0   498829.0    47276.0
1555   28       -2.00    5     9720.0    58182.0       65.0   523111.0    45734.0

1558                     8      475.0
1600                     7                                                            32.384
1617   29        0.00    4    11038.0        0.0        0.0   556689.1        0.0
1624   30        0.00    4    11740.0        0.0        0.0   582788.1        0.0
1632   31       -2.00    5     9395.0    44816.0      121.0   513281.0    39908.0
1650   32       -2.00    5    10017.0    48157.0        0.0   537743.1    39460.0
1707   33        0.00    4    10960.0        0.0        0.0   554861.1        0.0
```

```
1714   34     0.00   4   11740.0      0.0        0.0  583365.1       0.0
1722   35    -2.00   5    9333.0  46630.0       70.0  511067.0   41708.0
1739   36    -2.00   5    9978.0  49899.0       64.0  538365.1   40832.0
1744                 7                                                     32.394

1830                 8     325.0
```

```
                          DATA TAKEN DURING RUN  34 ON 14 AUG 74



THE CALIBRATION GASES ARE KNOWN TO BE
                    IGAS          H2         CO        CH4        CO2        H2O
                       1       25.17      24.94      24.97      24.94       0.00
                       2      100.00       0.00       0.00       0.00       0.00
                       3        0.00       0.00       0.00     100.00       0.00

CALIBRATION GAS SAMPLES FOR THIS RUN WERE ANALYSED AS

TIME SAMP       DELP IGAS          H2         CO        CH4        CO2        H2O          C
1023    1       0.00    1       25.18      24.89      24.91      25.00       0.00
1030    2       0.00    1       24.93      25.22      25.15      24.68       0.00
1037    3       0.00    1       25.32      24.72      24.91      25.04       0.00
1046    4       0.00    1       25.28      24.78      24.89      25.03       0.00
3300    8       0.00    2      100.00       0.00       0.00       0.00       0.00
3300    9      -1.00    2      100.00       0.00       0.00       0.00       0.00
3300   10       0.00    2      100.00       0.00       0.00       0.00       0.00
3300   11       0.00    2      100.00       0.00       0.00       0.00       0.00

THE RELATIVE CALIBRATION
AREA COEFFICENTS ARE       0.018919   0.886825   0.734074   1.000000   0.689999   0.027732

 ATMOSPHERIC PRESSURE WAS  759.96 .

 THE WEIGHT OF CATALYST INITIALLY CHARGED TO THE REACTOR IS  0.250 GRAMS.

 THE GROSS WEIGHT OF THE CATALYST CARRIER AND SUSPENSION MECHANISM IS  31.938 GRAMS.
```

```
                                   DATA TAKEN DURING RUN  34 ON 14 AUG 74

TIME SAMP       DELP IGAS          H2          CO          CH4          CO2          H2O          C
1000                                                                                              0.440 GRAMS CARBON DEPOSITED

1007 REACTOR TEMPERATURE 550. DEGREES CENTIGRADE


1015 CHANGED INLET GAS TO        49.80       0.00        0.00        50.19        0.00              TOTAL FLOW 19.9 CC/SEC (STP)
1054    5     -1.00    4         47.00       0.00        0.00        52.96        0.02
1109    6      0.00    4         47.15       0.00        0.00        52.84        0.00
1123    7     -2.00    5         40.54       5.75        0.00        47.35        6.34
1139    8     -2.00    5         40.56       6.05        0.00        47.20        6.17
1156    9      0.00    4         46.97       0.00        0.00        53.02        0.00
1205   10      0.00    4         47.12       0.00        0.00        52.87        0.00
1213   11     -1.00    5         39.84       6.25        0.00        46.73        7.15
1217                                                                                              0.443 GRAMS CARBON DEPOSITED
1230   12     -1.00    5         39.73       6.55        0.00        46.87        6.84

1235 REACTOR TEMPERATURE 525. DEGREES CENTIGRADE

1249   13      0.00    4         46.94       0.00        0.00        53.05        0.00
1256   14      0.00    4         47.06       0.00        0.00        52.93        0.00
1305   15     -1.00    5         40.03       5.99        0.00        46.96        6.99
1323   16     -2.00    5         40.39       6.18        0.00        47.12        6.28
1327                                                                                              0.449 GRAMS CARBON DEPOSITED
1340   17      0.00    4         47.02       0.00        0.00        52.97        0.00
1348   18      0.00    4         47.24       0.00        0.00        52.75        0.00
1355   19     -1.00    5         40.12       6.24        0.00        46.97        6.64
1413   20     -2.00    5         40.26       6.26        0.00        46.86        6.59

1413 REACTOR TEMPERATURE 500. DEGREES CENTIGRADE

1417                                                                                              0.446 GRAMS CARBON DEPOSITED
1431   21      0.00    4         47.05       0.00        0.00        52.94        0.00
1439   22      0.00    4         47.12       0.00        0.00        52.87        0.00
1449   23     -2.00    5         40.44       5.63        0.00        47.56        6.34
1506   24     -2.00    5         40.78       5.71        0.00        47.57        5.92
1522   25      0.00    4         47.04       0.00        0.00        52.95        0.00
1529   26      0.00    4         47.15       0.00        0.00        52.84        0.00
1539   27     -1.00    5         40.36       5.83        0.01        47.29        6.49
1555   28     -2.00    5         40.54       5.95        0.00        47.47        6.01

1558 REACTOR TEMPERATURE 475. DEGREES CENTIGRADE

1600                                                                                              0.445 GRAMS CARBON DEPOSITED
1617   29      0.00    4         47.00       0.00        0.00        52.99        0.00
1624   30      0.00    4         47.07       0.00        0.00        52.92        0.00
1632   31     -2.00    5         41.16       4.78        0.01        48.56        5.47
1650   32     -2.00    5         41.33       4.90        0.00        48.59        5.16
1707   33      0.00    4         46.95       0.00        0.00        53.04        0.00
1714   34      0.00    4         47.04       0.00        0.00        52.95        0.00
1722   35     -2.00    5         40.94       4.97        0.00        48.35        5.71
1739   36     -2.00    5         41.08       5.06        0.00        48.50        5.33
1744                                                                                              0.455 GRAMS CARBON DEPOSITED
```

```
                                DATA TAKEN DURING RUN  35 ON 15 AUG 74

TIME  SAMP          DELP IGAS          H2          CO         CH4         CO2         H2O           C
1230                        7                                                                  32.424

1240                        6        16.0         0.0         0.0        30.0         0.0

1240                        8       450.0
1229     1          0.00    1      4969.0    234596.0    192253.0    262519.0         0.0
1235     2          0.00    1      5327.0    247108.0    203149.0    276213.0         0.0
1243     3          0.00    1      5041.0    231992.0    192815.0    263970.0         0.0
1251     4         -1.00    1      5340.0    241552.0    200916.0    275751.0         0.0
3300     8          0.00    2     30982.0         0.0         0.0         0.0         0.0
3300     9         -1.00    2     28664.0         0.0         0.0         0.0         0.0
3300    10          0.00    2     30972.0         0.0         0.0         0.0         0.0
3300    11          0.00    2     28622.0         0.0         0.0         0.0         0.0
1258     5          0.00    4     10922.0         0.0         0.0    548549.1         0.0
1306     6          0.00    4     11611.0         0.0         0.0    575295.1         0.0
1313     7         -2.00    5      9726.0     31665.0        78.0    518364.0     30354.0
1330     8         -2.00    5     10480.0     33304.0        63.0    544564.1     27458.0
1346     9          0.00    4     11013.0         0.0         0.0    550337.1         0.0
1354    10          0.00    4     11721.0         0.0         0.0    576668.1         0.0
1402    11         -2.00    5      9723.0     34900.0        83.0    516900.0     32007.0
1418    12         -2.00    5     10371.0     36283.0       118.0    544060.1     39428.0
1425                        7                                                                  32.420

1426                        8       425.0
1435    13          0.00    4     11003.0         0.0         0.0    552735.1         0.0
1443    14          0.00    4     11691.0         0.0         0.0    578267.1         0.0
1451    15         -2.00    5      9985.0     24616.0       158.0    530790.1     23637.0
1509    16         -2.00    5     10796.0     23747.0       103.0    562274.1     20452.0
1525    17          0.00    4     11040.0         0.0         0.0    557512.1         0.0
1531    18          0.00    4     11745.0         0.0         0.0    582858.1         0.0
1540    19         -2.00    5     10092.0     22581.0       144.0    538027.1     21780.0
1559    20         -2.00    5     10762.0     22603.0       135.0    568167.1     27109.0
1609                        7                                                                  32.430

1610                        8       400.0
1613    21          0.00    4     11038.0         0.0         0.0    558579.1         0.0
1621    22          0.00    4     11762.0         0.0         0.0    586082.1         0.0
1630    23         -2.00    5     10313.0     13320.0        54.0    551712.1     14322.0
1640                        7                                                                  32.423
1646    24         -1.00    5     11116.0     13071.0        22.0    580201.1     12581.0
1703    25          0.00    4     10998.0         0.0         0.0    559885.1         0.0
1710    26          0.00    4     11773.0         0.0         0.0    589491.1         0.0
1719    27         -2.00    5     10331.0     12617.0        68.0    552720.1     12040.0
1735    28         -2.00    5     11070.0     13507.0        64.0    580434.1     13008.0
```

```
                              DATA TAKEN DURING RUN  35 ON 15 AUG 74



THE CALIBRATION GASES ARE KNOWN TO BE
                    IGAS         H2         CO         CH4        CO2         H2O
                       1      25.17      24.94       24.97      24.94        0.00
                       2     100.00       0.00        0.00       0.00        0.00
                       3       0.00       0.00        0.00     100.00        0.00

CALIBRATION GAS SAMPLES FOR THIS RUN WERE ANALYSED AS

TIME SAMP      DELP IGAS         H2         CO         CH4        CO2         H2O         C
1229    1      0.00    1      25.03      25.09       24.95      24.90        0.00
1235    2      0.00    1      25.07      25.06       25.00      24.84        0.00
1243    3      0.00    1      25.26      24.76       24.97      24.99        0.00
1251    4     -1.00    1      25.33      24.71       24.94      25.01        0.00
3300    8      0.00    2     100.00       0.00        0.00       0.00        0.00
3300    9     -1.00    2     100.00       0.00        0.00       0.00        0.00
3300   10      0.00    2     100.00       0.00        0.00       0.00        0.00
3300   11      0.00    2     100.00       0.00        0.00       0.00        0.00

THE RELATIVE CALIBRATION
AREA COEFFICENTS ARE      0.018990   0.886821   0.730846   1.000000   0.689999   0.027574

 ATMOSPHERIC PRESSURE WAS  759.96 .

 THE WEIGHT OF CATALYST INITIALLY CHARGED TO THE REACTOR IS  0.250 GRAMS.

 THE GROSS WEIGHT OF THE CATALYST CARRIER AND SUSPENSION MECHANISM IS  31.938 GRAMS.
```

```
                                   DATA TAKEN DURING RUN  35 ON 15 AUG 74

TIME SAMP      DELP IGAS        H2         CO         CH4        CO2        H2O          C
1230                                                                                   0.485 GRAMS CARBON DEPOSITED

1240 CHANGED INLET GAS TO     49.80       0.00       0.00      50.19       0.00             TOTAL FLOW 19.9 CC/SEC (STP)

1240 REACTOR TEMPERATURE 450. DEGREES CENTIGRADE

1258    5      0.00    4      47.20       0.00       0.00      52.79       0.00
1306    6      0.00    4      47.22       0.00       0.00      52.77       0.00
1313    7     -2.00    5      42.79       3.41       0.01      49.57       4.20
1330    8     -2.00    5      43.27       3.42       0.00      49.66       3.62
1346    9      0.00    4      47.28       0.00       0.00      52.71       0.00
1354   10      0.00    4      47.34       0.00       0.00      52.65       0.00
1402   11     -2.00    5      42.60       3.74       0.01      49.22       4.41
1419   12     -2.00    5      42.28       3.67       0.01      48.88       5.13
1425                                                                                   0.481 GRAMS CARBON DEPOSITED

1426 REACTOR TEMPERATURE 425. DEGREES CENTIGRADE

1435   13      0.00    4      47.16       0.00       0.00      52.83       0.00
1443   14      0.00    4      47.22       0.00       0.00      52.77       0.00
1451   15     -2.00    5      43.51       2.64       0.02      50.55       3.26
1509   16     -2.00    5      43.97       2.42       0.01      50.90       2.68
1525   17      0.00    4      47.01       0.00       0.00      52.98       0.00
1531   18      0.00    4      47.12       0.00       0.00      52.87       0.00
1540   19     -2.00    5      43.62       2.41       0.01      50.95       2.98
1558   20     -2.00    5      43.35       2.28       0.01      50.83       3.51
1608                                                                                   0.491 GRAMS CARBON DEPOSITED

1610 REACTOR TEMPERATURE 400. DEGREES CENTIGRADE

1613   21      0.00    4      46.96       0.00       0.00      53.03       0.00
1621   22      0.00    4      47.01       0.00       0.00      52.98       0.00
1630   23     -2.00    5      44.36       1.42       0.00      52.23       1.96
1640                                                                                   0.484 GRAMS CARBON DEPOSITED
1646   24     -1.00    5      44.77       1.32       0.00      52.25       1.64
1703   25      0.00    4      46.83       0.00       0.00      53.16       0.00
1710   26      0.00    4      46.88       0.00       0.00      53.11       0.00
1719   27     -2.00    5      44.53       1.35       0.00      52.45       1.65
1735   28     -2.00    5      44.63       1.37       0.00      52.28       1.69
```

```
                                DATA TAKEN DURING RUN  36 ON 20 AUG 74

TIME SAMP        DFLP IGAS          H2         CO        CH4        CO2          H2O         C
 900                        7                                                            32.451
 905    1        0.00       1     4728.0  234064.0  187423.0  252723.0          0.0
 912    2        0.00       1     5099.0  237018.0  196643.0  268714.0          0.0
 919    3        0.00       1     4849.0  225901.0  187913.0  257253.0          0.0
 926    4        1.00       1     5144.0  237034.0  197394.0  270441.0          0.0
 934    5        0.00       2    27568.0       0.0       0.0       0.0          0.0
 940    6        0.00       2    29764.0       0.0       0.0       0.0          0.0
 948    7        0.00       2    27732.0       0.0       0.0       0.0          0.0
 955    8        0.00       2    29847.0       0.0       0.0       0.0          0.0

 930                        8      550.0

 930                        6       32.0       0.0       0.0       0.0          0.0
1000                        7                                                            32.377

1004                        6       24.0       3.4       0.0      12.0          0.0
1008    9        0.00       4    18252.0   47697.0       0.0  224722.0          0.0
1014   10        0.00       4    19505.0   50023.0       0.0  236713.0          0.0
1031                        7                                                            32.414
1024   11       -1.00       5    15871.0  103256.0    1283.0  169061.0      45873.0
1039   12       -2.00       5    16924.0  116981.0    1851.0  169474.0      54682.0
1057   13       -2.00       5    15770.0  110310.0    1840.0  163826.0      53261.0
1101                        7                                                            32.436
1113   14       -2.00       5    17106.0  110927.0    1703.0  177215.0      54882.0
1129   15        0.00       4    18596.0   48788.0       0.0  232917.0          0.0
1133                        7                                                            32.465
1137   16        0.00       4    19878.0   50089.0       0.0  243193.0          0.0
1145   17       -2.00       5    15995.0  107841.0    1955.0  170345.0      55913.0
1202                        7                                                            32.481
1205   18       -2.00       5    17209.0  113574.0    2019.0  178343.0      54125.0
1221   19       -2.00       5    16022.0  107815.0    1887.0  171115.0      56000.0
1233                        7                                                            32.500
1240   20       -2.00       5    16881.0  123855.0    6446.0  175861.0      56696.0
1255   21        0.00       4    18584.0   47639.0       0.0  232806.0          0.0
1308                        7                                                            32.521
```

```
                          DATA TAKEN DURING RUN  36 ON 20 AUG 74



THE CALIBRATION GASES ARE KNOWN TO BE
                        IGAS          H2         CO        CH4        CO2         H2O
                           1       25.17      24.94      24.97      24.94        0.00
                           2      100.00       0.00       0.00       0.00        0.00
                           3        0.00       0.00       0.00     100.00        0.00

CALIBRATION GAS SAMPLES FOR THIS RUN WERE ANALYSED AS

TIME SAMP       DELP IGAS          H2         CO        CH4        CO2        H2O          C
 905    1       0.00    1       24.86      25.58      24.92      24.62       0.00
 912    2       0.00    1       25.21      24.76      24.99      25.02       0.00
 919    3       0.00    1       25.33      24.66      24.96      25.03       0.00
 926    4       1.00    1       25.28      24.65      24.98      25.07       0.00
 934    5       0.00    2      100.00       0.00       0.00       0.00       0.00
 940    6       0.00    2      100.00       0.00       0.00       0.00       0.00
 948    7       0.00    2      100.00       0.00       0.00       0.00       0.00
 955    8       0.00    2      100.00       0.00       0.00       0.00       0.00

THE RELATIVE CALIBRATION
AREA COEFFICENTS ARE       0.018711  0.891353  0.732463  1.000000  0.689999  0.027325

 ATMOSPHERIC PRESSURE WAS  759.96 .

 THE WEIGHT OF CATALYST INITIALLY CHARGED TO THE REACTOR IS  0.250 GRAMS.

 THE GROSS WEIGHT OF THE CATALYST CARRIER AND SUSPENSION MECHANISM IS  31.938 GRAMS.
```

```
                                    DATA TAKEN DURING RUN  36 ON 20 AUG 74

TIME SAMP        DELP IGAS          H2         CO        CH4        CO2        H2O        C
 900                                                                                   0.512 GRAMS CARBON DEPOSITED

 930 REACTOR TEMPERATURE 550. DEGREES CENTIGRADE


 930 CHANGED INLET GAS TO    100.00       0.00       0.00       0.00       0.00             TOTAL FLOW 19.8 CC/SEC (STP)
1000                                                                                   0.438 GRAMS CARBON DEPOSITED

1004 CHANGED INLET GAS TO     74.88       4.99       0.00      20.12       0.00             TOTAL FLOW 19.8 CC/SEC (STP)
1009    9       0.00    4     72.58       5.27       0.00      22.14       0.00
1014   10       0.00    4     72.59       5.25       0.00      22.14       0.00
1031                                                                                   0.475 GRAMS CARBON DEPOSITED
1024   11      -1.00    5     65.13      11.43       0.17      16.68       6.56
1039   12      -2.00    5     64.45      12.19       0.23      15.74       7.36
1057   13      -2.00    5     64.11      12.09       0.24      16.00       7.54
1101                                                                                   0.497 GRAMS CARBON DEPOSITED
1113   14      -2.00    5     64.58      11.49       0.21      16.36       7.34
1129   15       0.00    4     72.20       5.28       0.00      22.50       0.00
1133                                                                                   0.526 GRAMS CARBON DEPOSITED
1137   16       0.00    4     72.45       5.17       0.00      22.37       0.00
1145   17      -2.00    5     63.89      11.64       0.25      16.39       7.80
1202                                                                                   0.542 GRAMS CARBON DEPOSITED
1205   18      -2.00    5     64.49      11.69       0.25      16.36       7.19
1221   19      -2.00    5     63.87      11.62       0.24      16.44       7.80
1233                                                                                   0.562 GRAMS CARBON DEPOSITED
1240   20      -2.00    5     63.04      12.65       0.80      16.01       7.48
1255   21       0.00    4     72.29       5.17       0.00      22.53       0.00
1308                                                                                   0.582 GRAMS CARBON DEPOSITED
```

```
                                        DATA TAKEN DURING RUN  37 ON 22 AUG 74

TIME SAMP          DELP IGAS         H2         CO        CH4        CO2        H2O           C
1053    1          0.00    1     5066.0   243231.0   197131.0   267266.0        0.0
1100    2          0.00    1     4871.0   226680.0   188604.0   257433.0        0.0
1107    3          0.00    1     5190.0   237186.0   197486.0   270317.0        0.0
1113    4          0.00    1     4845.0   225409.0   187699.0   257399.0        0.0
1120    5          0.00    2    30035.0        0.0        0.0        0.0        0.0
1128    6          0.00    2    27942.0        0.0        0.0        0.0        0.0
1134    7          0.00    2    30078.0        0.0        0.0        0.0        0.0
1140    8          0.00    2    27982.0        0.0        0.0        0.0        0.0
1100                       7                                                             31.881

1101                       6       32.0        0.0        0.0        0.0        0.0

1102                       8      550.0
1130                       7                                                             31.887

1146                       6       24.0       17.0        0.0        0.0        0.0
1149    9          0.00    4    20397.0   252420.0        0.0       52.0        0.0
1156   10          0.00    4    18965.0   240510.0        0.0        0.0        0.0
1204   11         -2.00    5    20241.0   251805.0      415.0      311.0     3925.0
1208                       7                                                             31.915
1217   12         -2.00    5    18732.0   239052.0      176.0      392.0     2909.0
1230                       7                                                             31.950
1233   13         -2.00    5    20152.0   252805.0     1716.0     1132.0     3447.0
1248   14         -2.00    5    18706.0   239136.0      508.0      315.0     4216.0
1301                       7                                                             32.003
1305   15         -2.00    5    20066.0   250025.0      276.0      305.0     3302.0
1319   16         -2.00    5    18614.0   238302.0      273.0      277.0     3867.0
1330                       7                                                             32.053
1335   17         -2.00    5    20152.0   252017.0     1280.0      667.0     3059.0
1350   18          0.00    4    19787.0   239774.0        0.0        0.0        0.0
1359   19          0.00    4    20232.0   252516.0        0.0        0.0        0.0
1402                       7                                                             32.113

1406                       6       24.0        6.8        0.0        9.0        0.0
1412   20          0.00    4    18430.0    96433.0        0.0   171846.0        0.0
1420   21          0.00    4    19830.0   101143.0        0.0   179931.0        0.0
1429   22         -2.00    5    17713.0   107407.0      960.0   157814.0    17366.0
1431                       7                                                             32.160
1443   23         -2.00    5    18912.0   116441.0     1280.0   160626.0    21799.0
1500   24         -2.00    5    17260.0   116249.0     1527.0   146467.0    28654.0
1503                       7                                                             32.230
1516   25         -2.00    5    18300.0   129165.0     2243.0   146224.0    34301.0
1525   26         -2.00    5    16923.0   123133.0     2230.0   139315.0    35820.0
1532                       7                                                             32.311
1552    0         -2.00    5    17873.0   137471.0     2732.0   135930.0    43219.0
1600                       7                                                             32.403
1608   28         -2.00    5    16435.0   133805.0     2963.0   127379.0    46477.0
1624   29         -2.00    5    17448.0   145315.0     5080.0   129740.0    48553.0
1631                       7                                                             32.512
1640   30         -2.00    5    16119.0   140411.0     4727.0   121744.0    51483.0
1657   31         -2.00    5    17228.0   150016.0     3630.0   122476.0    52121.0
1702                       7                                                             32.622
```

```
1714   32      -2.00     5   16054.0  145828.0     5290.0  117665.0    55426.0
1730   33      -2.00     5   17203.0  153232.0     4061.0  121178.0    50592.0
   0                     7                                                         32.741
```

```
                         DATA TAKEN DURING RUN  37 ON 22 AUG 74




THE CALIBRATION GASES ARE KNOWN TO BE
                       IGAS       H2        CO        CH4        CO2        H2O
                          1    25.17     24.94      24.97      24.94       0.00
                          2   100.00      0.00       0.00       0.00       0.00
                          3     0.00      0.00       0.00     100.00       0.00

CALIBRATION GAS SAMPLES FOR THIS RUN WERE ANALYSED AS

TIME SAMP      DELP IGAS        H2         CO        CH4        CO2        H2O          C
1053    1      0.00    1     24.88      25.39      24.95      24.75       0.00
1100    2      0.00    1     25.26      24.77      24.99      24.96       0.00
1107    3      0.00    1     25.32      24.72      24.95      24.99       0.00
1113    4      0.00    1     25.25      24.72      24.96      25.05       0.00
1120    5      0.00    2    100.00       0.00       0.00       0.00       0.00
1128    6      0.00    2    100.00       0.00       0.00       0.00       0.00
1134    7      0.00    2    100.00       0.00       0.00       0.00       0.00
1140    8      0.00    2    100.00       0.00       0.00       0.00       0.00

THE RELATIVE CALIBRATION
AREA COEFFICENTS ARE     0.018796  0.887130  0.731644  1.000000  0.689999  0.027498

 ATMOSPHERIC PRESSURE WAS  759.96 .

 THE WEIGHT OF CATALYST INITIALLY CHARGED TO THE REACTOR IS  0.250 GRAMS.

 THE GROSS WEIGHT OF THE CATALYST CARRIER AND SUSPENSION MECHANISM IS  31.881 GRAMS.
```

```
                              DATA TAKEN DURING RUN  37 ON 22 AUG 74

TIME SAMP      DELP IGAS         H2         CO        CH4         CO2        H2O         C
1100                                                                                  0.000 GRAMS CARBON DEPOSITED

1101 CHANGED INLET GAS TO    100.00       0.00       0.00        0.00       0.00            TOTAL FLOW 19.8 CC/SEC (STP)

1102 REACTOR TEMPERATURE 550. DEGREES CENTIGRADE

1130                                                                                  0.006 GRAMS CARBON DEPOSITED

1146 CHANGED INLET GAS TO     74.99      25.00       0.00        0.00       0.00            TOTAL FLOW 19.8 CC/SEC (STP)
1149    9      0.00    4      73.77      26.22       0.00        0.00       0.00
1155   10      0.00    4      73.60      26.39       0.00        0.00       0.00
1204   11     -2.00    5      73.24      26.14       0.05        0.02       0.52
1208                                                                                  0.034 GRAMS CARBON DEPOSITED
1217   12     -2.00    5      73.17      26.34       0.02        0.03       0.41
1230                                                                                  0.069 GRAMS CARBON DEPOSITED
1233   13     -2.00    5      72.97      26.24       0.21        0.10       0.46
1248   14     -2.00    5      72.98      26.31       0.06        0.03       0.59
1301                                                                                  0.122 GRAMS CARBON DEPOSITED
1305   15     -2.00    5      73.32      26.16       0.03        0.02       0.44
1318   16     -2.00    5      73.03      26.34       0.03        0.02       0.54
1330                                                                                  0.171 GRAMS CARBON DEPOSITED
1335   17     -2.00    5      73.14      26.22       0.16        0.06       0.40
1350   18      0.00    4      73.52      26.47       0.00        0.00       0.00
1358   19      0.00    4      73.64      26.35       0.00        0.00       0.00
1402                                                                                  0.232 GRAMS CARBON DEPOSITED

1406 CHANGED INLET GAS TO     74.90       9.99       0.00       15.09       0.00            TOTAL FLOW 19.8 CC/SEC (STP)
1412   20      0.00    4      72.49      10.65       0.00       16.85       0.00
1420   21      0.00    4      72.70      10.58       0.00       16.70       0.00
1429   22     -2.00    5      70.10      11.85       0.12       15.44       2.46
1431                                                                                  0.278 GRAMS CARBON DEPOSITED
1443   23     -2.00    5      69.77      12.19       0.16       14.92       2.93
1500   24     -2.00    5      68.60      12.80       0.20       14.31       4.05
1503                                                                                  0.348 GRAMS CARBON DEPOSITED
1516   25     -2.00    5      68.07      13.48       0.28       13.54       4.60
1525   26     -2.00    5      67.47      13.55       0.29       13.60       5.06
1532                                                                                  0.430 GRAMS CARBON DEPOSITED
1552    0     -2.00    5      66.87      14.36       0.34       12.60       5.80
1600                                                                                  0.522 GRAMS CARBON DEPOSITED
1608   28     -2.00    5      65.89      14.71       0.39       12.42       6.57
1624   29     -2.00    5      65.61      15.18       0.64       12.02       6.52
1631                                                                                  0.630 GRAMS CARBON DEPOSITED
1640   30     -2.00    5      64.81      15.42       0.62       11.86       7.27
1657   31     -2.00    5      65.32      15.76       0.46       11.41       7.04
1702                                                                                  0.740 GRAMS CARBON DEPOSITED
1714   32     -2.00    5      64.21      15.91       0.70       11.39       7.77
1730   33     -2.00    5      65.25      16.10       0.51       11.29       6.83
                                                                                      0.860 GRAMS CARBON DEPOSITED
```

```
                                   DATA TAKEN DURING RUN  38 ON 28 AUG 74

TIME SAMP       DELP IGAS        H2         CO        CH4        CO2        H2O           C
 930                    7                                                               31.850

 935                    8     550.0

 935                    6      32.0        0.0        0.0        0.0        0.0
 943    1       0.00    1    4751.0   235753.0   188753.0   254786.0        0.0
 950    2       0.00    1    5162.0   238590.0   197707.0   270345.0        0.0
 958    3      -1.00    1    4838.0   225923.0   188478.0   257595.0        0.0
1005    4       0.00    1    5192.0   238321.0   198252.0   271246.0        0.0
1012    5       0.00    2   27906.0        0.0        0.0        0.0        0.0
1019    6       0.00    2   30045.0        0.0        0.0        0.0        0.0
1026    7       0.00    2   27837.0        0.0        0.0        0.0        0.0
1032    8       0.00    2   29983.0        0.0        0.0        0.0        0.0
1036                    7                                                               31.858

1040                    6      24.0       17.0        0.0        0.0        0.0
1043    9       0.00    4   19006.0   231396.0        0.0        0.0        0.0
1051   10       0.00    4   20462.0   246288.0        0.0        0.0        0.0
1100   11      -1.00    5   18697.0   235561.0        0.0      318.0     1747.0
1105                    7                                                               31.872
1114   12      -2.00    5   20189.0   247672.0       72.0      199.0     1447.0
1129   13      -2.00    5   18797.0   236086.0      108.0      130.0     3164.0
1132                    7                                                               31.895
1144   14      -2.00    5   20260.0   247183.0       75.0      155.0     2525.0
1204                    7                                                               31.927
1214   16      -2.00    5   20261.0   247524.0       87.0      170.0     3669.0
1229   17      -2.00    5   18737.0   235057.0       71.0      218.0     2865.0
1232                    7                                                               31.959
1245   18      -2.00    5   20209.0   247128.0      118.0      185.0     2529.0
1300   19      -2.00    5   18742.0   234550.0      102.0      283.0     2880.0
1303                    7                                                               32.000
1314   20      -1.00    5   20052.0   245087.0      120.0      207.0     3598.0
1329   21      -2.00    5   18684.0   233478.0      149.0      180.0     3721.0
1332                    7                                                               32.053
1345   22      -2.00    5   20052.0   245045.0      245.0      418.0     4279.0
1400                    7                                                               32.108

1402                    6      24.0       10.2        0.0        6.0        0.0
1406   23       0.00    4   18706.0   140042.0        0.0   112951.0        0.0
1419   25       0.00    4   19618.0   139276.0        0.0   114232.0        0.0
1427   26      -2.00    5   19429.0   150570.0      546.0   117292.0     9719.0
1432                    7                                                               32.180
1443   27      -2.00    5   18010.0   144045.0      710.0   110700.0    11620.0
1500   28      -2.00    5   19241.0   152327.0     1064.0   113808.0    14746.0
1503                    7                                                               32.281
1515   29      -2.00    5   17769.0   145629.0     1246.0   105853.0    17711.0
1532   30      -2.00    5   18960.0   155593.0     1956.0   107727.0    22912.0
1536                    7                                                               32.429
```

```
                              DATA TAKEN DURING RUN  38 ON 28 AUG 74



THE CALIBRATION GASES ARE KNOWN TO BE
                         IGAS         H2         CO        CH4        CO2        H2O
                            1      25.17      24.94      24.97      24.94       0.00
                            2     100.00       0.00       0.00       0.00       0.00
                            3       0.00       0.00       0.00     100.00       0.00

CALIBRATION GAS SAMPLES FOR THIS RUN WERE ANALYSED AS

TIME SAMP       DELP IGAS         H2         CO        CH4        CO2        H2O          C
 943    1       0.00    1      24.79      25.59      24.93      24.66       0.00
 950    2       0.00    1      25.29      24.75      24.95      25.00       0.00
 959    3      -1.00    1      25.26      24.64      25.02      25.05       0.00
1005    4       0.00    1      25.34      24.66      24.96      25.02       0.00
1012    5       0.00    2     100.00       0.00       0.00       0.00       0.00
1019    6       0.00    2     100.00       0.00       0.00       0.00       0.00
1026    7       0.00    2     100.00       0.00       0.00       0.00       0.00
1032    8       0.00    2     100.00       0.00       0.00       0.00       0.00

THE RELATIVE CALIBRATION
AREA COEFFICENTS ARE       0.018741   0.891592   0.732714   1.000000   0.689999   0.027385

 ATMOSPHERIC PRESSURE WAS  759.96 .

 THE WEIGHT OF CATALYST INITIALLY CHARGED TO THE REACTOR IS  0.249 GRAMS.

 THE GROSS WEIGHT OF THE CATALYST CARRIER AND SUSPENSION MECHANISM IS  31.850 GRAMS.
```

```
                          DATA TAKEN DURING RUN  38 ON 28 AUG 74

TIME SAMP      DELP IGAS        H2         CO        CH4        CO2        H2O       C
 930                                                                              0.000 GRAMS CARBON DEPOSITED

 935 REACTOR TEMPERATURE 550. DEGREES CENTIGRADE


 935 CHANGED INLET GAS TO   100.00       0.00       0.00       0.00       0.00         TOTAL FLOW 19.8 CC/SEC (STP)
1036                                                                              0.007 GRAMS CARBON DEPOSITED

1040 CHANGED INLET GAS TO    74.99      25.00       0.00       0.00       0.00         TOTAL FLOW 19.8 CC/SEC (STP)
1043    9       0.00    4    74.54      25.45       0.00       0.00       0.00
1051   10       0.00    4    74.45      25.54       0.00       0.00       0.00
1100   11      -1.00    5    73.73      25.98       0.00       0.03       0.24
1105                                                                              0.021 GRAMS CARBON DEPOSITED
1114   12      -2.00    5    73.97      25.80       0.00       0.01       0.19
1129   13      -2.00    5    73.62      25.89       0.01       0.01       0.44
1132                                                                              0.044 GRAMS CARBON DEPOSITED
1144   14      -2.00    5    73.95      25.67       0.00       0.01       0.33
1204                                                                              0.076 GRAMS CARBON DEPOSITED
1214   16      -2.00    5    73.81      25.66       0.01       0.01       0.49
1229   17      -2.00    5    73.69      25.96       0.00       0.02       0.40
1232                                                                              [illegible]9 GRAMS CARBON DEPOSITED
1245   18      -2.00    5    73.91      25.70       0.01       0.01       0.33
1300   19      -2.00    5    73.72      25.92       0.01       0.02       0.40
1303                                                                              0.150 GRAMS CARBON DEPOSITED
1314   20      -1.00    5    73.85      25.62       0.01       0.01       0.48
1329   21      -2.00    5    73.68      25.74       0.01       0.01       0.53
1332                                                                              0.202 GRAMS CARBON DEPOSITED
1345   22      -2.00    5    73.75      25.59       0.03       0.03       0.57
1400                                                                              0.257 GRAMS CARBON DEPOSITED

1402 CHANGED INLET GAS TO    74.93      14.99       0.00      10.06       0.00         TOTAL FLOW 19.8 CC/SEC (STP)
1406   23       0.00    4    73.54      15.39       0.00      11.06       0.00
1419   25       0.00    4    73.43      15.34       0.00      11.21       0.00
1427   26      -2.00    5    71.96      15.72       0.06      10.92       1.31
1432                                                                              0.329 GRAMS CARBON DEPOSITED
1443   27      -2.00    5    71.51      15.96       0.09      10.87       1.65
1500   28      -2.00    5    71.37      15.90       0.13      10.59       1.98
1503                                                                              0.430 GRAMS CARBON DEPOSITED
1515   29      -2.00    5    70.83      16.06       0.16      10.40       2.52
1532   30      -2.00    5    70.43      16.21       0.24      10.01       3.08
1536                                                                              0.578 GRAMS CARBON DEPOSITED
```

```
                              DATA TAKEN DURING RUN  39 ON 17 SEP 74

TIME SAMP      DELP IGAS        H2        CO       CH4       CO2        H2O         C
 942    2      2.00   1     4905.0  231325.0  190354.0  257197.0        0.0
 949    3      2.00   1     4632.0  216907.0  180416.0  246169.0        0.0
 956    4      2.00   1     4967.0  227800.0  189759.0  259336.0        0.0
1002    5      2.00   1     4674.0  217227.0  181098.0  247314.0        0.0
1013    6      0.00   2    28522.0       0.0       0.0       0.0        0.0
1020    7      0.00   2    26513.0       0.0       0.0       0.0        0.0
1032    9      0.00   2    26557.0       0.0       0.0       0.0        0.0
1039   10      0.00   2    28690.0       0.0       0.0       0.0        0.0
1045   11      0.00   2    26631.0       0.0       0.0       0.0        0.0
1009                  7                                                          31.042

1010                  6       32.0       0.0       0.0       0.0        0.0

1010                  8      500.0
1056                  7                                                          31.022

1058                  6       24.0      17.0       0.0       0.0        0.0
1100   12      0.00   4    19594.0  235004.0       0.0       0.0        0.0
1107   12      0.00   4    18278.0  224241.0       0.0       0.0        0.0
1115   13     -2.00   5    19489.0  240691.0       0.0     203.0     1322.0
1129                  7                                                          31.[illegible]46
1131   14     -2.00   5    18238.0  228637.0       0.0     183.0     1638.0
1145   15      0.00   4    19836.0  242029.0       0.0       0.0        0.0
1154   16      0.00   4    18439.0  228658.0       0.0       0.0        0.0
1159                  7                                                          31.071
1202   17     -1.00   5    19516.0  242884.0      71.0     168.0     2023.0
1219   18     -2.00   5    18092.0  230199.0      87.0     175.0     3020.0
1231                  7                                                          31.093
1234   19     -2.00   5    19455.0  240655.0      83.0     189.0     1926.0
1249   20     -2.00   5    17993.0  228501.0      57.0     163.0     1688.0
1309   21     -2.00   5    19360.0  240025.0      92.0     194.0     2126.0
1304                  7                                                          31.144
1324   22     -2.00   5    18074.0  230083.0      68.0     189.0     1663.0
1331                  7                                                          31.130
1339   23     -2.00   5    19316.0  240219.0     139.0     197.0     1295.0
1353   24     -2.00   5    17876.0  229449.0    1952.0    1085.0     1700.0
1405                  7                                                          31.151
1409   25     -2.00   5    19222.0  238824.0      76.0     171.0     1618.0
1423   26     -1.00   5    17807.0  228000.0     700.0     366.0     1672.0
1438   27     -1.00   5    19212.0  239508.0       0.0     344.0     1988.0
1434                  7                                                          31.168
1501                  7                                                          31.185
1506   29     -2.00   5    19192.0  239105.0     110.0     321.0     1232.0
1521   30      0.00   4    17976.0  224664.0       0.0       0.0        0.0
1526   31     -1.00   4    19371.0  236767.0       0.0       0.0        0.0
1530                  7                                                          31.201
```

```
                         DATA TAKEN DURING RUN  39 ON 17 SEP 74



THE CALIBRATION GASES ARE KNOWN TO BE
                   IGAS          H2          CO         CH4         CO2         H2O
                      1       25.17       24.94       24.97       24.94        0.00
                      2      100.00        0.00        0.00        0.00        0.00
                      3        0.00        0.00        0.00      100.00        0.00

CALIBRATION GAS SAMPLES FOR THIS RUN WERE ANALYSED AS

TIME SAMP        DELP IGAS         H2          CO         CH4         CO2         H2O          C
 942    2        2.00    1      25.01       25.17       25.01       24.78        0.00
 949    3        2.00    1      25.18       24.86       24.96       24.98        0.00
 956    4        2.00    1      25.26       24.79       24.93       24.99        0.00
1002    5        2.00    1      25.25       24.79       24.95       24.99        0.00
1013    6        0.00    2     100.00        0.00        0.00        0.00        0.00
1023    7        0.00    2     100.00        0.00        0.00        0.00        0.00
1032    9        0.00    2     100.00        0.00        0.00        0.00        0.00
1039   10        0.00    2     100.00        0.00        0.00        0.00        0.00
1045   11        0.00    2     100.00        0.00        0.00        0.00        0.00

THE RELATIVE CALIBRATION
AREA COEFFICENTS ARE      0.018806    0.885465    0.733390    1.000000    0.689999    0.027117

 ATMOSPHERIC PRESSURE WAS  759.96 .

 THE WEIGHT OF CATALYST INITIALLY CHARGED TO THE REACTOR IS  0.250 GRAMS.

 THE GROSS WEIGHT OF THE CATALYST CARRIER AND SUSPENSION MECHANISM IS  31.022 GRAMS.
```

```
                                   DATA TAKEN DURING RUN  39 ON 17 SEP 74

TIME SAMP       DELP IGAS         H2         CO         CH4        CO2        H2O         C
1009                                                                                   0.020 GRAMS CARBON DEPOSITED

1010 CHANGED INLET GAS TO   100.00       0.00       0.00       0.00       0.00               TOTAL FLOW 19.8 CC/SEC (STP)

1010 REACTOR TEMPERATURE 500. DEGREES CENTIGRADE

1056                                                                                   0.000 GRAMS CARBON DEPOSITED

1059 CHANGED INLET GAS TO     74.99      25.00       0.00       0.00       0.00               TOTAL FLOW 19.8 CC/SEC (STP)
1100   12       0.00    4     74.49      25.50       0.00       0.00       0.00
1107   12       0.00    4     74.33      25.66       0.00       0.00       0.00
1115   13      -2.00    5     73.79      26.00       0.00       0.01       0.18
1129                                                                                   0.023 GRAMS CARBON DEPOSITED
1131   14      -2.00    5     73.73      26.00       0.00       0.01       0.23
1145   15       0.00    4     74.11      25.88       0.00       0.00       0.00
1154   16       0.00    4     74.09      25.90       0.00       0.00       0.00
1159                                                                                   0.048 GRAMS CARBON DEPOSITED
1202   17      -1.00    5     73.57      26.12       0.00       0.01       0.27
1218   18      -2.00    5     73.32      26.20       0.01       0.01       0.44
1231                                                                                   0.070 GRAMS CARBON DEPOSITED
1234   19      -2.00    5     73.70      26.00       0.01       0.01       0.26
1248   20      -2.00    5     73.52      26.19       0.00       0.01       0.24
1309   21      -2.00    5     73.65      26.01       0.01       0.01       0.29
1304                                                                                   0.121 GRAMS CARBON DEPOSITED
1324   22      -2.00    5     73.46      26.26       0.00       0.01       0.24
1331                                                                                   0.107 GRAMS CARBON DEPOSITED
1339   23      -2.00    5     73.68      26.09       0.01       0.01       0.18
1353   24      -2.00    5     73.08      26.28       0.26       0.11       0.24
1405                                                                                   0.128 GRAMS CARBON DEPOSITED
1409   25      -2.00    5     73.69      26.05       0.01       0.01       0.22
1423   26      -1.00    5     73.33      26.28       0.09       0.03       0.24
1438   27      -1.00    5     73.59      26.09       0.00       0.03       0.27
1434                                                                                   0.145 GRAMS CARBON DEPOSITED
1501                                                                                   0.162 GRAMS CARBON DEPOSITED
1506   29      -2.00    5     73.67      26.10       0.01       0.03       0.17
1521   30       0.00    4     74.05      25.94       0.00       0.00       0.00
1526   31      -1.00    4     74.17      25.82       0.00       0.00       0.00
1530                                                                                   0.178 GRAMS CARBON DEPOSITED
```

```
                                   DATA TAKEN DURING RUN  40 ON 19 SEP 74

TIME SAMP        DELP IGAS         H2         CO        CH4        CO2          H2O          C
1029    1        0.00    1     4626.0   223452.0   182198.0   246200.0          0.0
1035    2        0.00    1     4968.0   230186.0   191023.0   260668.0          0.0
1042    3        0.00    1     4699.0   218628.0   181968.0   248948.0          0.0
1054    4        0.00    1     5008.0   229960.0   191735.0   262770.0          0.0
1106    5        0.00    2    26987.0        0.0        0.0        0.0          0.0
1112    6        0.00    2    29133.0        0.0        0.0        0.0          0.0
1118    7        0.00    2    27192.0        0.0        0.0        0.0          0.0
1124    8        0.00    2    29257.0        0.0        0.0        0.0          0.0
1022                    7                                                                31.207

1057                    6       32.0        0.0        0.0        0.0          0.0

1057                    8      500.0
1129                    7                                                                31.210

1131                    6       24.0       17.0        0.0        0.0          0.0
1133    9        0.00    4    18491.0   230818.0        0.0        0.0          0.0
1139   10        0.00    4    19833.0   243015.0        0.0        0.0          0.0
1147   11       -2.00    5    18119.0   233267.0      151.0      202.0       2081.0
1201   12       -2.00    5    19484.0   243831.0      138.0      248.0       1961.0
1207                    7                                                                31.241
1215   13       -2.00    5    18027.0   232435.0      247.0      230.0       3081.0
1230   14       -2.00    5    19490.0   245444.0      526.0      218.0       2132.0
1234                    7                                                                31.267
1245   15       -2.00    5    18132.0   233292.0      189.0      223.0       2655.0
1258                    7                                                                31.290
1301   16       -2.00    5    19465.0   245048.0      290.0      258.0       2341.0
1316   17       -2.00    5    18048.0   232612.0      201.0      284.0       2738.0
1329                    7                                                                31.318

1332                    6       24.0        6.8        0.0        9.0          0.0
1335   18        0.00    4    19367.0    93764.0        0.0   173922.0          0.0
1343   19        0.00    4    17943.0    88104.0        0.0   166099.0          0.0
1350   20       -2.00    5    18818.0    97111.0      637.0   173920.0       4548.0
1402                    7                                                                31.342
1405   21       -2.00    5    17433.0    92731.0      436.0   165985.0       6417.0
1421   22       -2.00    5    18780.0    97334.0      422.0   173957.0       6619.0
1434                    7                                                                31.365
1437   23       -2.00    5    17377.0    92930.0      600.0   165769.0       7418.0
1453   24       -2.00    5    18713.0    97879.0      509.0   174081.0       6498.0
1459                    7                                                                31.385
1508   25       -2.00    5    17414.0    93451.0      485.0   166048.0       7019.0
1524   26       -2.00    5    19695.0    97854.0      531.0   172907.0       5146.0
1530                    7                                                                31.406
1538   27       -2.00    5    17434.0    93786.0      516.0   166543.0       6194.0
1554                    7                                                                31.421
```

```
                    DATA TAKEN DURING RUN  40 ON 19 SEP 74



THE CALIBRATION GASES ARE KNOWN TO BE
                         IGAS        H2        CO       CH4       CO2       H2O
                            1     25.17     24.94     24.97     24.94      0.00
                            2    100.00      0.00      0.00      0.00      0.00
                            3      0.00      0.00      0.00    100.00      0.00

CALIBRATION GAS SAMPLES FOR THIS RUN WERE ANALYSED AS

TIME SAMP       DELP IGAS        H2        CO       CH4       CO2       H2O         C
1028    1       0.00    1     24.98     25.30     24.98     24.72      0.00
1035    2       0.00    1     25.19     24.86     24.98     24.96      0.00
1042    3       0.00    1     25.29     24.75     24.95     25.00      0.00
1054    4       0.00    1     25.24     24.73     24.96     25.06      0.00
1106    5       0.00    2    100.00      0.00      0.00      0.00      0.00
1112    6       0.00    2    100.00      0.00      0.00      0.00      0.00
1118    7       0.00    2    100.00      0.00      0.00      0.00      0.00
1124    8       0.00    2    100.00      0.00      0.00      0.00      0.00

THE RELATIVE CALIBRATION
AREA COEFFICENTS ARE       0.018769  0.886829  0.732413  1.000000  0.689999  0.027562

 ATMOSPHERIC PRESSURE WAS  759.96 .

 THE WEIGHT OF CATALYST INITIALLY CHARGED TO THE REACTOR IS  0.250 GRAMS.

 THE GROSS WEIGHT OF THE CATALYST CARRIER AND SUSPENSION MECHANISM IS  31.022 GRAMS.
```

```
                                    DATA TAKEN DURING RUN  40 ON 19 SEP 74

TIME SAMP        DELP IGAS         H2          CO         CH4         CO2         H2O        C
1022                                                                                       0.184 GRAMS CARBON DEPOSITED

1057 CHANGED INLET GAS TO   100.00        0.00        0.00        0.00        0.00             TOTAL FLOW 19.8 CC/SEC (STP)

1057 REACTOR TEMPERATURE 500. DEGREES CENTIGRADE

1129                                                                                       0.187 GRAMS CARBON DEPOSITED


1131 CHANGED INLET GAS TO     74.99       25.00        0.00        0.00        0.00             TOTAL FLOW 19.8 CC/SEC (STP)
1133    9     0.00    4       73.85       26.14        0.00        0.00        0.00
1139   10     0.00    4       73.91       26.08        0.00        0.00        0.00
1147   11    -2.00    5       73.07       26.57        0.02        0.02        0.30
1201   12    -2.00    5       73.34       26.34        0.01        0.02        0.27
1207                                                                                       0.218 GRAMS CARBON DEPOSITED
1215   13    -2.00    5       72.94       26.54        0.03        0.02        0.45
1230   14    -2.00    5       73.16       26.44        0.06        0.02        0.29
1234                                                                                       0.244 GRAMS CARBON DEPOSITED


1245   15    -2.00    5       73.01       26.54        0.02        0.02        0.38
1258                                                                                       0.267 GRAMS CARBON DEPOSITED
1301   16    -2.00    5       73.17       26.43        0.03        0.02        0.32
1316   17    -2.00    5       72.98       26.55        0.02        0.02        0.40
1329                                                                                       0.295 GRAMS CARBON DEPOSITED

1332 CHANGED INLET GAS TO     74.90        9.99        0.00       15.09        0.00             TOTAL FLOW 19.8 CC/SEC (STP)
1335   18     0.00    4       73.16       10.14        0.00       16.69        0.00
1343   19     0.00    4       73.01       10.10        0.00       16.88        0.00
1350   20    -2.00    5       71.91       10.57        0.08       16.79        0.63
1402                                                                                       0.319 GRAMS CARBON DEPOSITED
1406   21    -2.00    5       71.44       10.64        0.06       16.90        0.94
1421   22    -2.00    5       71.67       10.57        0.05       16.76        0.92
1434                                                                                       0.342 GRAMS CARBON DEPOSITED
1437   23    -2.00    5       71.27       10.67        0.08       16.88        1.09
1453   24    -2.00    5       71.57       10.65        0.06       16.79        0.90
1458                                                                                       0.362 GRAMS CARBON DEPOSITED
1509   25    -2.00    5       71.29       10.71        0.06       16.88        1.03

1524   26    -2.00    5       71.77       10.68        0.07       16.74        0.72
1530                                                                                       0.383 GRAMS CARBON DEPOSITED
1538   27    -2.00    5       71.33       10.75        0.07       16.93        0.91
1554                                                                                       0.398 GRAMS CARBON DEPOSITED
```

```
                                DATA TAKEN DURING RUN  41 ON 27 SEP 74

TIME SAMP       DELP IGAS          H2        CO       CH4       CO2        H2O          C
 858    1       1.00    1      4681.0  237052.0  184971.0  246479.0        0.0
 905    2       1.00    1      4564.0  214242.0  177619.0  241558.0        0.0
 912    3       1.00    1      4860.0  224776.0  186641.0  254927.0        0.0
 920    4       0.00    1      4569.0  213180.0  177510.0  242893.0        0.0
 926    5       1.00    1      4891.0  224327.0  187077.0  255264.0        0.0
 934    6       0.00    2     26043.0       0.0       0.0       0.0        0.0
 939    7       0.00    2     28197.0       0.0       0.0       0.0        0.0
 952    9       0.00    2     28254.0       0.0       0.0       0.0        0.0
 913                    7                                                           31.818

 854                    6        32.0       0.0       0.0       0.0        0.0

 854                    8       550.0
 957                    7                                                           31.836

 959                    6        24.0      17.0       0.0       0.0        0.0
1031                    7                                                           31.903
1034   13       0.00    4     19316.0  242022.0       0.0       0.0      423.0
1048   14       0.00    4     17913.0  233218.0       0.0       0.0        0.0
1055   15      -1.00    5     18975.0  240688.0     274.0     591.0     4283.0
1109                    7                                                           32.067
1111   16      -2.00    5     17713.0  228457.0     252.0     618.0     8345.0
1126   17      -2.00    5     19152.0  240511.0     474.0    1422.0     6434.0
1132                    7                                                           32.213
```

```
                        DATA TAKEN DURING RUN  41 ON 27 SEP 74




THE CALIBRATION GASES ARE KNOWN TO BE
                        IGAS        H2        CO       CH4       CO2       H2O
                           1     25.17     24.94     24.97     24.94      0.00
                           2    100.00      0.00      0.00      0.00      0.00
                           3      0.00      0.00      0.00    100.00      0.00

CALIBRATION GAS SAMPLES FOR THIS RUN WERE ANALYSED AS

TIME SAMP       DELP IGAS        H2        CO       CH4       CO2       H2O         C
 858    1       1.00    1     24.65     26.09     24.87     24.37      0.00
 905    2       1.00    1     25.30     24.68     25.00     25.00      0.00
 912    3       1.00    1     25.27     24.63     24.99     25.09      0.00

 920    4       0.00    1     25.31     24.56     24.99     25.14      0.00
 926    5       1.00    1     25.35     24.54     25.00     25.09      0.00
 934    6       0.00    2    100.00      0.00      0.00      0.00      0.00
 939    7       0.00    2    100.00      0.00      0.00      0.00      0.00
 952    9       0.00    2    100.00      0.00      0.00      0.00      0.00

THE RELATIVE CALIBRATION
AREA COEFFICENTS ARE      0.018805  0.898310  0.735398  1.000000  0.689999  0.027657

 ATMOSPHERIC PRESSURE WAS  759.96 .


 THE WEIGHT OF CATALYST INITIALLY CHARGED TO THE REACTOR IS  0.249 GRAMS.

 THE GROSS WEIGHT OF THE CATALYST CARRIER AND SUSPENSION MECHANISM IS  31.818 GRAMS.
```

```
                              DATA TAKEN DURING RUN  41 ON 27 SEP 74

TIME SAMP       DELP IGAS       H2         CO        CH4        CO2        H2O         C
 813                                                                                0.000 GRAMS CARBON DEPOSITED

 954 CHANGED INLET GAS TO   100.00       0.00       0.00       0.00       0.00            TOTAL FLOW 19.8 CC/SEC (STP)

 954 REACTOR TEMPERATURE 550. DEGREES CENTIGRADE

 957                                                                                0.018 GRAMS CARBON DEPOSITED

 959 CHANGED INLET GAS TO    74.99      25.00       0.00       0.00       0.00            TOTAL FLOW 19.8 CC/SEC (STP)
1031                                                                                0.085 GRAMS CARBON DEPOSITED
1034   13       0.00    4    73.64      26.29       0.00       0.00       0.05
1048   14       0.00    4    73.25      26.74       0.00       0.00       0.00
1055   15      -1.00    5    73.00      26.29       0.03       0.05       0.60
1109                                                                                0.248 GRAMS CARBON DEPOSITED
1111   16      -2.00    5    72.49      26.16       0.03       0.06       1.24
1126   17      -2.00    5    72.85      26.04       0.06       0.13       0.90
1132                                                                                0.395 GRAMS CARBON DEPOSITED
```

```
                                DATA TAKEN DURING RUN  42 ON 03 OCT 74

TIME SAMP       DELP IGAS         H2         CO        CH4        CO2        H2O          C
 850    1       0.00    1     4436.0   220343.0   175559.0   236538.0        0.0
 857    2       0.00    1     4819.0   223765.0   186408.0   253338.0        0.0
 907    3       1.00    1     4578.0   213729.0   178003.0   242745.0        0.0
 915    4       0.00    1     4827.0   226732.0   188531.0   254420.0        0.0
 922    5       0.00    2    26055.0        0.0        0.0        0.0        0.0
 927    6       0.00    2    28205.0        0.0        0.0        0.0        0.0
 941    7       0.00    3    25495.0        0.0        0.0        0.0    14990.0
 955    8       0.00    3    27498.0        0.0        0.0        0.0    13331.0
 955                    7                                                            32.264

 912                    6       32.0        0.0        0.0        0.0        0.0

 913                    8      550.0
 930                    7                                                            32.267

 935                    6       32.0        0.0        0.0        0.0       14.7
1002                    7                                                            32.224
1010    9       0.00    5    25460.0        0.0       80.0       58.0    14962.0
1025   10       0.00    5    27657.0        0.0       10.0       22.0    13240.0
1031                    7                                                            32.212

1039                    6       24.0       17.0        0.0        0.0       14.7
1042   11       0.00    4    17042.0   231264.0        0.0        0.0    15832.0
1056   12       0.00    4    18454.0   243907.0        0.0       16.0    15732.0

1102                    7                                                            32.320
1111   13      -2.00    5    16856.0   224665.0      391.0     3409.0    24021.0
1129   14      -2.00    5    18321.0   235704.0     1655.0     6174.0    17574.0
1132                    7                                                            32.469
1143   15      -1.00    5    17062.0   217965.0     2334.0     8728.0    22637.0

1144                    6       24.0        0.0        0.0        0.0        0.0
```

```
                                   DATA TAKEN DURING RUN  42 ON 03 OCT 74



THE CALIBRATION GASES ARE KNOWN TO BE
                         IGAS         H2          CO          CH4         CO2         H2O
                            1      25.17       24.94       24.97       24.94        0.00
                            2     100.00        0.00        0.00        0.00        0.00
                            3       0.00        0.00        0.00       98.06        1.93

CALIBRATION GAS SAMPLES FOR THIS RUN WERE ANALYSED AS

TIME SAMP        DELP IGAS         H2          CO         CH4         CO2         H2O          C
 950    1        0.00    1      24.95       25.58       24.81       24.64        0.00
 957    2        0.00    1      25.27       24.66       25.00       25.05        0.00
 907    3        1.00    1      25.36       24.60       24.94       25.07        0.00
 915    4        0.00    1      25.11       24.80       25.10       24.97        0.00
 922    5        0.00    2     100.00        0.00        0.00        0.00        0.00
 927    6        0.00    2     100.00        0.00        0.00        0.00        0.00
 941    7        0.00    3      97.89        0.00        0.00        0.00        2.10
 955    8        0.00    3      98.22        0.00        0.00        0.00        1.77

THE RELATIVE CALIBRATION
AREA COEFFICENTS ARE        0.018724   0.897267   0.737180   1.000000   0.739392   0.027429

 ATMOSPHERIC PRESSURE WAS  759.96 .

 THE WEIGHT OF CATALYST INITIALLY CHARGED TO THE REACTOR IS  0.249 GRAMS.

 THE GROSS WEIGHT OF THE CATALYST CARRIER AND SUSPENSION MECHANISM IS  31.818 GRAMS.
```

```
                                DATA TAKEN DURING RUN  42 ON 03 OCT 74

TIME SAMP      DELP IGAS        H2        CO       CH4       CO2       H2O        C
 855                                                                           0.446 GRAMS CARBON DEPOSITED

 912 CHANGED INLET GAS TO   100.00      0.00      0.00      0.00      0.00           TOTAL FLOW 19.8 CC/SEC (STP)

 913 REACTOR TEMPERATURE 550. DEGREES CENTIGRADE

 930                                                                           0.449 GRAMS CARBON DEPOSITED

 935 CHANGED INLET GAS TO    98.10      0.00      0.00      0.00      1.89           TOTAL FLOW 20.2 CC/SEC (STP)
1002                                                                           0.406 GRAMS CARBON DEPOSITED
1010    9      0.00    5     97.87      0.00      0.01      0.00      2.10
1025   10      0.00    5     98.24      0.00      0.00      0.00      1.75
1031                                                                           0.394 GRAMS CARBON DEPOSITED

1039 CHANGED INLET GAS TO    73.56     24.53      0.00      0.00      1.89           TOTAL FLOW 20.2 CC/SEC (STP)
1042   11      0.00    4     71.11     26.67      0.00      0.00      2.21
1056   12      0.00    4     71.39     26.53      0.00      0.00      2.07
1102                                                                           0.502 GRAMS CARBON DEPOSITED
1111   13     -2.00    5     70.36     25.87      0.05      0.35      3.35
1129   14     -2.00    5     71.13     25.71      0.21      0.60      2.32
1132                                                                           0.650 GRAMS CARBON DEPOSITED
1143   15     -1.00    5     70.66     24.96      0.32      0.89      3.14

1144 CHANGED INLET GAS TO   100.00      0.00      0.00      0.00      0.00           TOTAL FLOW 14.8 CC/SEC (STP)
```

```
                                  DATA TAKEN DURING RUN  43 ON 16 OCT 74

TIME SAMP       DELP IGAS       H2        CO       CH4       CO2       H2O          C
1401    1       0.00    1    4632.0 230405.0 177960.0 236966.0       0.0
1408    2       0.00    1    4489.0 206342.0 171086.0 231948.0       0.0
1415    3       0.00    1    4795.0 215087.0 179153.0 244427.0       0.0
1422    4       0.00    1    4507.0 206443.0 171863.0 232669.0       0.0
1429    5      -1.00    1    4834.0 215603.0 179463.0 245458.0       0.0
1437    6       0.00    2   25572.0      0.0      0.0      0.0       0.0
1443    7       0.00    2   27565.0      0.0      0.0      0.0       0.0
1449    8       0.00    2   25659.0      0.0      0.0      0.0       0.0
1455    9       0.00    2   27518.0      0.0      0.0      0.0       0.0
1430                    7                                                      31.807

1432                    6      32.0      0.0      0.0      0.0       0.0

1433                    8     550.0
1504                    7                                                      31.821

1506                    6      24.0     17.0      0.0      0.0       0.0
1509   10       0.00    4   17334.0 212629.0      0.0      0.0       0.0
1515   11       0.00    4   18689.0 224674.0      0.0      0.0       0.0
1521   12       0.00    5   17065.0 213645.0    214.0    470.0    3681.0
1531                    7                                                      31.872
1535   13      -1.00    5   18384.0 223448.0    297.0    500.0    3193.0
1549   14      -1.00    5   17050.0 212856.0    352.0    471.0    3954.0
1602                    7                                                      31.945
1605   15      -1.00    5   18416.0 223925.0    405.0    500.0    5164.0
1620   16      -1.00    5   17077.0 211512.0    350.0    510.0    4991.0
1632                    7                                                      32.024
1636   17      -1.00    5   18537.0 223468.0    509.0    478.0    4616.0
1651   18      -1.00    5   17047.0 211145.0    414.0    425.0    4513.0
1701                    7                                                      32.107
1705   19       0.00    5   18573.0 224891.0   1273.0    563.0    4931.0
1721   20       0.00    5   17208.0 213031.0    531.0    472.0    5150.0
1730                    7                                                      32.199

1732                    6      24.0      0.0      0.0      0.0       0.0
```

```
                              DATA TAKEN DURING RUN  43 ON 16 OCT 74



THE CALIBRATION GASES ARE KNOWN TO BE
                            IGAS        H2        CO       CH4       CO2       H2O
                               1     25.17     24.94     24.97     24.94      0.00
                               2    100.00      0.00      0.00      0.00      0.00
                               3      0.00      0.00      0.00    100.00      0.00

CALIBRATION GAS SAMPLES FOR THIS RUN WERE ANALYSED AS

TIME SAMP        DELP IGAS        H2        CO       CH4       CO2       H2O         C
1401    1        0.00    1     24.63     26.22     24.79     24.34      0.00
1408    2        0.00    1     25.24     24.67     25.04     25.03      0.00
1415    3        0.00    1     25.35     24.51     24.99     25.14      0.00
1422    4        0.00    1     25.25     24.62     25.08     25.03      0.00
1429    5       -1.00    1     25.41     24.48     24.94     25.15      0.00
1437    6        0.00    2    100.00      0.00      0.00      0.00      0.00
1443    7        0.00    2    100.00      0.00      0.00      0.00      0.00
1449    8        0.00    2    100.00      0.00      0.00      0.00      0.00
1455    9        0.00    2    100.00      0.00      0.00      0.00      0.00

THE RELATIVE CALIBRATION
AREA COEFFICENTS ARE      0.019333  0.902387  0.737297  1.000000  0.689999  0.027809

 ATMOSPHERIC PRESSURE WAS  759.96 .

 THE WEIGHT OF CATALYST INITIALLY CHARGED TO THE REACTOR IS  0.243 GRAMS.

 THE GROSS WEIGHT OF THE CATALYST CARRIER AND SUSPENSION MECHANISM IS  31.807 GRAMS.
```

```
                                 DATA TAKEN DURING RUN  43 ON 16 OCT 74

TIME SAMP      DELP IGAS        H2        CO       CH4       CO2       H2O        C
1400                                                                           0.000 GRAMS CARBON DEPOSITED

1432 CHANGED INLET GAS TO   100.00      0.00      0.00      0.00      0.00           TOTAL FLOW 19.8 CC/SEC (STP)

1433 REACTOR TEMPERATURE 550. DEGREES CENTIGRADE

1504                                                                           0.013 GRAMS CARBON DEPOSITED

1506 CHANGED INLET GAS TO    74.99     25.00      0.00      0.00      0.00           TOTAL FLOW 19.8 CC/SEC (STP)
1509   10      0.00    4     74.30     25.69      0.00      0.00      0.00
1515   11      0.00    4     74.39     25.60      0.00      0.00      0.00
1521   12      0.00    5     73.48     25.84      0.03      0.05      0.58
1531                                                                           0.064 GRAMS CARBON DEPOSITED
1535   13     -1.00    5     73.81     25.61      0.04      0.05      0.47
1549   14     -1.00    5     73.48     25.78      0.05      0.05      0.62
1602                                                                           0.138 GRAMS CARBON DEPOSITED
1605   15     -1.00    5     73.57     25.54      0.05      0.05      0.77
1620   16     -1.00    5     73.51     25.59      0.05      0.05      0.78
1632                                                                           0.216 GRAMS CARBON DEPOSITED
1636   17     -1.00    5     73.76     25.42      0.07      0.04      0.68
1651   18     -1.00    5     73.57     25.60      0.06      0.04      0.71
1701                                                                           0.299 GRAMS CARBON DEPOSITED
1705   19      0.00    5     73.56     25.47      0.17      0.05      0.73
1721   20      0.00    5     73.46     25.59      0.07      0.05      0.80
1730                                                                           0.391 GRAMS CARBON DEPOSITED

1732 CHANGED INLET GAS TO   100.00      0.00      0.00      0.00      0.00           TOTAL FLOW 14.8 CC/SEC (STP)
```

```
                                   DATA TAKEN DURING RUN  44 ON 17 OCT 74

TIME SAMP      DELP IGAS        H2        CO       CH4       CO2       H2O          C
1321    1     -1.00    1    4717.0  212033.0  175902.0  239842.0       0.0
1328    2      0.00    1    4464.0  201393.0  168097.0  229819.0       0.0
1333    3      0.00    1    4733.0  211360.0  176176.0  241039.0       0.0
1339    4     -1.00    1    4446.0  200611.0  167412.0  229141.0       0.0
1346    5      0.00    2   27101.0       0.0       0.0       0.0       0.0
1351    6      0.00    2   25056.0       0.0       0.0       0.0       0.0
   0    0      0.00    3       0.0       0.0       0.0  931500.1   14060.0
1315                   7                                                       32.190

1317                   6      32.0       0.0       0.0       0.0       0.0

1318                   8     550.0
1359                   7                                                       32.164


1401                   6       0.0       0.0       0.0      60.0       0.0
1405    7      0.00    4       0.0       0.0       0.0  972993.1       0.0
1413    8     -1.00    4       0.0       0.0       0.0  921296.1       0.0
1421    9     -1.00    5       0.0       0.0       0.0  971212.1     446.0
1431                   7                                                       32.161
1435   10     -1.00    5       0.0       0.0       0.0  922374.1     336.0
1449   11     -1.00    5       0.0       0.0       0.0  970892.1     390.0
1500                   7                                                       32.165
1504   12     -1.00    5       0.0       0.0       0.0  922257.1       0.0
1520   13     -1.00    5       0.0       0.0       0.0  972691.1     248.0
1532                   7                                                       32.160

1534                   6       0.0       0.0       0.0      60.0      15.6
1537   14     -1.00    4       0.0       0.0       0.0  909265.1   13541.0
1553   15      0.00    4       0.0       0.0       0.0  958149.1   13934.0
1601                   7                                                       32.145
1614   16     -1.00    5       0.0       0.0       0.0  907360.1   14729.0
1629   17     -2.00    5       0.0       0.0       0.0  952698.1   14458.0
1631                   7                                                       32.147
1644   18     -1.00    5       0.0       0.0       0.0  906275.1   14249.0
1659   19     -2.00    5       0.0       0.0       0.0  956442.1   13453.0
1701                   7                                                       32.150

1703                   6       0.0       0.0       0.0      60.0       0.0
```

```
                         DATA TAKEN DURING RUN  44 ON 17 OCT 74


THE CALIBRATION GASES ARE KNOWN TO BE
                    IGAS         H2         CO        CH4        CO2        H2O
                       1      25.17      24.94      24.97      24.94       0.00
                       2     100.00       0.00       0.00       0.00       0.00
                       3       0.00       0.00       0.00      97.93       2.06

CALIBRATION GAS SAMPLES FOR THIS RUN WERE ANALYSED AS

TIME SAMP       DELP IGAS        H2         CO        CH4        CO2        H2O          C
1321    1      -1.00    1     25.14      25.01      24.96      24.87       0.00
1329    2       0.00    1     25.19      24.86      24.97      24.95       0.00
1333    3       0.00    1     25.17      24.89      24.96      24.96       0.00
1339    4      -1.00    1     25.20      24.86      24.96      24.97       0.00
1346    5       0.00    2    100.00       0.00       0.00       0.00       0.00
1351    6       0.00    2    100.00       0.00       0.00       0.00       0.00
   0    0       0.00    3      0.00       0.00       0.00      97.95       2.04

THE RELATIVE CALIBRATION
AREA COEFFICENTS ARE      0.019349   0.879289   0.730720   1.000000   0.723178   0.027663

 ATMOSPHERIC PRESSURE WAS  759.96 .

 THE WEIGHT OF CATALYST INITIALLY CHARGED TO THE REACTOR IS  0.243 GRAMS.

 THE GROSS WEIGHT OF THE CATALYST CARRIER AND SUSPENSION MECHANISM IS  31.807 GRAMS.
```

```
                                DATA TAKEN DURING RUN  44 ON 17 OCT 74

TIME SAMP     DELP IGAS           H2         CO        CH4        CO2        H2O      C
1315                                                                                0.382 GRAMS CARBON DEPOSITED

1317 CHANGED INLET GAS TO     100.00       0.00       0.00       0.00       0.00          TOTAL FLOW 19.8 CC/SEC (STP)

1318 REACTOR TEMPERATURE 550. DEGREES CENTIGRADE

1359                                                                                0.356 GRAMS CARBON DEPOSITED

1401 CHANGED INLET GAS TO       0.00       0.00       0.00     100.00       0.00          TOTAL FLOW 20.0 CC/SEC (STP)
1405    7     0.00    4         0.00       0.00       0.00     100.00       0.00
1413    8    -1.00    4         0.00       0.00       0.00     100.00       0.00
1421    9    -1.00    5         0.00       0.00       0.00      99.93       0.06
1431                                                                                0.353 GRAMS CARBON DEPOSITED
1435   10    -1.00    5         0.00       0.00       0.00      99.94       0.05
1449   11    -1.00    5         0.00       0.00       0.00      99.94       0.05
1500                                                                                0.357 GRAMS CARBON DEPOSITED
1504   12    -1.00    5         0.00       0.00       0.00     100.00       0.00
1520   13    -1.00    5         0.00       0.00       0.00      99.96       0.03
1532                                                                                0.352 GRAMS CARBON DEPOSITED

1534 CHANGED INLET GAS TO       0.00       0.00       0.00      97.97       2.02          TOTAL FLOW 20.4 CC/SEC (STP)
1537   14    -1.00    4         0.00       0.00       0.00      97.98       2.01
1553   15     0.00    4         0.00       0.00       0.00      98.02       1.97
1601                                                                                0.337 GRAMS CARBON DEPOSITED
1614   16    -1.00    5         0.00       0.00       0.00      97.80       2.19
1629   17    -2.00    5         0.00       0.00       0.00      97.94       2.05
1631                                                                                0.339 GRAMS CARBON DEPOSITED
1644   18    -1.00    5         0.00       0.00       0.00      97.97       2.12
1659   19    -2.00    5         0.00       0.00       0.00      98.09       1.90
1701                                                                                0.342 GRAMS CARBON DEPOSITED

1703 CHANGED INLET GAS TO       0.00       0.00       0.00     100.00       0.00          TOTAL FLOW 20.0 CC/SEC (STP)
```

```
                              DATA TAKEN DURING RUN  45 ON 31 OCT 74

TIME SAMP      DELP IGAS        H2         CO        CH4        CO2        H2O           C
1359                   7                                                              31.762
1408    1      0.00    1    4743.0   231120.0   183691.0   245693.0        0.0
1415    2      0.00    1    5172.0   234242.0   192803.0   262526.0        0.0
1423    3     -1.00    1    4855.0   222396.0   183659.0   249735.0        0.0
1429    4      0.00    1    5164.0   235561.0   194317.0   263074.0        0.0

1432                   6      32.0        0.0        0.0        0.0        0.0
1437    5     -1.00    2   27373.0        0.0        0.0        0.0        0.0
1442    6     -1.00    2   29571.0        0.0        0.0        0.0        0.0
1447    7      0.00    2   27459.0        0.0        0.0        0.0        0.0

1450                   8     550.0
1453    8      0.00    2   29664.0        0.0        0.0        0.0        0.0
1500                   7                                                              31.771
1505    9      0.00    5   27505.0        0.0        0.0        0.0        0.0
1510   10     -1.00    5   29700.0        0.0        0.0        0.0        0.0
1529                   7                                                              31.771

1532                   6      30.4        3.4        0.0        0.0        0.0
1536   11      0.00    4   25890.0    51017.0        0.0        0.0        0.0
1542   12      0.00    4   27756.0    52409.0        0.0        0.0        0.0
1547   13     -1.00    5   25692.0    49551.0      326.0      114.0     3093.0
1600                   7                                                              31.790
1602   14     -1.00    5   27705.0    53096.0        0.0     3826.0     2392.0
1621   15      0.00    5   25719.0    45274.0      755.0      143.0     3297.0
1633                   7                                                              31.815
1637   16      0.00    5   27614.0    47424.0     1268.0      131.0     3602.0
1652   17      0.00    5   25709.0    44750.0      864.0       90.0     3074.0
1701                   7                                                              31.837
1708   18      0.00    5   27697.0    47522.0     1089.0      139.0     3647.0
1721   19     -1.00    5   25728.0    45429.0     1136.0      108.0     1902.0
1732                   7                                                              31.854
1735   20      0.00    5   27698.0    47350.0     1189.0      211.0     2940.0
1750   21     -1.00    5   25567.0    45404.0     1651.0      341.0     4144.0
1803                   7                                                              31.884
1806   22     -1.00    5   27731.0    47031.0     1413.0      218.0     2966.0
1821   23      0.00    5   25796.0    44422.0     1226.0      112.0     2921.0
1833                   7                                                              31.909
1836   24     -1.00    5   27656.0    46728.0     1507.0      119.0     3055.0
1850   25     -1.00    5   25626.0    44309.0     1396.0      183.0     4007.0
1902                   7                                                              31.932
```

```
                              DATA TAKEN DURING RUN  45 ON 31 OCT 74



THE CALIBRATION GASES ARE KNOWN TO BE
                     IGAS        H2        CO       CH4       CO2       H2O
                        1     25.17     24.94     24.97     24.94      0.00
                        2    100.00      0.00      0.00      0.00      0.00
                        3      0.00      0.00      0.00    100.00      0.00

CALIBRATION GAS SAMPLES FOR THIS RUN WERE ANALYSED AS

TIME SAMP       DELP IGAS        H2        CO       CH4       CO2       H2O         C
1409    1       0.00    1     24.84     25.58     24.94     24.62      0.00
1415    2       0.00    1     25.32     24.68     24.92     25.05      0.00
1423    3      -1.00    1     25.32     24.64     24.96     25.05      0.00
1429    4       0.00    1     25.20     24.74     25.03     25.01      0.00
1437    5      -1.00    2    100.00      0.00      0.00      0.00      0.00
1442    6      -1.00    2    100.00      0.00      0.00      0.00      0.00
1447    7       0.00    2    100.00      0.00      0.00      0.00      0.00
1453    8       0.00    2    100.00      0.00      0.00      0.00      0.00

THE RELATIVE CALIBRATION
AREA COEFFICENTS ARE      0.019337  0.905387  0.738042  1.000000  0.689999  0.027871

 ATMOSPHERIC PRESSURE WAS  759.96 .

 THE WEIGHT OF CATALYST INITIALLY CHARGED TO THE REACTOR IS  0.249 GRAMS.

 THE GROSS WEIGHT OF THE CATALYST CARRIER AND SUSPENSION MECHANISM IS  31.771 GRAMS.
```

```
                                  DATA TAKEN DURING RUN  45 ON 31 OCT 74

TIME SAMP      DELP IGAS         H2          CO         CH4         CO2         H2O          C
1359                                                                                    -0.009 GRAMS CARBON DEPOSITED

1432 CHANGED INLET GAS TO    100.00        0.00        0.00        0.00        0.00           TOTAL FLOW 19.8 CC/SEC (STP)

1450 REACTOR TEMPERATURE 550. DEGREES CENTIGRADE

1500                                                                                     0.000 GRAMS CARBON DEPOSITED
1505    9      0.00    5     100.00        0.00        0.00        0.00        0.00
1510   10     -1.00    5     100.00        0.00        0.00        0.00        0.00
1529                                                                                     0.000 GRAMS CARBON DEPOSITED

1532 CHANGED INLET GAS TO     94.99        5.00        0.00        0.00        0.00           TOTAL FLOW 19.8 CC/SEC (STP)
1536   11      0.00    4      94.38        5.61        0.00        0.00        0.00
1542   12      0.00    4      94.53        5.46        0.00        0.00        0.00
1547   13     -1.00    5      94.03        5.46        0.04        0.01        0.44
1600                                                                                     0.018 GRAMS CARBON DEPOSITED
1602   14     -1.00    5      93.81        5.50        0.00        0.35        0.32
1621   15      0.00    5      94.39        5.00        0.10        0.01        0.47
1633                                                                                     0.043 GRAMS CARBON DEPOSITED
1637   16      0.00    5      94.37        4.95        0.16        0.01        0.49
1652   17      0.00    5      94.47        4.95        0.11        0.00        0.44
1701                                                                                     0.065 GRAMS CARBON DEPOSITED
1709   18      0.00    5      94.39        4.95        0.13        0.01        0.49
1721   19     -1.00    5      94.52        5.02        0.15        0.01        0.27
1732                                                                                     0.082 GRAMS CARBON DEPOSITED
1735   20      0.00    5      94.48        4.94        0.15        0.01        0.40
1750   21     -1.00    5      94.10        5.02        0.22        0.03        0.60
1803                                                                                     0.112 GRAMS CARBON DEPOSITED
1806   22     -1.00    5      94.48        4.90        0.18        0.02        0.40
1821   23      0.00    5      94.49        4.90        0.16        0.01        0.42
1833                                                                                     0.137 GRAMS CARBON DEPOSITED
1836   24     -1.00    5      94.49        4.88        0.19        0.01        0.41
1850   25     -1.00    5      94.30        4.90        0.18        0.01        0.58
1902                                                                                     0.160 GRAMS CARBON DEPOSITED
```

```
                                DATA TAKEN DURING RUN  46 ON 14 NOV 74

TIME SAMP       DELP IGAS        H2         CO        CH4        CO2        H2O          C
 913                    7                                                            31.880

 915                    6      32.0        0.0        0.0        0.0        0.0
 921    1       0.00    1    5146.0   235488.0   192886.0   261487.0        0.0
 927    2      -1.00    1    4813.0   219341.0   182511.0   249416.0        0.0
 950    3       0.00    1    5148.0   232197.0   192838.0   263276.0        0.0
1005                    7                                                            31.886
1007    5       0.00    1    5195.0   231209.0   192862.0   263704.0        0.0
1020    6       0.00    2   27426.0        0.0        0.0        0.0        0.0
1025    7       0.00    2   29658.0        0.0        0.0        0.0        0.0
1029                    7                                                            31.889
1031    8       0.00    2   27551.0        0.0        0.0        0.0        0.0
1036    9       0.00    2   29720.0        0.0        0.0        0.0        0.0
1059                    7                                                            31.889

1059                    8     550.0

1101                    6      28.8        6.8        0.0        0.0        0.0
1105   10       0.00    4   23814.0    95480.0        0.0        0.0        0.0
1112   11       0.00    4   25636.0    99667.0        0.0        0.0        0.0
1118   12       0.00    5   23695.0    93753.0      190.0      152.0     2148.0
1131                    7                                                            31.915
1134   13       0.00    5   25658.0    99490.0      326.0      116.0     2366.0
1149   14       0.00    5   23767.0    94081.0      296.0      138.0     2320.0
1201                    7                                                            31.943
1204   15       0.00    5   25674.0    99381.0      313.0      157.0     2239.0
1231                    7                                                            31.974
1234   17      -1.00    5   25642.0    99545.0      389.0      111.0     2680.0
1249   18      -1.00    5   23823.0    94325.0      367.0      130.0     2424.0
1301                    7                                                            32.010
1305   19       0.00    5   25752.0    99659.0      458.0      157.0     2690.0
1319   20      -1.00    5   23819.0    94103.0      446.0      104.0     3000.0
1331                    7                                                            32.044
1334   21      -1.00    5   25708.0    98710.0      497.0      135.0     2918.0
1348   22      -1.00    5   23752.0    93353.0      507.0      151.0     2513.0
1402                    7                                                            32.078
1405   23      -1.00    5   25682.0    98873.0      569.0      165.0     3139.0
1420   24      -1.00    5   23812.0    93419.0      493.0      146.0     3222.0
1432                    7                                                            32.115
1435   25       0.00    5   25652.0    98194.0      571.0      157.0     3691.0
1450   26      -1.00    5   23808.0    93029.0      462.0      158.0     3979.0
1504                    7                                                            32.148
1507   27       0.00    5   25728.0    98488.0      628.0      191.0     3555.0
1522   28      -1.00    5   23795.0    93482.0      637.0      183.0     3585.0
1539                    7                                                            32.209
1556   30      -1.00    5   23862.0    93323.0      647.0      177.0     4393.0
1600                    7                                                            32.256
```

```
                         DATA TAKEN DURING RUN  46 ON 14 NOV 74



THE CALIBRATION GASES ARE KNOWN TO BE
                          IGAS        H2         CO        CH4        CO2        H2O
                             1     25.17      24.94      24.97      24.94       0.00
                             2    100.00       0.00       0.00       0.00       0.00
                             3      0.00       0.00       0.00     100.00       0.00

CALIBRATION GAS SAMPLES FOR THIS RUN WERE ANALYSED AS

TIME SAMP        DELP IGAS        H2         CO        CH4        CO2        H2O          C
 921    1        0.00    1     25.09      25.18      24.94      24.77       0.00
 927    2       -1.00    1     25.17      24.83      24.99      25.00       0.00
 952    3        0.00    1     25.14      24.87      24.98      24.98       0.00
1007    5        0.00    1     25.29      24.74      24.96      24.99       0.00
1020    6        0.00    2    100.00       0.00       0.00       0.00       0.00
1025    7        0.00    2    100.00       0.00       0.00       0.00       0.00
1031    8        0.00    2    100.00       0.00       0.00       0.00       0.00
1036    9        0.00    2    100.00       0.00       0.00       0.00       0.00

THE RELATIVE CALIBRATION
AREA COEFFICENTS ARE      0.019374   0.885782   0.732435   1.000000   0.689999   0.027470

 ATMOSPHERIC PRESSURE WAS  759.96 .

 THE WEIGHT OF CATALYST INITIALLY CHARGED TO THE REACTOR IS  0.249 GRAMS.

 THE GROSS WEIGHT OF THE CATALYST CARRIER AND SUSPENSION MECHANISM IS  31.880 GRAMS.
```

```
                              DATA TAKEN DURING RUN  46 ON 14 NOV 74

TIME SAMP       DELP  IGAS         H2         CO        CH4        CO2        H2O        C
 913                                                                                     0.000 GRAMS CARBON DEPOSITED

 915 CHANGED INLET GAS TO     100.00       0.00       0.00       0.00       0.00              TOTAL FLOW 19.8 CC/SEC (STP)
1005                                                                                     0.006 GRAMS CARBON DEPOSITED
1029                                                                                     0.009 GRAMS CARBON DEPOSITED
1059                                                                                     0.009 GRAMS CARBON DEPOSITED

1059 REACTOR TEMPERATURE 550. DEGREES CENTIGRADE


1101 CHANGED INLET GAS TO      89.99      10.00       0.00       0.00       0.00              TOTAL FLOW 19.8 CC/SEC (STP)
1105   10       0.00   4       89.29      10.70       0.00       0.00       0.00
1112   11       0.00   4       89.44      10.55       0.00       0.00       0.00
1118   12       0.00   5       89.12      10.52       0.02       0.01       0.30
1131                                                                                     0.034 GRAMS CARBON DEPOSITED
1134   13       0.00   5       89.13      10.48       0.04       0.01       0.32
1149   14       0.00   5       89.07      10.53       0.04       0.01       0.33
1201                                                                                     0.062 GRAMS CARBON DEPOSITED
1204   15       0.00   5       89.16      10.47       0.03       0.01       0.30
1231                                                                                     0.094 GRAMS CARBON DEPOSITED
1234   17      -1.00   5       89.08      10.49       0.04       0.01       0.36
1249   18      -1.00   5       89.04      10.54       0.04       0.01       0.34
1301                                                                                     0.129 GRAMS CARBON DEPOSITED
1305   19       0.00   5       89.09      10.46       0.05       0.01       0.36
1319   20      -1.00   5       88.98      10.51       0.06       0.01       0.43
1331                                                                                     0.164 GRAMS CARBON DEPOSITED
1334   21      -1.00   5       89.13      10.39       0.06       0.01       0.39
1348   22      -1.00   5       89.09      10.46       0.06       0.01       0.36
1402                                                                                     0.197 GRAMS CARBON DEPOSITED
1405   23      -1.00   5       89.07      10.41       0.07       0.01       0.42
1420   24      -1.00   5       89.01      10.44       0.06       0.01       0.46
1432                                                                                     0.235 GRAMS CARBON DEPOSITED
1435   25       0.00   5       89.06      10.34       0.07       0.01       0.49
1450   26      -1.00   5       88.95      10.39       0.06       0.01       0.57
1504                                                                                     0.267 GRAMS CARBON DEPOSITED
1507   27       0.00   5       89.07      10.35       0.07       0.01       0.47
1522   28      -1.00   5       88.93      10.44       0.08       0.01       0.51
1539                                                                                     0.329 GRAMS CARBON DEPOSITED
1556   30      -1.00   5       88.87      10.39       0.08       0.01       0.62
1600                                                                                     0.375 GRAMS CARBON DEPOSITED
```

```
                              DATA TAKEN DURING RUN  48 ON 16 DEC 74

TIME SAMP      DELP IGAS        H2        CO       CH4       CO2        H2O          C
 922    1      0.00    1    4491.0  231985.0  175757.0  234954.0        0.0
 934    2      0.00    1    4960.0  225428.0  187077.0  254847.0        0.0
 940    3      0.00    1    4674.0  213413.0  178220.0  243302.0        0.0
 946    4      0.00    1    5002.0  224568.0  187629.0  256705.0        0.0
 953    5      0.00    2   26564.0       0.0       0.0       0.0        0.0

1000                   8     550.0
1001    6      0.00    2   28662.0       0.0       0.0       0.0        0.0
1007    7      0.00    2   26549.0       0.0       0.0       0.0        0.0
1013    8      0.00    2   28733.0       0.0       0.0       0.0        0.0
 910                   7                                                        32.142

 924                   6      32.0       0.0       0.0       0.0        0.0
 954                   7                                                        32.141
1032                   7                                                        32.123
1035    9      0.00    5   26764.0       0.0       0.0       0.0        0.0
1043   10      0.00    5   28763.0       0.0       0.0       0.0        0.0

1055                   6      24.0      17.0       0.0       0.0        0.0
1058                   7                                                        32.115
1103   11      0.00    4   18168.0  226636.0       0.0       0.0        0.0
1106   12      0.00    4   19422.0  238172.0       0.0       0.0        0.0
1115   13      0.00    5   17743.0  233816.0       0.0     127.0      413.0
1129                   7                                                        32.115
1132   14      0.00    5   19215.0  244270.0       0.0     101.0      292.0
1146   15      0.00    5   17789.0  231968.0       0.0     109.0      283.0
1202                   7                                                        32.111
1206   16      0.00    5   19187.0  244804.0       0.0     130.0       86.0
1220   17      0.00    4   18080.0  226608.0       0.0       0.0        0.0
1233                   7                                                        32.113
1235   18      0.00    4   19602.0  239545.0       0.0       0.0        0.0
1250   19      0.00    5   17839.0  231446.0       0.0     148.0      215.0
1302                   7                                                        32.113

1305                   6      16.0       0.0       0.0      30.0        0.0
1308   20      0.00    4   10927.0       0.0       0.0  539227.1        0.0
1322   21      0.00    4   10219.0       0.0       0.0  516210.0        0.0
1331                   7                                                        32.110
1339   22      0.00    5   10657.0    2064.0       0.0  546637.1     1854.0
1354   23      0.00    5    9903.0    1772.0       0.0  519840.0     2197.0
1402                   7                                                        32.105
```

```
                         DATA TAKEN DURING RUN  48 ON 16 DEC 74


THE CALIBRATION GASES ARE KNOWN TO BE
                   IGAS          H2         CO        CH4        CO2        H2O
                      1       25.17      24.94      24.97      24.94       0.00
                      2      100.00       0.00       0.00       0.00       0.00
                      3        0.00       0.00       0.00     100.00       0.00

CALIBRATION GAS SAMPLES FOR THIS RUN WERE ANALYSED AS

TIME SAMP         DELP IGAS          H2         CO        CH4        CO2        H2O          C
 922    1         0.00    1       24.56      26.46      24.69      24.27       0.00
 934    2         0.00    1       25.32      24.51      25.05      25.10       0.00
 940    3         0.00    1       25.38      24.37      25.07      25.16       0.00
 946    4         0.00    1       25.40      24.34      25.04      25.20       0.00
 953    5         0.00    2      100.00       0.00       0.00       0.00       0.00
1001    6         0.00    2      100.00       0.00       0.00       0.00       0.00
1007    7         0.00    2      100.00       0.00       0.00       0.00       0.00
1013    8         0.00    2      100.00       0.00       0.00       0.00       0.00

THE RELATIVE CALIBRATION
AREA COEFFICENTS ARE       0.019139   0.905703   0.735301   1.000000   0.689999   0.027844

 ATMOSPHERIC PRESSURE WAS  759.96 .

 THE WEIGHT OF CATALYST INITIALLY CHARGED TO THE REACTOR IS  0.423 GRAMS.

 THE GROSS WEIGHT OF THE CATALYST CARRIER AND SUSPENSION MECHANISM IS  32.145 GRAMS.
```

```
                                 DATA TAKEN DURING RUN  48 ON 16 DEC 74

TIME SAMP      DELP IGAS        H2        CO       CH4       CO2       H2O        C

1000 REACTOR TEMPERATURE 550. DEGREES CENTIGRADE

 919                                                                          -0.002 GRAMS CARBON DEPOSITED

 924 CHANGED INLET GAS TO   100.00      0.00      0.00      0.00      0.00            TOTAL FLOW 19.8 CC/SEC (STP)
 958                                                                          -0.003 GRAMS CARBON DEPOSITED
1032                                                                          -0.022 GRAMS CARBON DEPOSITED
1035    9      0.00    5    100.00      0.00      0.00      0.00      0.00
1043   10      0.00    5    100.00      0.00      0.00      0.00      0.00

1055 CHANGED INLET GAS TO    74.99     25.00      0.00      0.00      0.00            TOTAL FLOW 19.6 CC/SEC (STP)
1058                                                                          -0.029 GRAMS CARBON DEPOSITED
1100   11      0.00    4     74.03     25.96      0.00      0.00      0.00
1106   12      0.00    4     74.09     25.90      0.00      0.00      0.00
1115   13      0.00    5     73.01     26.90      0.00      0.01      0.06
1129                                                                          -0.029 GRAMS CARBON DEPOSITED
1132   14      0.00    5     73.40     26.54      0.00      0.00      0.04
1146   15      0.00    5     73.22     26.71      0.00      0.01      0.04
1202                                                                          -0.034 GRAMS CARBON DEPOSITED
1206   16      0.00    5     73.35     26.61      0.00      0.01      0.01
1220   17      0.00    4     73.96     26.03      0.00      0.00      0.00
1233                                                                          -0.031 GRAMS CARBON DEPOSITED
1235   18      0.00    4     74.12     25.87      0.00      0.00      0.00
1250   19      0.00    5     73.31     26.63      0.00      0.01      0.03
1302                                                                          -0.031 GRAMS CARBON DEPOSITED

1305 CHANGED INLET GAS TO    49.80      0.00      0.00     50.19      0.00            TOTAL FLOW 19.9 CC/SEC (STP)
1308   20      0.00    4     47.01      0.00      0.00     52.98      0.00
1322   21      0.00    4     46.78      0.00      0.00     53.21      0.00
1331                                                                          -0.035 GRAMS CARBON DEPOSITED
1339   22      0.00    5     45.96      0.22      0.00     53.55      0.26
1354   23      0.00    5     45.75      0.20      0.00     53.71      0.32
1402                                                                          -0.040 GRAMS CARBON DEPOSITED
```

```
                                     DATA TAKEN DURING RUN  49 ON 19 DEC 74

TIME SAMP       DELP IGAS        H2        CO       CH4       CO2        H2O          C
 917    1       0.00    1    4897.0  229782.0  187723.0  253189.0        0.0
 924    2       0.00    1    4665.0  213257.0  177982.0  242837.0        0.0
 930    3       0.00    1    4993.0  224696.0  187863.0  256760.0        0.0
 937    4       0.00    1    4710.0  212992.0  178401.0  244487.0        0.0
4800    5       0.00    2   26564.0       0.0       0.0       0.0        0.0
4800    6       0.00    2   29662.0       0.0       0.0       0.0        0.0
4800    7       0.00    2   26549.0       0.0       0.0       0.0        0.0
4800    8       0.00    2   28733.0       0.0       0.0       0.0        0.0
 908                    7                                                       32.000
 940                    7                                                       32.013

 942                    8     550.0
1021                    7                                                       32.020

1023                    6       0.0       0.0       0.0      60.0        0.0
1027    5       0.00    4       0.0       0.0       0.0 1031627.1      184.0
1047    6       0.00    4       0.0       0.0       0.0  978812.1        0.0
1058    7      -2.00    5       0.0       0.0       0.0 1029820.1        0.0
1103                    7                                                       32.010
1113    8      -2.00    5       0.0       0.0       0.0  976291.1        0.0
1130                    7                                                       32.013
1140    9      -2.00    5       0.0       0.0       0.0   17615.0        0.0
1150   10      -2.00    5       0.0       0.0       0.0     528.0        0.0
1158   11      -2.00    5       0.0       0.0       0.0     330.0        0.0
1202                    7                                                       32.015

1205                    6      24.0      17.0       0.0       0.0        0.0
1207   12       0.00    4   17960.0  226374.0       0.0     617.0        0.0
1214   13       0.00    4   19311.0  238923.0       0.0     798.0        0.0
1222   14      -1.00    5   17375.0  143760.0    3441.0   16500.0    32719.0
1232                    7                                                       32.798
1238   15      -2.00    5   18794.0  196183.0    2897.0   16859.0    30652.0
1253   16      -1.00    5   17375.0  183554.0    3926.0   18321.0    32512.0
1300                    7                                                       33.433
```

```
                                   DATA TAKEN DURING RUN  49 ON 19 DEC 74



THE CALIBRATION GASES ARE KNOWN TO BE
                    IGAS          H2          CO          CH4          CO2          H2O
                       1       25.17       24.94        24.97        24.94         0.00
                       2      100.00        0.00         0.00         0.00         0.00
                       3        0.00        0.00         0.00       100.00         0.00

CALIBRATION GAS SAMPLES FOR THIS RUN WERE ANALYSED AS

TIME SAMP       DELP IGAS          H2          CO          CH4          CO2          H2O          C
 917    1       0.00    1       24.90       25.37        25.00        24.72         0.00
 924    2       0.00    1       25.24       24.80        24.97        24.97         0.00
 930    3       0.00    1       25.23       24.76        24.97        25.02         0.00
 937    4       0.00    1       25.33       24.67        24.93        25.04         0.00
4900    5       0.00    2      100.00        0.00         0.00         0.00         0.00
4900    6       0.00    2      100.00        0.00         0.00         0.00         0.00
4900    7       0.00    2      100.00        0.00         0.00         0.00         0.00
4900    8       0.00    2      100.00        0.00         0.00         0.00         0.00

THE RELATIVE CALIBRATION
AREA COEFFICENTS ARE      0.019133    0.884199    0.733088    1.000000    0.689999    0.027636

 ATMOSPHERIC PRESSURE WAS  759.96 .

 THE WEIGHT OF CATALYST INITIALLY CHARGED TO THE REACTOR IS  0.251 GRAMS.

 THE GROSS WEIGHT OF THE CATALYST CARRIER AND SUSPENSION MECHANISM IS  32.000 GRAMS.
```

```
                                   DATA TAKEN DURING RUN  49 ON 19 DEC 74

TIME SAMP      DELP IGAS        H2         CO         CH4        CO2        H2O            C
 908                                                                                  0.000 GRAMS CARBON DEPOSITED
 940                                                                                  0.012 GRAMS CARBON DEPOSITED

 942 REACTOR TEMPERATURE 550. DEGREES CENTIGRADE

1021                                                                                  0.019 GRAMS CARBON DEPOSITED

1023 CHANGED INLET GAS TO      0.00       0.00       0.00     100.00       0.00             TOTAL FLOW 20.0 CC/SEC (STP)
1027    5       0.00    4      0.00       0.00       0.00      99.97       0.02
1042    6       0.00    4      0.00       0.00       0.00     100.00       0.00
1058    7      -2.00    5      0.00       0.00       0.00     100.00       0.00
1103                                                                                  0.009 GRAMS CARBON DEPOSITED
1113    8      -2.00    5      0.00       0.00       0.00     100.00       0.00
1130                                                                                  0.012 GRAMS CARBON DEPOSITED
THE SUM OF THE FOLLOWING DATA DIFFERED FROM 100 PERCENT BY MORE THAN 10 PERCENT BEFORE JUSTIFICATION
1140    9      -2.00    5      0.00       0.00       0.00     100.00       0.00
THE SUM OF THE FOLLOWING DATA DIFFERED FROM 100 PERCENT BY MORE THAN 10 PERCENT BEFORE JUSTIFICATION
1150   10      -2.00    5      0.00       0.00       0.00     100.00       0.00
THE SUM OF THE FOLLOWING DATA DIFFERED FROM 100 PERCENT BY MORE THAN 10 PERCENT BEFORE JUSTIFICATION
1159   11      -2.00    5      0.00       0.00       0.00     100.00       0.00
1202                                                     .                            0.014 GRAMS CARBON DEPOSITED

1205 CHANGED INLET GAS TO     74.99      25.00       0.00       0.00       0.00             TOTAL FLOW 19.8 CC/SEC (STP)
1207   12       0.00    4     73.49      26.44       0.00       0.06       0.00
1214   13       0.00    4     73.54      26.37       0.00       0.07       0.00
1222   14      -1.00    5     71.49      21.43       0.49       1.70       4.89
1232                                                                                  0.797 GRAMS CARBON DEPOSITED
1239   15      -2.00    5     71.96      21.66       0.39       1.64       4.33
1253   16      -1.00    5     71.34      21.37       0.55       1.88       4.85
1300                                                                                  1.432 GRAMS CARBON DEPOSITED
```

8.4.3 Data Conversion Computer Program

A listing of the FORTRAN program employed to convert data readings to tabular summaries of experimental operating conditions and results follows:

```
PAGE    1

 // JOB T

 LOG DRIVE   CART SPEC   CART AVAIL  PHY DRIVE
   0000        02FA        02FA        0000

 V2 M12   ACTUAL  8K  CONFIG  8K

 // FOR
 *IOCS(TYPEWRITER,KEYBOARD,DISK,CARD,1132PRINTER,PLOTTER)
 *LIST SOURCE PROGRAM
       DIMENSION ITIME(99),DELP(99),IGAS(99),DATA(99,5),CAL(6),
      1CALCO(6),SUMD(6),ISAMP(99),RCC(6),IDATE(5),MSG(160)
    01 READ (2,101)NRUN,NSAMP,PATM,PH2O,IDATE,CZERO,FEZER
        IF(NRUN)68,68,02
     02 WRITE(3,102)NRUN,IDATE
    101 FORMAT(5X,I5,5X,I5,5X,F5.2,5X,F6.3,4X,5A2,5X,2F10.3)
    102 FORMAT(1H1,33X,21HDATA TAKEN DURING RUN,I4,3H ON,5A2)
        WRITE(3,116)
        IH2O=PH2O
        PATM=PATM*25.4
        CAL(1)=25.18
        CAL(2)=24.91
        CAL(3)=24.97
        CAL(4)=24.94
        CAL(5)=PH2O*100./PATM
        CAL(6)=100.
        NSUM1=0
        NSUM2=0
        NSUM3=0
        DO 05 N=1,6,1
        SUMD(N)=0.
     05 CONTINUE
        DO 11 I=1,NSAMP,1
     11 READ (2,103)ITIME(I),ISAMP(I),DELP(I),IGAS(I),(DATA(I,J),J=1,5)
        DO 10 I=1,NSAMP,1
        IF(IGAS(I)-6)18,51,51
     18 WRITE(3,103)ITIME(I),ISAMP(I),DELP(I),IGAS(I),(DATA(I,J),J=1,5)
    103 FORMAT(2I5,5X,F5.2,I5,5F10.1)
        DO 20 K=1,5,1
        DATA(I,K)=DATA(I,K)*PATM/(PATM+DELP(I))
     20 CONTINUE
        K=IGAS(I)
        GO TO (30,40,50,10,10),K
     30 DO 70 J=1,4,1
        SUMD(J)=SUMD(J)+DATA(I,J)
     70 CONTINUE
        NSUM1=NSUM1+1
        GO TO 10
     40 SUMD(6)=SUMD(6)+DATA(I,1)
        NSUM2=NSUM2+1
        GO TO 10
     50 SUMD(5)=SUMD(5)+DATA(I,5)
        NSUM3=NSUM3+1
```

```
PAGE    2

      GO TO 10
   51 K=IGAS(I)-5
      GO TO (52,53,54),K
   52 WRITE(3,106)ITIME(I),IGAS(I),(DATA(I,J),J=1,5)
  106 FORMAT(1H0,I4,15X,I5,5F10.1)
      GO TO 10
   53 WRITE(3,107)ITIME(I),IGAS(I),DATA(I,1)
  107 FORMAT(I5,15X,I5,50X,F10.3)
      GO TO 10
   54 WRITE(3,106)ITIME(I),IGAS(I),DATA(I,1)
   10 CONTINUE
      DO 45 L=1,4,1
      CALCO(L)=SUMD(L)*100./(NSUM1*CAL(L))
   45 CONTINUE
      IF(IH2O)68,46,47
   46 CALCO(5)=CALCO(4)*0.69
      GO TO 48
   47 CALCO(5)=SUMD(5)*100./(NSUM3*CAL(5))
   48 CALCO(6)=SUMD(6)*100./(NSUM2*CAL(6))
      A=SUMD(6)/NSUM2
      B=SUMD(1)/NSUM1
      HSLOP=(ALOG(100.)- ALOG(25.18))/(ALOG(A)-ALOG(B))
      NCAL =0
      NCAL1=0
      NCAL2=0
   71 DO 65 I=1,NSAMP,1
      IF(NCAL1)68,80,81
   80 WRITE(3,102)NRUN,IDATE
      READ (2,112)MSG
      WRITE(3,112)MSG
  112 FORMAT(40A2)
      WRITE(3,113)
  113 FORMAT(//38H THE CALIBRATION GASES ARE KNOWN TO BE/21X,55HIGAS
     1      H2          CO          CH4          CO2          H2O    )
      SUM=100.-CAL(5)
      WRITE(3,114)SUM,CAL(5)
  114 FORMAT(24X,52H1          25.17       24.94       24.97       24.94       0.00
     1        /24X,52H2       100.00        0.00        0.00        0.00       0.00
     2        /24X,36H3         0.00        0.00        0.00       ,F6.2,5X,F5.2)
      WRITE(3,115)
  115 FORMAT(/54H CALIBRATION GAS SAMPLES FOR THIS RUN WERE ANALYSED AS)
      WRITE(3,116)
  116 FORMAT(1H0,  9HTIME SAMP,5X,70H DELP IGAS          H2          CO
     1  CH4          CO2          H2O          C    )
      NCAL1=NCAL1+1
   81 IF(NCAL)68,82,83
   82 IF(IGAS(I)-4)72,65,65
   83 IF(NCAL2)68,84,85
   84 WRITE(3,102)NRUN,IDATE
      WRITE(3,116)
      NCAL2=NCAL2+1
   85 IF(IGAS(I)-4)65,86,86
   86 IF(IGAS(I)-6)72,69,69
```

```
   72 J=1
      DATA(I,J)=EXP(ALOG(100.)-(ALOG(A)-ALOG(DATA(I,J)))*HSLOP)
      SUM=DATA(I,J)
      DO 66 J=2,5,1
      DATA(I,J)=DATA(I,J)*100./CALCO(J)
      SUM=SUM+DATA(I,J)
   66 CONTINUE
      DO 67 J=1,5
      DATA(I,J)=DATA(I,J)*100./SUM
   67 CONTINUE
      INDEX=(SUM-100.)/10.
      IF(INDEX)690,691,690
  690 WRITE(3,108)
  108 FORMAT(1X,100HTHE SUM OF THE FOLLOWING DATA DIFFERED FROM 100 PERC
     1ENT BY MORE THAN 10 PERCENT BEFORE JUSTIFICATION)
  691 WRITE(3,105)ITIME(I),ISAMP(I),DELP(I),IGAS(I),(DATA(I,J),J=1,5)
  105 FORMAT(2I5,5X,F5.2,I5,5F10.2)
      GO TO 65
   69 K=IGAS(I)-5
      GO TO (152,156,157),K
  152 DATA(I,1)=DATA(I,1)/1.6125
      DATA(I,2)=DATA(I,2)/3.4250
      DATA(I,3)=DATA(I,3)/ 4.3125
      DATA(I,4)=DATA(I,4)/3.0000
      SUM=0.
      DO 153 K=1,4
  153 SUM=SUM+DATA(I,K)
      DATA(I,5)=SUM*DATA(I,5)/PATM
      SUM=SUM+DATA(I,5)
      DO 154 K=1,5
  154 DATA(I,K)=100.*DATA(I,K)/SUM
      WRITE(3,109)ITIME(I),(DATA(I,K),K=1,5),SUM
  109 FORMAT(1H0,I4,21H CHANGED INLET GAS TO,F9.2,4F10.2,11X,11HTOTAL FL
     1OW ,F4.1,13H CC/SEC (STP))
      GO TO 65
  156 C=DATA(I,1)-CZERO
      WRITE(3,110)ITIME(I),C
  110 FORMAT(I5,70X,F10.3,23H GRAMS CARBON DEPOSITED)
      GO TO 65
  157 WRITE(3,111)ITIME(I),DATA(I,1)
  111 FORMAT(/I5,21H REACTOR TEMPERATURE ,F4.0,19H DEGREES CENTIGRADE/)
   65 CONTINUE
      NCAL =NCAL +1
      IF(NCAL2)68,89,90
   89 DO 55 I=1,6,1
      RCC(I)=CALCO(I)/CALCO(4)
   55 CONTINUE
      WRITE(3,104)(RCC(I),I=1,6)
      WRITE(3,117)PATM
      WRITE(3,118)FEZER
      WRITE(3,119)CZERO
  118 FORMAT(1H0,60H THE WEIGHT OF CATALYST INITIALLY CHARGED TO THE REA
     1CTOR IS  ,F6.3,7H GRAMS.)
```

```
  119 FORMAT(1H0,70H THE GROSS WEIGHT OF THE CATALYST CARRIER AND SUSPEN
     1SION MECHANISM IS  ,F7.3,7H GRAMS.)
  117 FORMAT(1H0,26H ATMOSPHERIC PRESSURE WAS  ,F7.2,2H .)
      GO TO 71
   90 GO TO 91
  104 FORMAT(1H0,24HTHE RELATIVE CALIBRATION/25H AREA COEFFICENTS ARE
     1  ,6F10.6)
   68 CALL EXIT
      END

FEATURES SUPPORTED
 IOCS

CORE REQUIREMENTS FOR
 COMMON       0  VARIABLES   2220  PROGRAM   1866

END OF COMPILATION

// XEQ
```

8.5 Nomenclature

a	area, cm^2
b	exponent, dimensionless
$C_o, C_1, C_2, C_3, C_4, C_5, C_6$	constants in polynomial equation
C_p	heat capacity, cal/mole-K
D	diameter, cm
$\mathcal{D}$	diffusion coefficient, cm^2/sec
G	superficial mass flow rate, g/cm^2-sec
G_m	superficial molar flow rate, moles/cm^2-sec
j_D	Chilton - Colburn j-factor
k_i	calibration constant, moles/cm^2
k_G	mass transfer coefficient, moles/cm^2-sec-atm
$K_1, K_2, K_3, K_4, K_5, K_6$	equilibrium constants
L	length, cm
M	molecular weight
n	hydrogen recycle per mole inlet CO_2, moles
n_i	moles of component i
P	pressure or partial pressure, atm
P_{BM}	logarithmic mean of component pressure in bulk and at interface
$\Delta P_{\ell M}$	logarithmic mean pressure difference
Q	rate of heat input, cal/sec
r	total gas recycle in Bosch reactor per mole inlet CO_2, moles
R	gas constant, 82 cc-atm/mole-K
T	temperature, K
u	superficial velocity, cm/sec
V	specific volume, cm^3/g
x	number of moles converted

μ	viscosity, g/cm-sec
ρ	density, g/cm^3

Subscripts

1	component 1
2	component 2
i	component i
av	average

8.6 Literature References

Baker, R.T.K., and P.S. Harris, "Controlled Atmosphere Electron Microscopy," *J. Phys.*, *Sect. E*, *Scientific Instruments*, *5*, 793 (1972).

Baker, R.T.K., M.A. Barber, P.S. Harris, F.S. Feates, and R.J. Waite, "Nucleation and Growth of Carbon Deposits from the Nickel Catalyzed Decomposition of Acetylene," *J. Catalysis*, *26*, 51 (1972).

Baker, R.T.K., P.S. Harris, R.B. Thomas, and R.J. Waite, "Formation of Filamentous Carbon from Iron, Coablt and Chromium Catalyzed Decomposition of Acetylene," *J. Catalysis*, *30*, 86 (1973).

Baker, R.T.K., and R.J. Waite, "Formation of Carbonaceous Deposits from the Platinum-Iron Catalyzed Decomposition of Acetylene," *J. Catalysis*, *37*, 101 (1975).

Barkley, L.W., T.E. Corrigan, H.W. Wainwright, and A.E. Sands, "Catalytic Reverse Shift Reaction: A Kinetic Study," *Ind. Eng. Chem.*, *44*, 1066 (1952).

Berry, T.F., R.N. Ames, and R.B. Snow, "Influence of Impurities and Role of Iron Carbides in Deposition of Carbon from Carbon Monoxide," *J. Am. Ceramic Soc.*, *39*, 308 (1956).

Boehm, H.P., "Carbon from Carbon Monoxide Disproportionation on Nickel and Iron Catalysts: Morphological Studies and Possible Growth Mechanisms," *Carbon*, *11*, 583 (1973).

Bohlbro, H., "The Kinetics of the Water-Gas Conversion at Atmospheric Pressure," *Acta Chem. Scand.*, *15*, 502 (1961).

Browning, L.C., T.W. DeWitt, and P.H. Emmett, "Equilibria in the Systems Fe_2C-Fe-CH_4-H_2 and Fe_3C-Fe-CH_4-H_2," *J. Am. Chem. Soc.*, *72*, 4211 (1950).

Browning, L.C., and P.H. Emmett, "Equilibrium Measurements in the System C-CH_4-H_2," *J. Am. Chem. Soc.*, *73*, 581 (1951).

Chatterjee, B., and P.P. Das, "Nature of the Catalyst in the Decomposition of Carbon Monoxide in the Presence of Iron," *Nature*, *173*, 1046 (1954).

Dal Nogare, S., and R.S. Juvet, "Gas-Liquid Chromatography, Theory and Practice," Wiley, New York (1962), pp. 257-264.

Das, P.P., and B. Chatterjee, "Iron as a Catalyst in the Decomposition of Carbon Monoxide," Trans. Indian Inst. Metals, 6, 279 (1952).

Das, P.P., and B. Chatterjee, "The Nature of the Catalyst in the Decomposition of Carbon Monoxide in the Presence of Iron," Trans. Indian Inst. Metals, 7, 189 (1955).

Davis, W.R., R.J. Slawson, and G.R. Ribgy, "CO Attack on Firebricks: The Physical State of the Deposited Carbon," Trans. Br. Ceram. Soc., 56, 67 (1957).

Dietz, W.A., "Response Factors for Gas Chromatographic Analyses," J. Gas Chromatog., 5, 68 (1967).

Duggin, M.J., and L.J.E. Hofer, "Nature of X-Iron Carbide," Nature, 212, 248 (1966).

Eckstrom, H.C., and W.A. Adcock, "A New Iron Carbide in Hydrocarbon Synthesis Catalysts," J. Am. Chem. Soc., 72, 1042 (1950).

Elliott, R.P., "Constitution of Binary Alloys, First Supplement," McGraw-Hill, New York (1965).

Evans, E.L., J.M. Thomas, P.A. Thrower, and P.L. Walker, "Growth of Filamentary Carbon on Metallic Surfaces During the Pyrolysis of Methane and Acetone," Carbon, 11, 441 (1973).

Everett, M.R., and D.V. Kinsey, "Some Aspects of Carbon Transport in High Temperature Gas Cooled Reactors," D.P. Report 365, Atomic Energy Establishment, Winfrith (1965).

Everett, M.R., "The Kinetics of Carbon Deposition Reactions in High-Temperature Gas-Cooled Reactors," D.P. Report 500, Atomic Energy Establishment, Winfrith (January 1967).

Fischer, F., and H.A. Bahr, "Ges. Abhandl. Kenntnis. Kohle., 8, 225 (1928) cited as footnote 31, Walker et al. (1959).

Fleureau, B., "Sur la formation de graphite par decomposition catalytique de l'oxyde de carbone," Compt. rend., 237, 330 (1953).

Hansen, M., editor, "Constitution of Binary Alloys," 2nd ed., McGraw-Hill, New York (1958).

Herbstein, F.H., and J.A. Snyman, "Identification of Eckstrom-Adcock Iron Carbide as Fe_7C_3," Inorg. Chem., 3, 894 (1964).

Hofer, L.J.E., E.M. Cohn, and W.C. Peebles, "The Modifications of the Carbide, Fe_2C; Their Properties and Identification," J. Am. Chem. Soc., 71, 189 (1949).

Hollis, O.L., and M.V. Hayes, "Water Analysis by Gas Chromatography Using Porous Polymer Columns," J. Gas Chromatography, 4, 235 (1966).

Holmes, R.F., E.E. Keller, and C.D. King, "A Carbon Dioxide Reduction Unit Using Bosch Reaction and Expendable Catalyst Cartridges," NASA CR-1682, (November 1970).

Jack, K.H., "Iron-Nitrogen, Iron-Carbon, and Iron-Carbon-Nitrogen Interstitial Alloys: Their Occurrence in Tempered Martensite," Nature, No. 4002, 61 (July 13, 1946).

Jack, K.H., and S. Wild, "Nature of χ-Carbide and Its Possible Occurrence in Steels," Nature, 212, 248 (1966).

Karcher, W., and P. Glaude, "Inhibition of Carbon Deposition on Iron and Steel Surfaces," Carbon, 9, 617 (1971).

Karcher, W., and P. Glaude, "Reaction of Nuclear Graphites with Hydrogen at Total Pressures Between 1 and 40 Atmospheres," Carbon, 1972. Preprints of the International Carbon Conference, Baden-Baden, 1972, pp. 71-73.

Kohn, J.A., and D.W. Eckart, "X-Ray Study of Synthetic Diamond and Associated Phases," Am. Mineralogist, 47, 1422 (1962).

Kusner, R.E., "Kinetics of the Iron Catalyzed Reverse Water-Gas Shift Reaction," Ph.D. Thesis, Case Institute of Technology, Ohio (1962).

Louw, J.D., J.P. Van Den Berg, L.C. Ferreira, and J.J. Pienaar, "Appearance of FeC in a Hydrocarbon Synthesis Catalyst," J. Am. Chem. Soc., 79, 5899 (1957).

MacIver, D.S., and P.H. Emmett, "Surface Area Measurements on Carbon Black Produced by the Catalytic Decomposition of Carbon Monoxide Over Iron," J. Phys. Chem., 59, 1109 (1955).

Mars, P., "Factors Governing the Behavior of the Adiabatic Water-Gas Shift Reactor," Chem. Eng. Sci., 14, 375 (1961).

McCartney, J.T., L.J.E. Hofer, B. Seligman, J.A. Lecky, W.C. Peebles, and R.B. Anderson, "Electron and x-Ray Diffraction Studies of Iron Fischer-Tropsch Catalysts," J. Phys. Chem., 57, 730 (1953).

Nelson, H.R., "The Primary Oxide Film on Iron," J. Chem. Phys., 5, 252 (1937).

Podgurski, H.H., J.T. Kummer, T.W. DeWitt, and P.H. Emmett, "Preparation, Stability, and Adsorptive Properties of the Carbides of Iron," J. Am. Chem. Soc., 72, 5382 (1950).

Podolski, W.F., and Y.G. Kim, "Modeling the Water-Gas Shift Reaction," Ind. Eng. Chem. Proc. Des. Develop., 13, 415 (1974).

Purcell, J.E., and L.S. Ettre, "Analysis of Hydrogen with Thermal Conductivity Detectors," J. Gas Chromatog., 3, 69 (1965).

Ratliff, J.T., "Early Stages in the Interaction of Carbon Monoxide with Single Crystal Films," Ph.D. Thesis, Georgia Institute of Technology (1968).

Renshaw, G.D., C. Roscoe, and P.L. Walker, Jr., "Disproportionation of CO Over Iron and Silicon-Iron Single Crystals," J. Catalysis, 18, 164 (1970).

Robertson, S.D., "Carbon Formation from Methane Pyrolysis Over Some Transition Metal Surfaces I. Nature and Properties of the Carbon Formed," Carbon, 8, 365 (1970).

Ruston, W.R., M. Warzee, J. Hennaut, and J. Waty, "The Solid Reaction Products of the Catalytic Decomposition of Carbon Monoxide on Iron at 550°C," Carbon, 7, 47 (1969).

Ruston, W.R., M. Warzee, J. Hennaut, and J. Waty, "Basic Studies on the Growth of Carbon Deposition from Carbon Monoxide on a Metal Catalyst," D.P. Report 394, Atomic Energy Establishment, Winfrith (1966).

Ruthven, D.M., "A Simple Method of Calculating Mass Transfer Factors for Heterogeneous Catalytic Gas Reactors," Chem. Eng. Sci., 23, 759 (1968).

Satterfield, C.N., and D.H. Cortez, "Mass Transfer Characteristics of Woven-Wire Screen Catalysts," I&EC Fund., 9, 613 (1970).

Sherwood, T.K., and R.L. Pigford, "Absorption and Extraction," McGraw-Hill, New York (1952).

Shunk, F.A., "Constitution of Binary Alloys, Second Supplement," McGraw-Hill, New York (1969).

Stricoff, R.S., "The Reduction of Carbon Dioxide with Hydrogen Over Iron Catalysts," S.M. Thesis, Massachusetts Institute of Technology (1972).

Stull, D.R., and H. Prophet, "JANAF Thermochemical Tables," 2nd ed., National Bureau of Standards, Washington (1971).

Tamar, Y., Y. Nishiyama, and M. Takahashi, "The Effects of Helium Upon Carbon Deposition Onto Metal Surfaces," Carbon, 7, 209 (1969).

Tesner, P.A., E.Y. Rabinovich, I.S. Rafalkes, and E.F. Arefieva, "Formation of Carbon Fibers from Acetylene," Carbon, 8, 435 (1970).

Tevebaugh, A.D., and E.J. Cairns, "CHO Gas Phase Compositions in Equilibrium with Carbon and Carbon Deposition Boundaries at One Atmosphere," J. Chem. Eng. Data, 9, 453 (1964).

Tevebaugh, A.D., and E.J. Cairns, "Carbon Deposition Boundaries in the CHO System at Several Pressures," J. Chem. Eng. Data, 10, 359 (1965).

Walker, P.L., Jr., J.F. Rakszawski, and G.R. Imperial, "Carbon Formation from Carbon Monoxide-Hydrogen Mixtures Over Iron Catalysts I. Properties of Carbon Formed," J. Phys. Chem., 73, 133 (1959), "II. Rates of Carbon Formation," Ibid., 140 (1959).

Warzee, M., C. Sonnen, J. Hennaut, and W.R. Ruston, "Study of Catalytic Decomposition of Carbon Monoxide on Pure Iron, Mild Steels, and Alloyed Steels," D.P. Report-530, Atomic Energy Establishment, Winfrith (1967).

Watase, T., J. Chem. Soc. Japan, 54, 110 (1933).

Wert, C.A., "Precipitation from Solid Solutions of C and N in α-Iron," J. App. Phys., 20, 943 (1949).

Wert, C.A., "Diffusion Coefficient of C in α-Iron," Phys. Rev., 79, 601 (1950).

Westerman, R.V., "Mechanism and Kinetics of Iron Deterioration in Carbon Monoxide," Ph.D. Thesis, Georgia Institute of Technology (1967).

Wilson, R.B., "Fundamental Investigation of the Bosch Reaction," S.M. Thesis, Massachusetts Institute of Technology (1971).

Wicke, E., K. Hedden, P. Hugo, and A. Löwe, "Corrosion Rate of Graphites by CO_2 and H_2O Vapor Taking into Account In-Pore Diffusion and Temperature Gradients," D.P. Report 391, Atomic Energy Establishment, Winfrith (1966).

Zener, C., "Theory of Growth of Spherical Precipitates from Solid Solution," J. App. Phys., 20, 950 (1949).