CONVERSION OF N-HEPTANE TO SUBSTITUTE NATURAL GAS

by

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ABSTRACT

The production of substitute natural gas (SNG) was investigated in this work by studying the chemical equilibria in the steam reforming of n-heptane. An isothermal tubular-flow reactor was used, together with a nickel-alumina catalyst. The reactions were investigated over a pressure range of 5 ~ 300 p.s.i.g., and a temperature range of 350 ~ 530°C. The mole ratio of steam to hydrocarbon varied from 8 to 24.

The results indicate that the condition of equilibrium was nearly reached for several different stages of decomposition of n-heptane. As a result, the composition of the products can be predicted at a given temperature, pressure and reactant ratio. It was found that the primary products of the decomposition, under the conditions adopted in this work, are carbon monoxide and hydrogen. The conversion of n-heptane is strongly temperature dependent; it was not affected by changing the partial pressure of steam. The optimum conditions for the production of a gas mixture rich in methane are at pressures above 200 psig and temperatures below 600°C. The activation energy of the reaction was calculated to be of the order of 20 Kcal/g-mole.

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NOMENCLATURE

English Letter Symbols

E	Activation energy
F	Rate of n-heptane feed
f	Fugacity
$\Delta G°$	Standard free energy change for a chemical reaction
$\Delta G_f°$	Standard free energy change of formation
$\Delta H°$	Standard heat of a chemical reaction
$\Delta H_f°$	Standard heat of formation
ΔH_o	Constant in the equation $\Delta H°_T = \Delta H_o + \Delta \alpha T + \frac{\Delta \beta}{2} T^2 + \frac{\Delta \gamma}{3} T^3$
I	Integration constant
K	Chemical-rection equilibrium constant
K_φ	Fugacity term for a reaction $aA + bB \rightleftharpoons cC + dD$ where $K_\varphi = \varphi_C^c \varphi_D^d / \varphi_A^a \varphi_B^b$
k	Reaction rate constant
N	Number of moles

NOMENCLATURE

English Letter Symbols

P	Pressure
R	Universal gas constant
r	Reaction rate
T	Temperature
W	Weight of catalyst, gm.
x	Conversion of n-heptane
Z	Active site of catalyst

Greek Letter Symbols

α, β, γ	Constant in the equation $C_P = \alpha + \beta T + \gamma T^2$
Δ	Indicate a finite change in the quantity, i. e., the final value minus the initial value
μ	Micron
φ	Fugacity coefficient (f/p)

I. INTRODUCTION

The advantage of natural gas

Natural gas is consumed in domestic heating and many industries, e.g. food, tobacco, textile, leather, rubber, paper, glass, cement, chemical, metal, etc.[1]. It is used in industries for boilers, kilns and central heating. The characteristics of natural gas are completely different from that of coal and oil. It is a clean fuel that can be transported to the places where combustion is required; it produces heat in a simple and controllable way; its combustion products do not pollute the environment. When natural gas is used as a fuel, the necessity to apply a heat transport medium for heat distribution is absent in many cases. The use of natural gas in direct-fired gas systems offers industry the benefits of high efficiency, especially for drying processes, as found in the paper, ceramic, textile, and food industries. The use of natural gas for boilers in industry has been increasing in recent years[2]. The burner installation of a gas-fired boiler is simpler and the space required to burn the gas is less than for oil, contributing to a lower installation cost. The combustion gases are also free from soot, ash and are usually free from or low in sulphur.

The shortage of natural gas

Unfortunately the reserves of natural gas are limited and not large. It has been observed[3] by the National Petroleum Council and Institute of Gas Technology (IGT) that to stimulate exploration and development of U. S. gas resources to a significant extent will require

huge investments and large price increases. Even with this, the increases in production are expected to fall far short of the requirements and depend on relatively high finding rates. It becomes clear that the path with the lowest investment cost and minimum time for supplemental clean fuel gas is the production of Substitute Natural Gas (SNG) from light/liquid hydrocarbons. The production of SNG from coal, or crude oil is also possible in the near future.

Although the problems is not as serious in Canada as in the United States, a search for an additional source of clean and convenient fuel is desirable to meet future demands.

The development of the SNG process

Industrial processes based on the catalytic reaction between steam and light liquid hydrocarbons to produce a gas rich in methane have been studied recently[4][3]. In these reforming processes, the operating conditions are generally in the range of temperature from 400°C to 600°C and pressures from 15 atm. to 25 atm. The complete steps for the production of SNG may include desulfurization, gasification, methanation, methane concentration and drying. Of these, only gasification, is unique to SNG processing. The calorific value[5] of the gas leaving the gasification reactor is typically between 850 and 930 Btu/s.c.f. on a CO_2 and water-free basis. It is increased to 990-1005 Btu/scf conventionally by methanation, carbon dioxide removal and drying. The principal operating steps of the currently important Low Temperature Catalyst Reforming (LTCR) processes are shown in a block flow diagram in Figure 1-1[6].

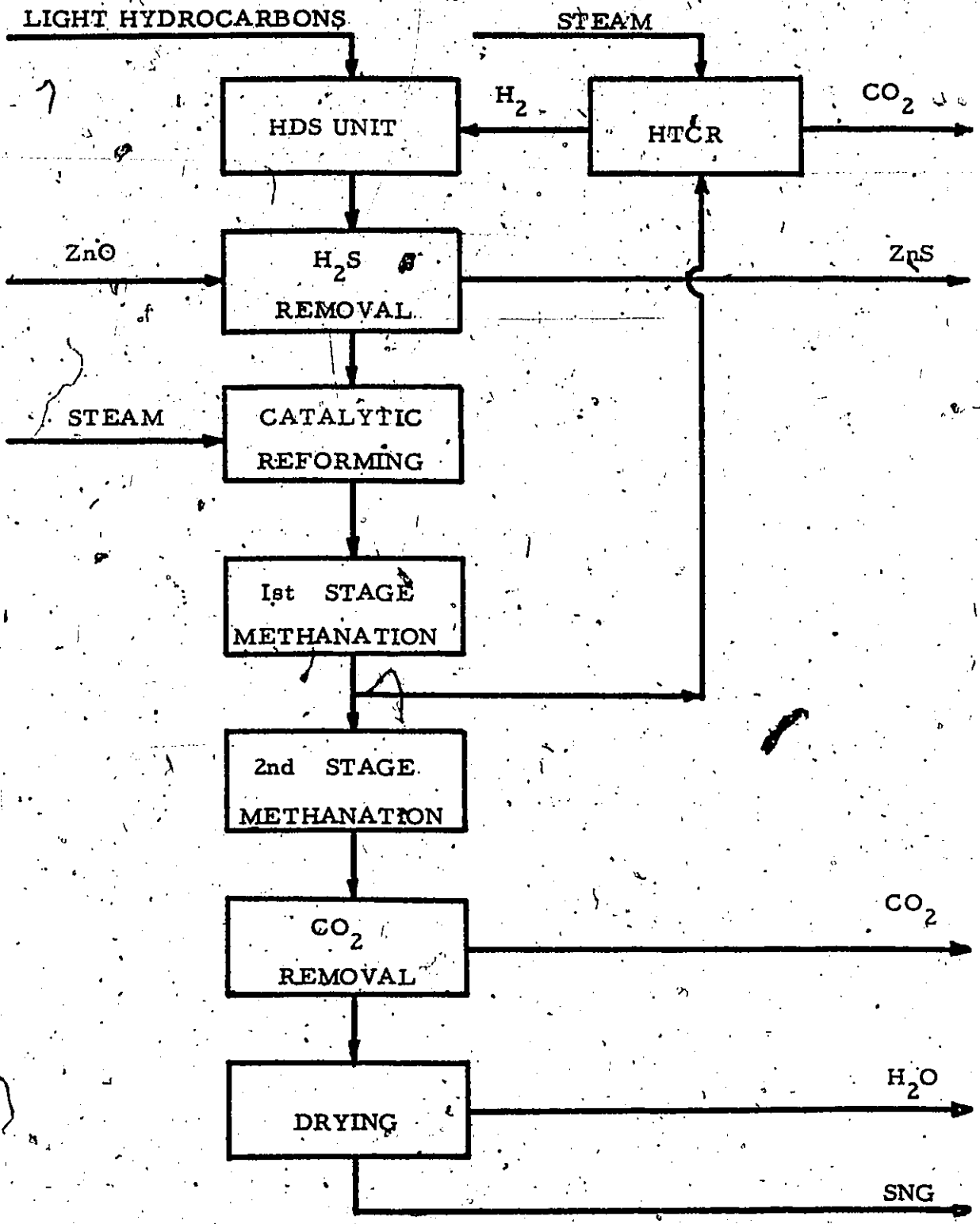


Figure 1-1 Low Temperature Catalytic Reforming Process

HDS - Hydrodesulfirization, this involves catalytic treatment of the vaporized feed with hydrogen. The organic sulfides are converted to H_2S

HTCR - High temperature catalytic reforming, a small amount of methane and large amount of hydrogen is formed.

The present investigation

It has been found that when light hydrocarbons are completely decomposed with steam in the presence of an active catalyst, the following reactions reach equilibrium[4][5]:

$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O \qquad (1\text{-}1)$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad (1\text{-}2)$$

To explain the phenomena observed in industrial plants, it has been suggested that these equilibria also apply when the feed is only partly decomposed[4].

The present work was carried out to test whether the reactions reach equilibrium for different stages of decomposition of n-heptane in the steam-reforming process. We also investigated the effect of temperature, pressure and reactant ratio on the fractional conversion of hydrocarbon and the yield of products. The thermodynamic equilibrium characteristics of a chemical reaction system are important and helpful to process design because they can predict the distribution of products and determine the most favourable conditions of temperature, pressure and reactant ratios for the maximum conversion of reactants and the desired composition of products. For the steam-reforming process with gaseous reactants, fast rate reactions and a low feed rate, a tubular-flow reactor is most suitable. The nickel-alumina catalyst was adopted because of its high activity and because it has been developed in many patents[7][8][9].

II. LITERATURE SURVEY

Steam-reforming of liquid hydrocarbons has been known as a potential process for the production of substitute natural gas (SNG). A study of the reaction equilibria and kinetics are necessary for the development of such processes. Thermodynamic and kinetic considerations are briefly reviewed in this chapter.

A. The Equilibrium Reaction

The steam reforming of low molecular weight hydrocarbons for the production of synthesis gas (H_2 & CO_2) started in the 1930's with the catalytic reforming of natural gas (Eqn 2-1) at atmospheric pressure in multi-tubular reactors operating at about 870°C, followed by water-gas shift (Eqn 2-2) reactors at 460°C[10]. The equilibrium system arising from two simultaneous reversible reactions has been studied by Dodge[11], who proposed that the equilibria of steam reforming of methane are as follows:

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \qquad (2\text{-}1)$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad (2\text{-}2)$$

Somer[12] has collected the information on the product composition from a plant reforming 600,000 scf/day of methane. The results for three different commercial catalysts with reaction temperatures above 750°C show that equilibrium is approached very closely. Besides the equilibrium reaction [2-1] & [2-2] he also considered the carbon reaction as one of major importance i. e.

$$CO_2 + C \rightleftharpoons 2CO \qquad (2\text{-}3)$$

This reaction might be applied to check the possibility of carbon formation. However, it should be noted that a theoretical analysis of carbon-formation equilibria is not always conclusive. According to Brester et al[13], there are many installations that operate successfully even though the equilibria indicate that the operations are in the range of carbon-formation.

Based on the previous work[14][15], the general forms of the initial reactions of steam with any paraffin C_nH_{2n+2} may be presented as follows:

$$C_nH_{2n+2} + 2n\,H_2O \longrightarrow nCO_2 + (3n+1)\,H_2 \qquad (2\text{-}4)$$

$$C_nH_{2n+2} + n\,H_2O \longrightarrow nCO + (2n+1)\,H_2 \qquad (2\text{-}5)$$

For the reaction of ethane with water over nickel catalysts, Balandin et al[14] suggested that the initial products were carbon dioxide and hydrogen, but most other workers[4][5][13][15][16] believed that the initial products were carbon monoxide and hydrogen rather than carbon dioxide.

Bhatta and Dixon[17] made a study of the reaction of n-butane with steam at a total pressure of 30 atm. in the temperature range 425-675°C over a 15% nickel-alumina catalyst. They found that equilibrium was achieved at all levels of conversions of butane in an isothermal tubular reactor. Rogers and Crooks[18], using n-butane as feedstock, found that their results did not agree with Bhatta completely. Their experimental results show that the product composition differed from

those predicted values at low levels of conversion. There was good agreement between the experimental and calculated equilibrium gas-composition at the condition of complete conversion.

Cockerham and co-workers[4] found that when light distillates were gasified with steam in the presence of a sufficiently active catalyst, the methanation reaction (Eqn 1-1) and the water-gas shift reaction (Eqn 1-2) were brought to equilibrium. These equilibria were closely approached in the Gas Council's rich-gas process for the production of town-gas[4].

Recently Phillips and his co-workers[16] tested the hypothesis that the equilibria were applicable when the hydrocarbon was only partly decomposed. Using n-heptane as feedstock and a 75% nickel-alumina catalyst, they found that the yields of hydrogen and carbon oxides were much higher than the predicted values.

B. Kinetic Study

A kinetic study was made by Akers and Camp[19], of the reactions of steam with natural gas over a nickel catalyst in a temperature range of 336°C to 638°C. They found that the rate of reaction was first order with respect to methane.

Two possible rate-controlling steps were given: (1) the mass transfer of the methane to the catalyst surface; (2) a first-order reaction, being either the chemisorption of the methane on the active centers of the catalyst or the decomposition of the absorbed methane to form free radicals. Their results indicate that the rate-controlling step is the decomposition of the adsorbed methane to form CH_2 radicals.

Mass transfer, although not rate controlling, can exert an effect on the rate.

Bodrov et al[20] studied the kinetics of the reaction of methane with steam on nickel foil at temperatures of 800° - 900°C. The mechanisms of the reforming reaction and the water-gas shift reaction were explained by the following sequence of reactions:

a) $CH_4 + Z \rightleftharpoons ZCH_2 + H_2$

b) $ZCH_2 + H_2O \rightleftharpoons ZCO + 2H_2$

c) $ZCO \rightleftharpoons Z + CO$

d) $H_2O + Z \rightleftharpoons ZO + H_2$

e) $CO + ZO \rightleftharpoons CO_2 + Z$

where Z denotes an active site on the surface of nickel, and, ZCH_2, ZCO, ZO denotes chemisorbed CH_2, CO and O.

According to Bhatta and Dixon[17], the order of reaction was zero with respect to butane and approximately first order with respect to water in the steam reforming process for n-butane at high pressure (30 atm.).

Phillips and co-workers[16] investigated the reactions of n-hexane and n-heptane with steam at 200 psig over a temperature range of 360 - 450°C. For most of this range, the order of reaction was zero with respect to steam and 0 to 0.3 with respect to the hydrocarbon. The results were interpreted by a Langmuir kinetic mechanism. The effect of diffusion was tested by repeating the experiments using a catalyst of different sized particles. The results indicated that the activation energy was almost constant when the particle size was changed from a range of 126-178 μ to a range of 853-1002 μ.

III. THERMODYNAMIC CONSIDERATION

According to Dodge et al.[11][12][17], the reactions which might occur on the catalyst, after the initial reaction of the hydrocarbon with steam, may be represented by the following equations:

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad (3\text{-}1)$$

$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O \qquad (3\text{-}2)$$

$$CH_4 + 2H_2O \rightleftharpoons CO_2 + 4H_2 \qquad (3\text{-}3)$$

$$2CO + 2H_2 \rightleftharpoons CO_2 + CH_4 \qquad (3\text{-}4)$$

$$CH_4 \rightleftharpoons C + 2H_2 \qquad (3\text{-}5)$$

$$2CO \rightleftharpoons C + CO_2 \qquad (3\text{-}6)$$

$$H_2O + C \rightleftharpoons CO + H_2 \qquad (3\text{-}7)$$

Many reactions are possible in such a system, but with a careful analysis and consideration the complex situation may be greatly simplified. For instance all the dependent reactions can be eliminated. Thus, [3-3] = [3-1] - [3-2] and [3-4] = [3-1] + [3-2]. Equations [3-5], [3-6] and [3-7] are the possible reactions of deposition and removal of carbon. These equations can also be eliminated by assuming the deposition of carbon is slow and that any carbon formed is consumed in reaction [3-7]. This leaves only reactions [3-1] and [3-2] to be considered. The equilibrium concentration of methane, carbon monoxide, carbon dioxide, hydrogen and water can then be determined by using equations [3-1] and [3-2].

In the calculation of the equilibrium composition, it has been assumed that the primary products of decomposition of n-heptane are hydrogen and carbon monoxide. Let the number of moles of carbon dioxide and methane at equilibrium be y and z respectively; the mole ratio of water to n-heptane be "a"; the mole ratio of nitrogen to n-heptane be "b". Then for a conversion x of heptane, the concentration of each constituent is as follows:

$CO_2 = y$	$H_2O = a - 7x - y + z$
$CH_4 = z$	$C_nH_{16} = 1 - x$
$CO = 7x - y - z$	$N_2 = b$
$H_2 = 15x + y - 3z$	$\text{Total} = a + b + 1 + 14x - 2z$

The equilibrium constant of Eqn (3-1) & (3-2) can be expressed as follows:

$$K_1 = K_{\varphi_1} \frac{y\,(15x + y - 3z)}{(7x - y - z)\,(a - 7x - y + z)} \qquad (3\text{-}8)$$

$$K_2 = K_{\varphi_2} \frac{z\,(a - 7x - y + z)}{(7x - y - z)\,(15x + y - 3z)^3} \cdot \frac{(a + b + 1 + 14x - 2z)^2}{P^2} \qquad (3\text{-}9)$$

Where P is the total pressure in atm. and K_{φ_1} and K_{φ_2} are the fugacity terms for eqn.[3-1]and[3-2] respectively. The fugacity coefficients of the pure components were taken from the tabulated data of Canjar and Manning[21]. These data were also compared with the value from the equation suggested by Pitzer and Brower[22] for the real gases. The

difference between them is generally less than 0.5%. Thermodynamic properties were obtained from the literature [23][24]. Equilibrium constants K were calculated from the free energy of reactions at temperature T.

$$\Delta G^\circ = - RT \ln K$$

The description of the calculations is given in Appendix C.

IV. EXPERIMENTAL

A. Apparatus

A tubular reactor of laboratory size was used in a flow system. The experimental set up was designed to study the reaction over a catalyst at controlled temperature and pressure. A schematic diagram of the experimental apparatus is shown in Figure 4-1.

The apparatus may be divided into the feed section, the reactor assembly and the product separation unit.

(1) Feed Section

This section consisted of two reactant streams. An additional nitrogen stream was used here to pressurize the system to the desired pressure and to allow the partial pressure of one of the reactants to be changed while keeping the other constant.

Water and n-heptane were transported along the 1/8" O.D. tubing to the evaporators by a propotional pump (Model No. 2213 BI, Ruska Industrument Corporation) which had two cylinders with a volume of 500 ml for the liquid feedstock. The discharge rate could be controlled from one ml to five hundred ml per hour. The heat was supplied by two temperature controllers (Model No. R7350 A 1123, Honeywell). Nitrogen gas was obtained from high pressure cylinders through two-stage pressure regulators. Traces of moisture were removed by

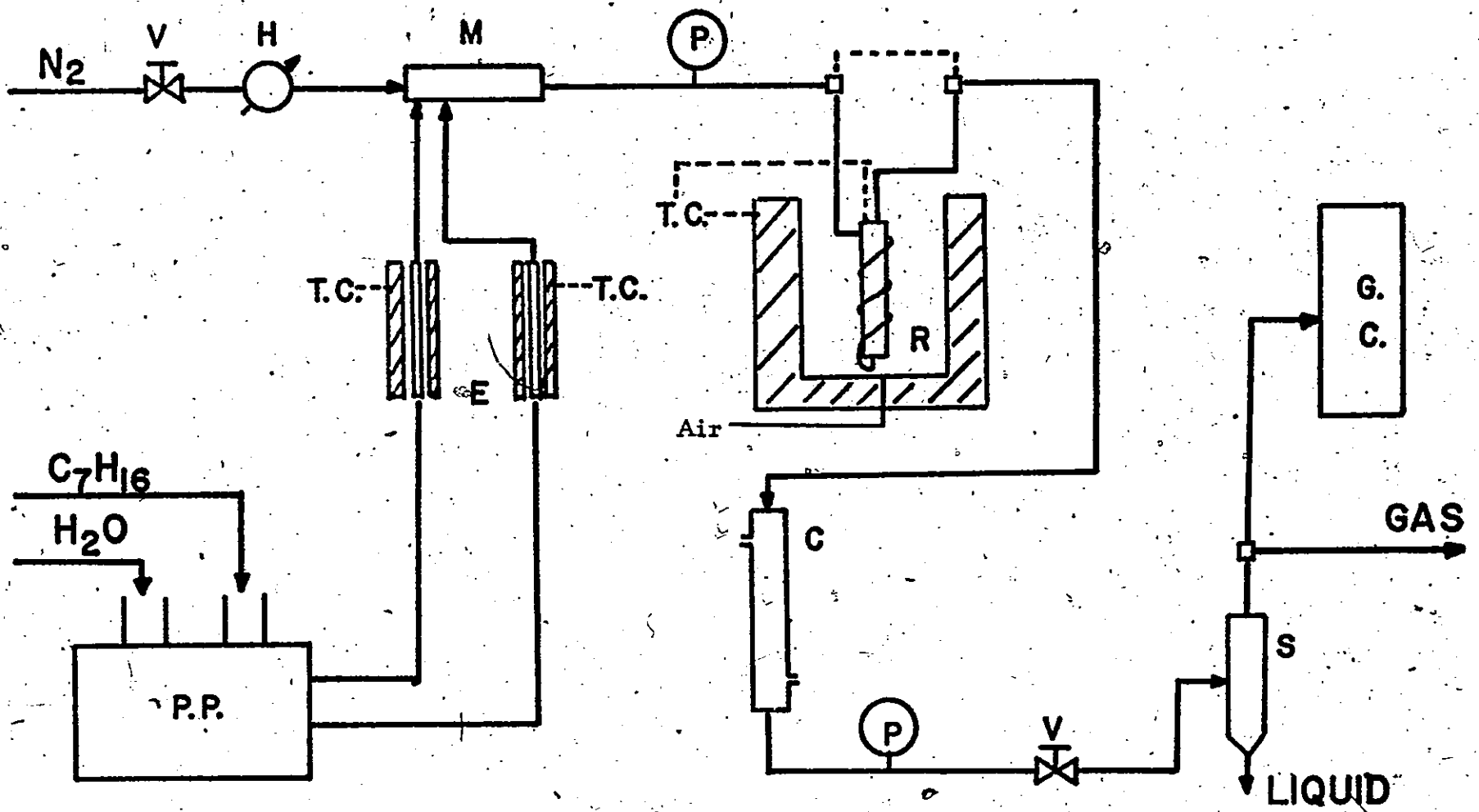


Figure 4-1 Schematic Diagram of the Apparatus

C: Water Condenser, E: Evaporator, G.C.: Gas Chromatograph Unit,
H: Heater, M: Mixer, P.P.: Proportioning Pump,
P: Pressure Gage, R: Reactor, S : Seperator,
TC: Temperature Controller, V: Pressure Control Valve,

passing the nitrogen through a drying tube packed with anhydrous calcium sulfate. The gas flow rate was controlled by an N.R.S. high accuracy valve (Metheson, Model 4183) and measured by a rotameter (Brooks, Model 2-1110) which was calibrated at different pressures. The heated gases of nitrogen, steam and hydrocarbon were introduced in a mixer fabricated from a 6" x 3/4" O.D. stainless steel tubing and then fed to the reactor. All the tubing which transported gases was covered by heating tapes to maintain the temperature.

(2) Reactor Assembly

The reactant stream from the mixer was bifurcated, one branch leading to the reactor through a preheater and the other by-passing the reactor and preheater. The preheater was made of an 8 ft long 1/8" O.D. 316 S.S. tube which was wound round the reactor. The preheated reactants entered the reactor from the bottom. The reactor was designed as a tube, 6 inches long and one half inch outside diameter with a porous plate fixed at the bottom of the tube. The pore diameter was about 65 microns, and the plate had a thickness of 1/16 inch.

A stainless steel tube, 1/16" O.D., containing two iron-constantan thermocouples was inserted into the reactor and was ajusted to keep the lower end of the thermocouple in contact with the catalyst bed. The first thermocouple in the protective tube was connected to the temperature controller for controlling the catalyst bed temperature; the second was connected to a potentiometer (Leeds & Northrup Co., Model No. 8686) for

measuring the temperature of the reaction zone.

The reactor and the preheater were kept immersed in a constant temperature fluidized bed furnace. The container for the fluidized bed was a steel cylinder, two feet long by 5" O. D., with a porous plate inserted at the bottom. Clean sand of 40-60 mesh was used as the heating medium of the fluidized bed and placed in the container on the porous plate. The reactor was held upright in the center of the bed, completely covered by the sand. During operation, compressed air was passed through the porous plate to keep the sand fluidized in order to obtain a uniform temperature around the reactor. For heating the reactor, two independent heating coils were wrapped around the cylinder. One was connected to a transformer and then to the temperature controller. The other was connected to another transformer only. This design reduced the heating load in the controller circuit and a more precise control of temperature was obtained.

(3) Product Separation Unit

This section consists of a condenser, separator, dryer, a gas chromatograph, a chart recorder and an integrater.

The products and unconverted reactants were conducted through a length of 1/8" O.D. tubing to a water condenser and then entered the separator which was kept cooled in an ice bath. Water and unreacted feedstock were condensed and could be drained from the bottom of the separator. The gas mixtures of

carbon dioxide, carbon monoxide, hydrogen, methane and other light hydrocarbons were transported from the separator and passed the dryer to the flowmeter where the gas flow rate was measured. Part of the gas flow was directed to a G. C. unit for the analysis.

A helical tube of 1/8" O. D. was housed in a one foot long by 1 1/2" O. D. copper tube to serve as a condenser. Cold water was used as a condensing medium between the two tubes. The seperator was made of 5 1/2" x 1 3/4" O. D. s. s. cylinder. The drying tube, made of a 5" x 2" O. D. acrylic tube was packed with 10-20 mesh indicating "drierite" (calcium sulfate anhydrous). The gas chromatograph (Hewlett Packard, Model 5712A) used a dual column system and a digital oven temperature programmer to program temperature from -50°C to 390°C, and included a thermal conductivity detector. A dual column system was used to minimize the baseline drift during temperature programming. Liquid nitrogen was employed for the purpose of temperature programming. The columns were made of 8' x 1/8" O. D. tubing packed with "Porapak Q". There are several advantages with this packing material. There is no adsorption of polar compounds such as water and alcohols; no change of retention time; the polymer beads, which are very rigid cross-linked polymers, can be used to a temperature of 250°C.

During the analysis operation, the signals were sent by the gas chromatograph to a chart recorder and an integrator (HP Model 3373B). The peak areas generated by the GC detector were measured by the integrator in units of microvolt-

seconds with an accuracy of 0.1%. The integrator used a voltage-to-frequency convertor which develops an output pulse rate directly proportional to the input signal. When the slope detector senses a peak, the pulses from the voltage to frequency convertor are accumulated and counted.

B. Preparation of Catalysts

A nickel catalyst was employed because its high activity and its ability to maintain the activity at relatively low reaction temperatures for the reactions of steam with hydrocarbons. The nickel-alumina catalyst was prepared by a coprecipitation technique (7).

The procedure was to prepare an aqueous solution of nickel nitrate and aluminum nitrate in the desired proportions. Ammonium bicarbonate was added gradually with stirring to the solution as a precipitating agent, and the temperature held constant at 50°C. After the precipitation was finished, the slurry was stirred continuously for an additional 2 hours at the same temperature. The precipitate was seperated from the excess solution by filtering without washing, and dried overnight in an oven at 177°C. The dried material was calcined in the presence of air for 4 hours at 400°C. Finally, the desired size (40-60 mesh) of catalyst was obtained by screening.

During the calcination, the nickel and alumina were in an oxidized form, but for the final activation the catalyst was treated with hydrogen overnight at a temperature about 450°C. The weight content of Ni in the catalyst after the calcination was calculated to be 50%.

C. Experimental Procedure

(1) Calibration of Equipment

The flow rates of the inlet gases were measured by the rotameter which was calibrated for different reactor pressures. The volumetric flow rates of the outlet gases were measured by the soap film bubble meter and a wet test gas meter. A calibration curve for the flow rate of nitrogen at 200 psig is given in Appendix B (Fig. 7-5).

The thermocouples in the reactor vessel were calibrated by inserting them into the fluidized bed furance with an ASTM thermometer attached to it. The temperatures were directly read from the thermometer and the thermocouple output in millivolts were measured by a potentiometer. A calibration curve of temperature against millivolts is shown in Appendix B (Fig. 7-6).

For the calibration of the gas chromatograph, research grade pure gases were used. The binary mixtures of CO_2, with CO, H_2, CH_4 or N_2 as a second component were prepared in various proportions on a gas train. These prepared samples were injected into the G.C. column and the peak areas were counted by an integrator as described. As a result the quantitative analysis could be based on the relative area ratios versus mole ratios. The calibration curves are given in Appendix B (Fig. 7-1 to 7-4).

(2) Operating Procedure

The following sequence of operation was carried out before and during each experiment: leakage test; experimental start up; experimental operation.

A leakage test for the experimental apparatus was carried out by pressurizing the system with nitrogen to the reaction pressure and holding at that pressure for at least one hour. Leaks were detected by soap bubbles.

After the satisfactory completion of the leakage test, the reactor was charged with the desired amount of fresh catalyst which was covered with a layer of glass wool to keep the catalyst fixed in position. The reactor was then reassembled and placed in the center of the fluidized bed furnace. It was again checked for any new leaks. The furnace, heater, heating tapes, controllers and transformers were switched on and the controllers set for the desired temperature. The system was then pressurized with nitrogen to the desired pressure and the flow rate was adjusted. At the same time, the power of the G.C., the recorder and the integrator was turned on, and helium gas used to purge the columns in preparation for the analysis.

As soon as the required temperature was attained at the reactor the reactants were fed at a fixed rate. The mixture of gases initially was led to the bypass of the reactor and maintained in this way for several hours to let the flow reach a steady state. With the onset of steady state flow the mixture was conducted through the reactor, and the bypass was closed.

During the course of an experiment, the temperature, pressure and flow rate of the system were kept constant. The condensate was drained from the separator for analysis in the G.C.; the flow rate of the outlet gases was measured and their composition analysed by the G.C. Unit.

(3) Analysis

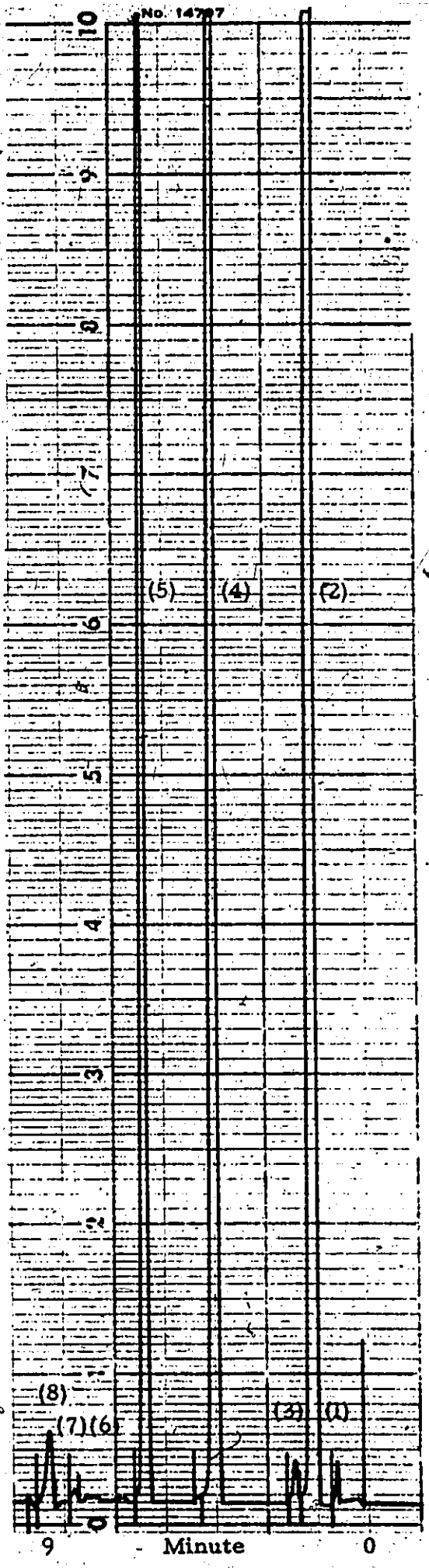
The product gases were fed to the gas chromatograph continuously. The injection of 0.5 ml. samples was operated automatically and controled by a timer. The signals of analysis were sent to the integrator and the recorder. The flow rate of helium was maintained at 20 ml/min. at 40 psig. A retention time of 10 minutes was required for separating the products. A typical analysis of the products from the gas chromatograph is shown in Figure 4-2.

Liquid samples drawn from the separator about every two hours were also injected into the gas chromatograph by a microliter syringe.

Fig. 4-2

A Typical Analysis of Products from Gas Chromatograph

(1) Hydrogen
(2) Nitrogen
(3) Carbon monoxide
(4) Methane
(5) Carbon dioxide
(6) Ethylene
(7) Ethane
(8) Moisture



D. Reactants and Chemicals

The materials which are used as reactants, diluent gases and for catalyst sythesis are n-heptane, steam, nitrogen, helium, nickel nitrate, aluminum nitrate and ammonium bicarbonate.

Normal heptane obtained from Phillips Petroleum Company with a stated purity of 99.7 mole% and a boiling point of 98.4°C was used as the hydrocarbon reactant in this study.

Distilled water used as one of the feeds was supplied by the department for the generation of steam.

The nitrogen diluent gas was supplied by the Union Carbide, Canada Limited in cylinders at a pressure of 2500 psig. Gas chromatographic analysis showed no significant impurity in the gas. The moisture was removed by passing it through a drying tube containing anhydrous calcium sulfate. The helium carrier gas was supplied by Canadian Liquid Air Ltd., with a minimum purity of 99.99%.

The chemicals used for the preparation of the catalyst are nickel nitrate ($Ni(NO_3)_2 \cdot 6H_2O$), aluminum nitrate ($Al(NO_3)_3 \cdot 9H_2O$) and ammonium bicarbonate (NH_4HCO_3). They were supplied by the Fisher Scientific Co. and correspond in purity to Fisher certified reagents.

V. RESULTS AND DISCUSSION

All the experimental data were obtained by means of an isothermal fixed bed reactor. Some of the experiments were carried out in the absence of catalyst at temperatures of 450°C and 500°C, but no decomposition of the n-heptane was detected. This indicated that the effects of the homogeneous reaction between n-heptane and water were negligible. The data were collected at different percentage of conversion of the n-heptane. At constant temperature, pressure and feed ratio, different values of conversion were obtained, either by changing the amount of catalyst, or by allowing the catalyst activity to decay over a longer period of time. The experimental results are discussed in the sequence as follows:

a) Chemical Reaction Equilibrium

Fig. 5-1 represents the experimental product gas composition and the theoretical values which were obtained according to the equilibrium reactions [3-1] and [3-2] at different fractions of conversion. The yields are expressed in terms of moles per mole of heptane feed. At higher conversions of n-heptane, traces of ethylene, ethane and propane were detected in the effluent, but the amount was always small in comparison with other products. They were ignored in the calculation of equilibrium compositions. As shown in Fig. 5-1 there is a change in the product dry gas composition as the extent of the reaction increases. The calculated equilibrium compositions change from predominantly H_2, CO and CO_2 initially to predominantly methane when

the heptane has been practically totally converted. The experimental results indicate a deficiency of CH_4 and an excess of H_2, CO and CO_2 in the earlier stages of conversion with a closer approximation to the expected distribution of H_2, CO and CO_2 at higher fraction of conversion.

An alternative method of presenting the results is given in Table 5-1 in which the calculated values of the equilibrium constants for reactions [3-1] and [3-2] are compared with the constants which were obtained from the outlet gas compositions. Both constants K_1 and K_2 were not good enough to match with the equilibrium values which were expected at the reaction temperature of 466°C. Because of the power expressions in the formula for K_2, a slight excess of hydrogen would magnify the value of the constant. The amount of carbon monoxide in most of the experiments was less than 1%, so that the accuracy of the quantitative evaluation in the analysis was reduced. The error in the determination of CO would definitely change the value of the constants K_1 and K_2. The temperature effect on the equilibrium constant was significant as shown in Table 5-1. A small error in temperature measurement would also cause a large deviation in the K value.

Due to the importance of the methane content in natural gas, a comparison of methane in the products with the equilibrium values is given in Table 5-2. From this we see that the concentration of methane approached the equilibrium value as the conversion approached totality.

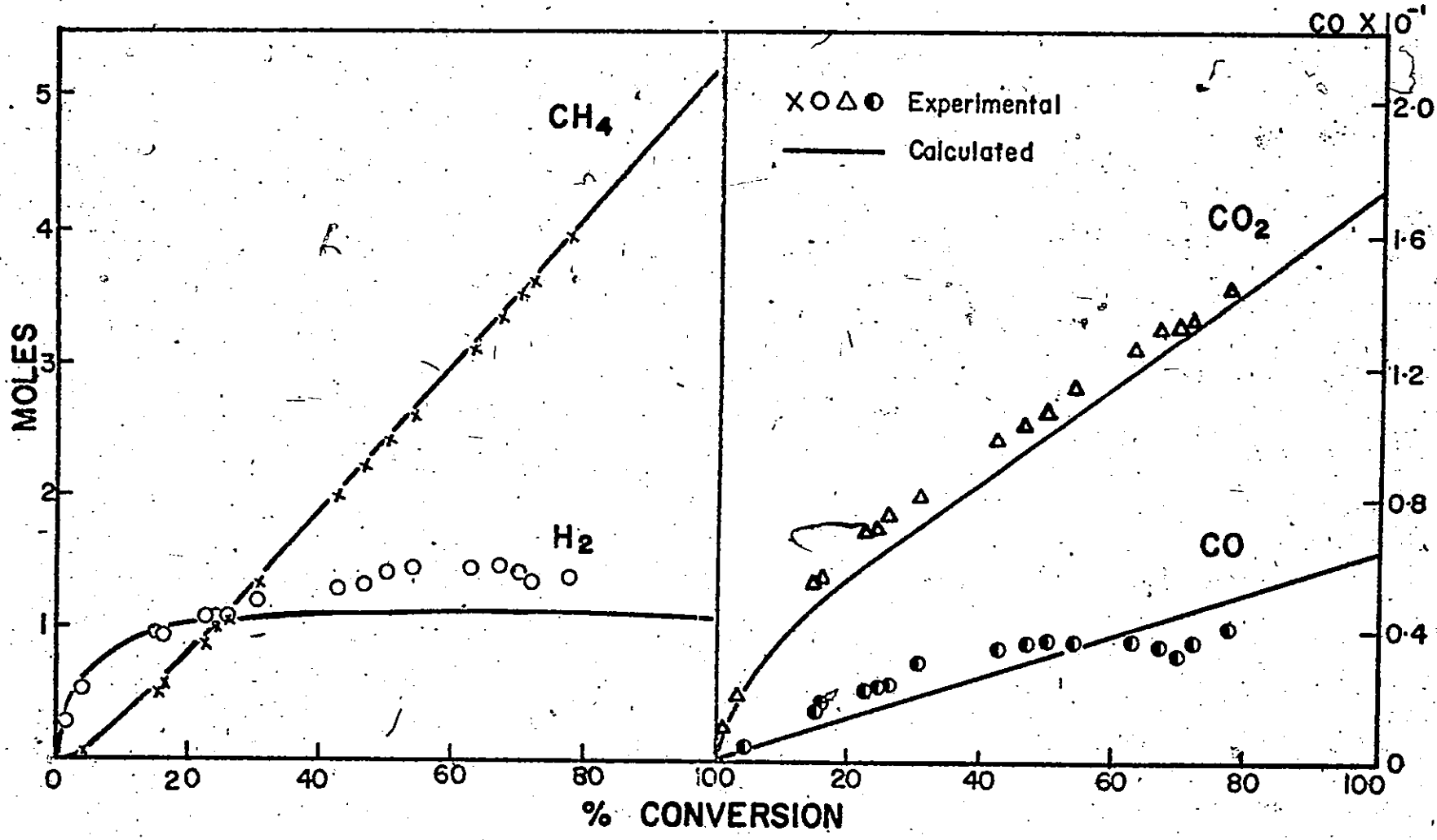


Figure 5-1 Comparison of the calculated and the experimental compositions of products ($T = 466°C$, $P = 200$ psig, $H_2O/C_7H_{16} = 8.2$)

Table 5-1

Experimental Values of Equilibrium Constants for Reactions [3-1] and [3-2] as a Function of % Conversion of n-Heptane. (T = 466°C, P = 200 psig, H_2O/C_7H_{16} = 8.2)

% Conversion	K_1	$K_2 \times 10^{-3}$	
3.98	2.06	0.704	
14.42	5.10	0.327	
15.91	4.17	0.298	
22.68	5.35	0.289	
24.45	4.90	0.332	
26.01	5.29	0.324	
30.63	5.03	0.200	
42.56	6.02	0.214	
46.69	6.37	0.219	
53.76	7.87	0.187	
62.45	8.93	0.229	
67.01	10.62	0.246	
69.66	10.64	0.308	
72.28	10.20	0.361	
77.47	10.42	0.332	
Theoretical Value	11.49	16.667	400°C
	6.29	0.478	466°C
	4.81	0.100	500°C

where $K_1 = (\hat{f}_{CO_2})(\hat{f}_{H_2}) / (\hat{f}_{CO})(\hat{f}_{H_2O})$

$K_2 = (\hat{f}_{CH_4})(\hat{f}_{H_2O}) / (\hat{f}_{CO})(\hat{f}_{H_2})^3$

Table 5-2

Comparison of the Calculated and the Experimental Methane Composition in the Products. (T = 466°C, P = 200 psig, H_2O/C_7H_{16} = 8.2)

% Conversion	Experimental		Calculated		% Deviation
	Moles	Vol. % (Dry)	Moles	Vol. % (Dry)	$\frac{\text{Moles(Cal)} - \text{Moles(Exp)}}{\text{Moles (Cal)}} \times 100$
3.98	0.061	7.4	0.051	5.4	- 19.6
14.42	0.497	24.7	0.571	28.1	12.9
15.91	0.551	26.6	0.625	29.5	11.8
22.68	0.880	33.0	0.982	37.2	10.4
24.45	0.991	36.0	1.073	38.7	7.6
26.01	1.064	36.7	1.164	40.2	8.6
30.63	1.308	38.8	1.411	43.6	7.3
42.66	1.979	48.1	2.059	50.3	3.9
46.69	2.219	48.2	2.283	52.0	2.8
50.07	2.415	49.0	2.467	53.3	2.1
53.76	2.589	49.5	2.669	54.6	3.0
62.45	3.107	53.2	3.155	57.3	1.5
67.01	3.355	54.4	3.397	58.5	1.2
69.66	3.528	56.0	3.566	59.2	0.5
72.28	3.617	57.2	3.684	59.7	1.8
77.47	3.953	58.2	3.969	60.8	0.4

b) Effect of Temperature on Conversion

Effect of temperature on the conversion with three different amounts of catalyst are given in Fig. 5-2. It appears that the conversion increased sharply with only a slight increase in temperature for temperatures above 450°C. At a reaction temperature of 530°C with one gram of catalyst, a 97% conversion was observed. When the temperature was below 400°C, the effect of temperature on reaction rate was much smaller, and the conversion approached zero at 300°C. The relation of temperature, conversion and weight of catalyst at fixed feed rates are presented in Fig. 5-3. At a constant temperature of 466°C the conversion was ploted against W/F in Fig. 5-4, where W is the mass of catalyst, and F in the rate of n-heptane feed. The trend shows that the conversion approached a limit with a high value of W/F.

The maximum temperature was limited to 530°C for the purpose of avoiding the chance of thermal cracking of the hydrocarbon. For testing the possibility of thermal decomposition, n-heptane was fed without steam and catalyst. Nothing was detected other than the reactant itself in the effluent at the temperature of 530°C. When the temperature was increased to 600°C traces of hydrogen, carbon oxides, methane, ethylene and ethane were observed.

The relations between the rate constant and the temperature can be expressed by Arrhenius law.

$$k = k_o \, e^{-E/RT}$$

where k is the rate constant; k_o is an integration constant; E is the activation energy. For the reaction of steam with n-heptane, the reaction rate can be expressed as follows:

$$r = k\,[P_{H_2O}]^n\,[P_{C_7H_{16}}]^m$$

$$= k_o\, e^{-E/RT}\,[P_{H_2O}]^n\,[P_{C_7H_{16}}]^m$$

where $[P_{H_2O}]$ and $[P_{C_7H_{16}}]$ represent the partial pressure of steam and n-heptane respectively.

According to Phillips et al.[6] which has been described in Chapter II, the reaction orders n and m were considered as zero, hence

$$r = k_o\, e^{-E/RT}$$

The reaction rate can also be determined from the relation, $r = (F/W)x$, where F is the feed rate of n-heptane, W is the mass of catalyst and x is the fraction of heptane converted.

The logarithm of r against 1/T was plotted in Fig. 5-5, and the activation energy of reaction was found to be around 20 kilo-calories per gram mole.

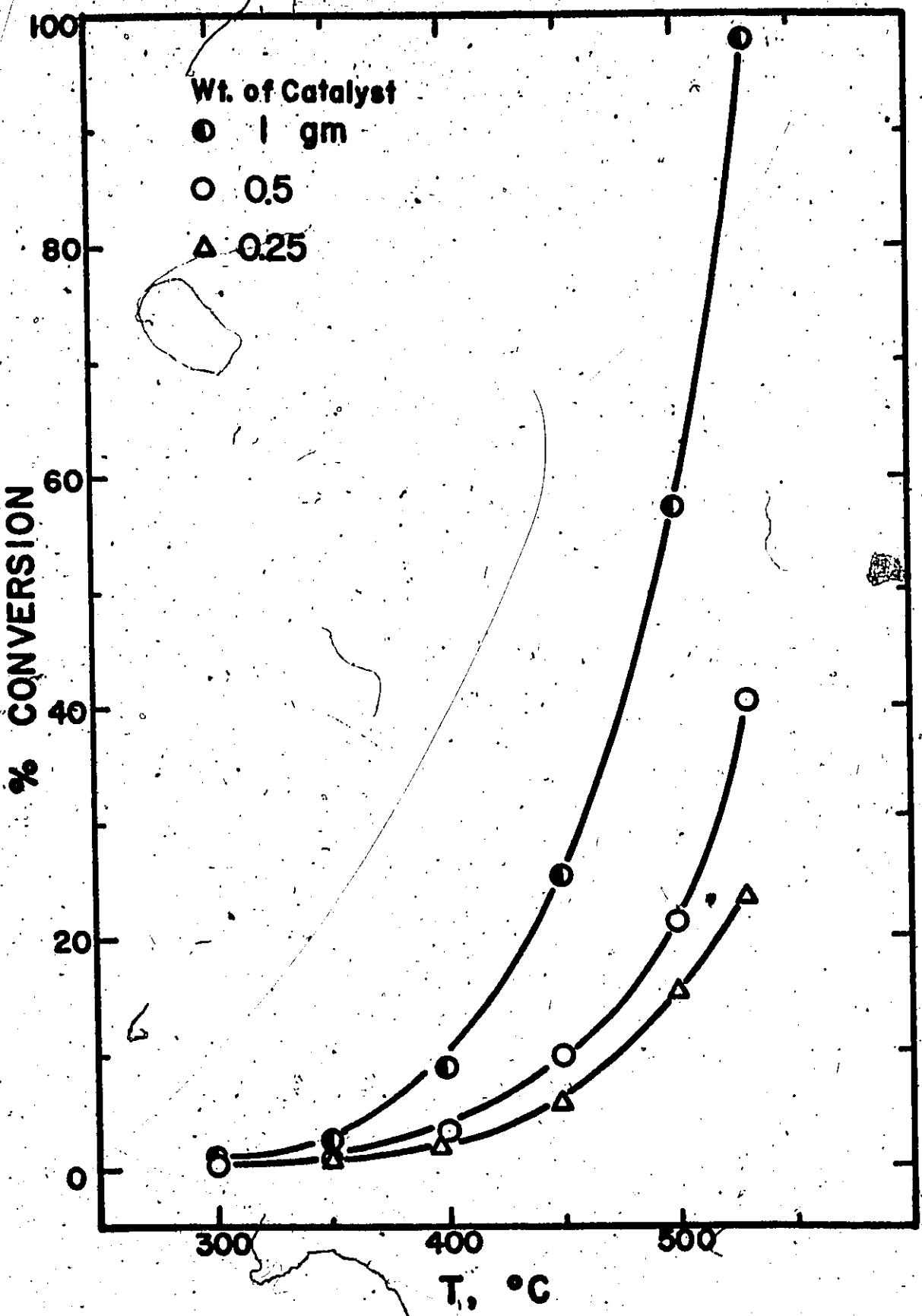


Figure 5-2 Effect of temperature on conversion using the wt. of catalyst as the parameter.
(P = 200 psig, H_2O/C_7H_{16} = 8.2)

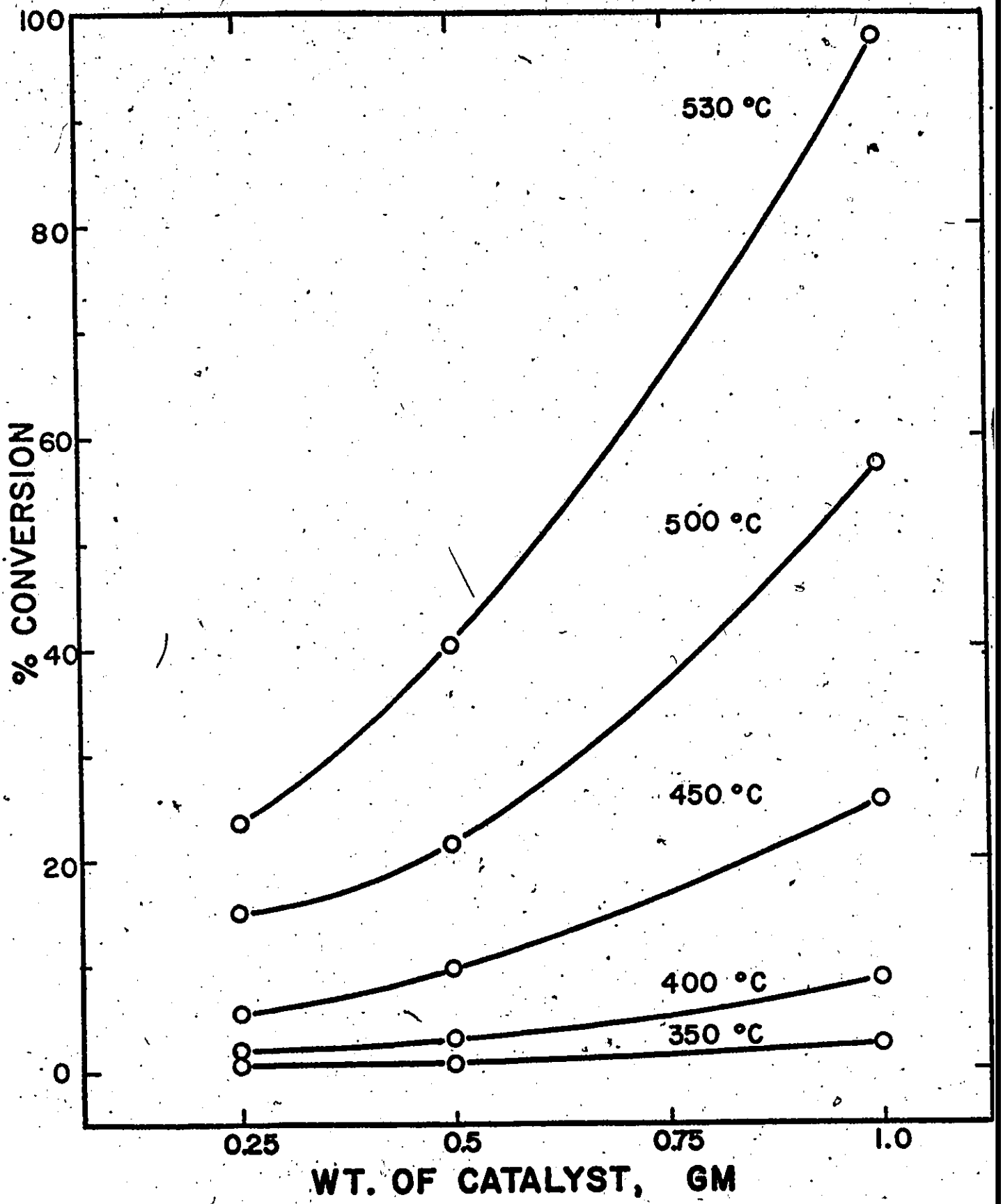
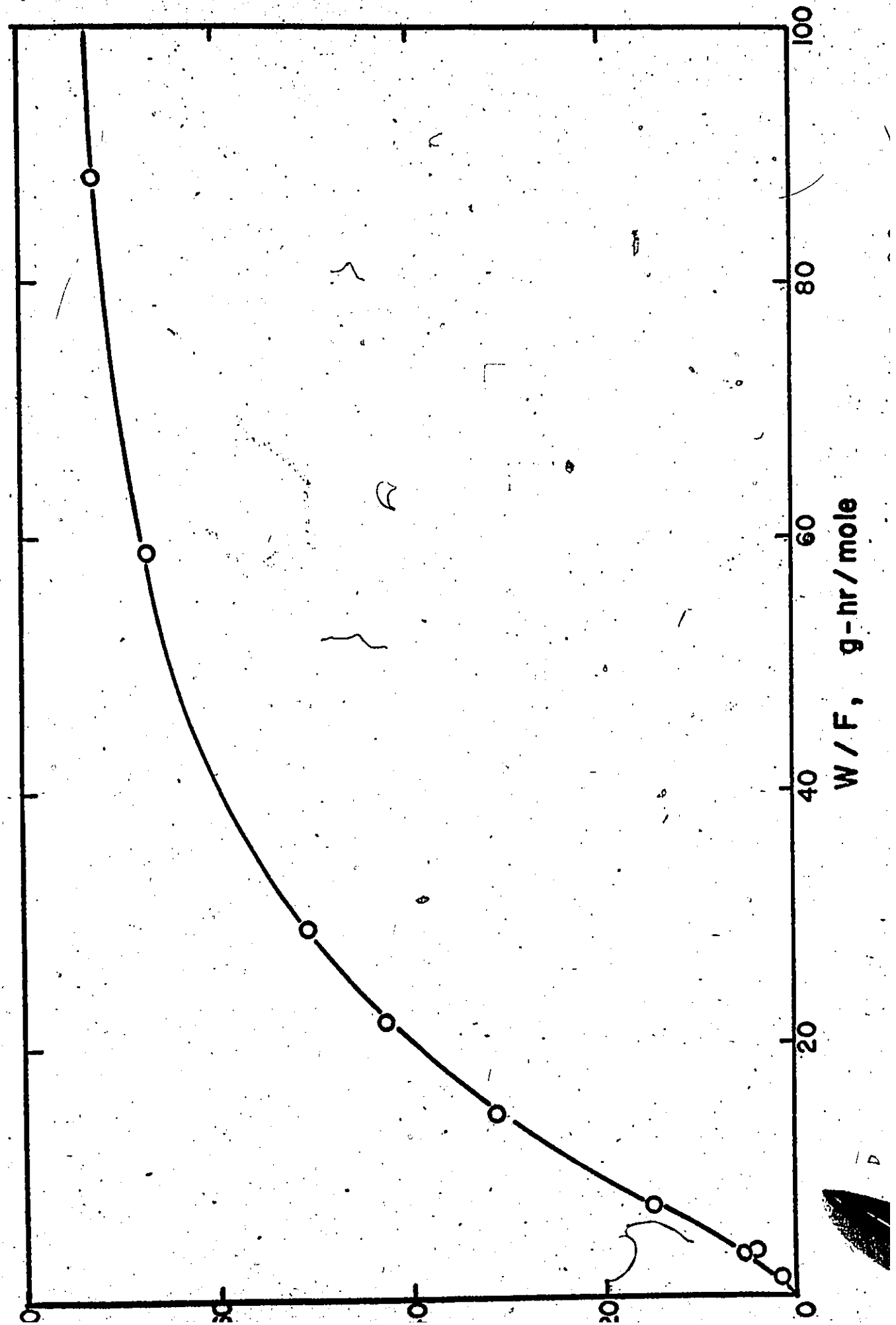


Figure 5-3 Effect of wt. of catalyst on conversion using temperature as the parameter
(P = 200 psig, H_2O/C_7H_{16} = 8.2)


0
20
40
60
80
100
W / F, g-hr/mole

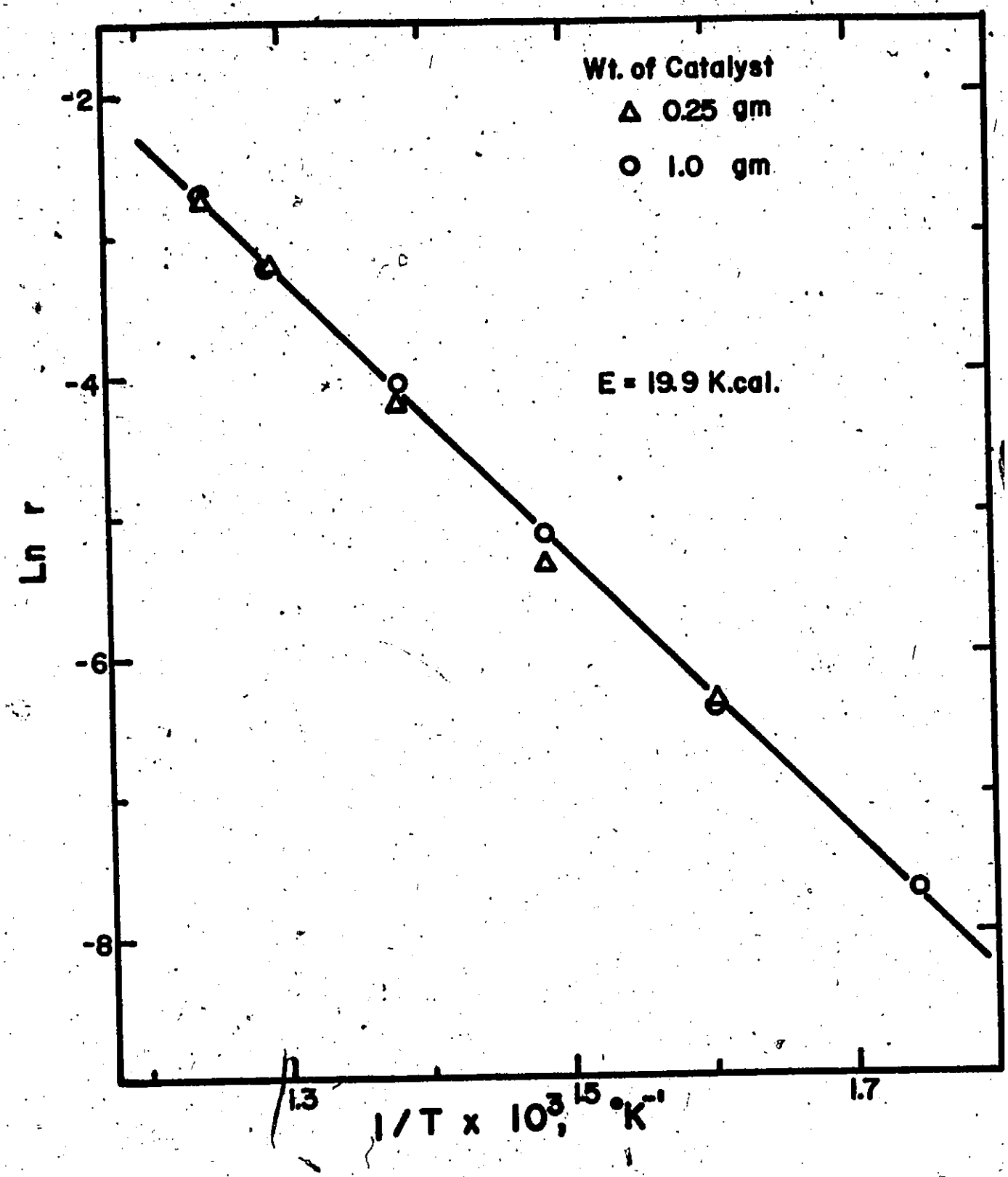


Figure 5-5 Reaction rate as a function of temperature
(P = 200 psig, H_2O/C_7H_{16} = 8.2)

c) Effect of Pressure on Conversion

A set of data was obtained by altering the reactor pressure while maintaining constant flows of the reactants and nitrogen. These data were plotted in Fig. 5-6 to represent the effect of pressure on conversion in the range of 5 ~ 300 psig. As the conversion and pressure increased the vol. % of methane increased, but the hydrogen changed in the inverse manner. We found it difficult to have constant conversions at different pressures in order to represent the effect of gas composition on the pressure. However the results in Table 5-3 can be applied to predict that at higher reaction pressures, the products will have higher yields of methane but lower yields of hydrogen and carbon monoxide. No significant effect of pressure on carbon formation was observed.

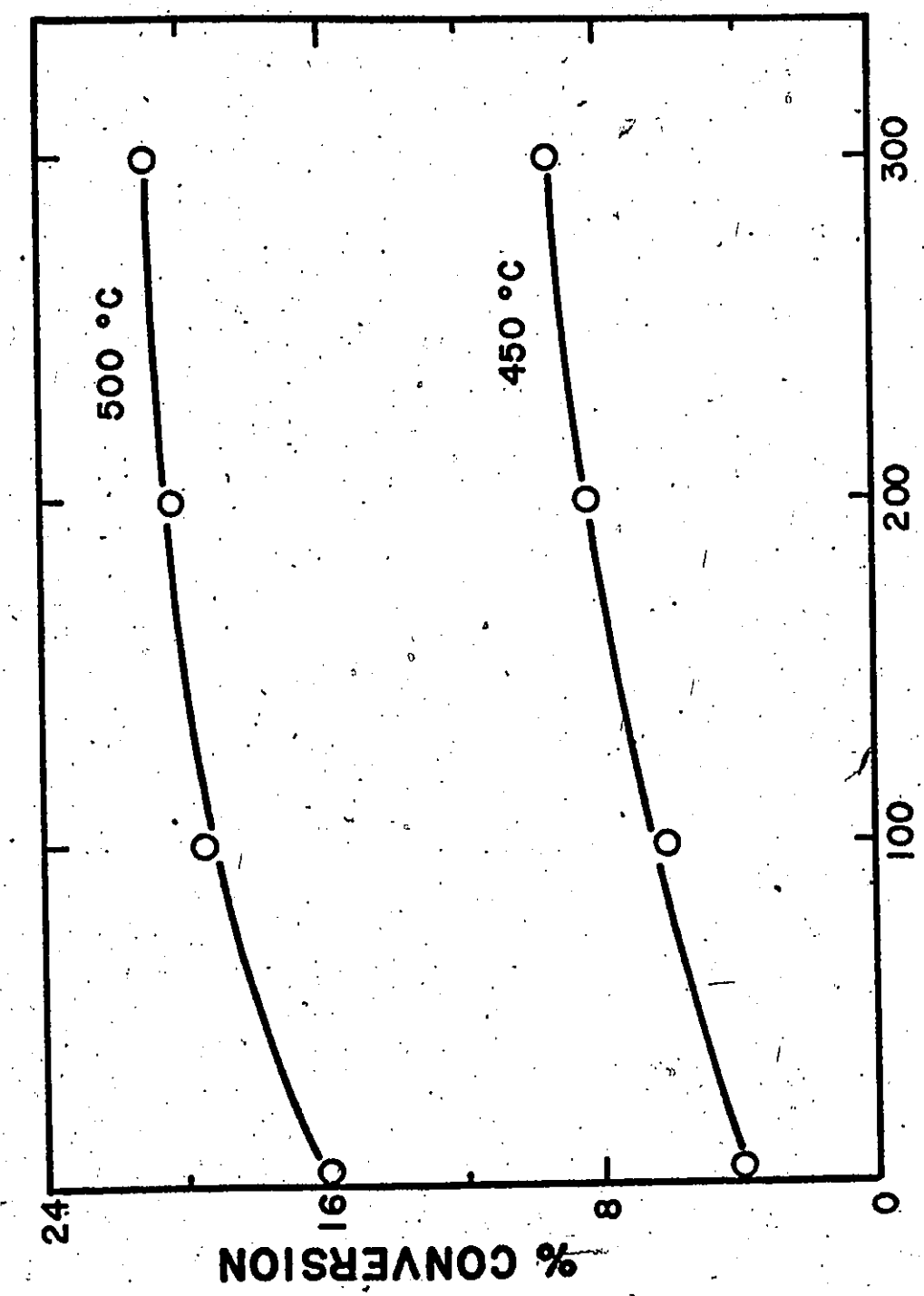


Figure 5-6 · Effect of pressure on conversion at 450°C and 500°C

Table 5-3

Dependance of Conversion and Gas Composition on Pressure

(T = 450°C, H_2O/C_7H_{16} = 8.2)

Pressure, psig	% Conversion	Experimental Product Composition (dry basis), Vol. %			
		CO_2	CO	CH_4	H_2
5	3.98	27.1	1.2	0.5	71.2
100	6.04	28.3	0.7	6.5	64.4
200	8.39	27.4	0.6	16.0	56.0
300	9.43	28.0	0.5	18.1	53.4

d) Effect of Reactant Ratio on Conversion

Several runs were tested by altering the mole ratio of water/heptane from 8 to 24. The results are plotted in Fig. 5-7. These experiments were carried out under a constant feed rate of n-heptane while changing the feed rate of the steam and nitrogen in order to maintain the total molar flow at a constant rate. Thus, the only variable was the partial pressure of steam. The conversion appears in this work to be independent of the partial pressure of steam.

Since the conversions were almost stable at different reactant ratios, we have tabulated the product distributions and reactant ratios in Table 5-4. We have found that the volume % of methane on a dry basis, decreases with an increase of the steam ratio, but hydrogen under the same conditions increases. The content of carbon monoxide and carbon dioxide in the products was almost independent of steam ratio.

According to Hougen et al.[25], the minimum steam ratio for preventing the formation of carbon deposit can be estimated by using Equations [3-5], [3-6] and [3-7]. By means of this calculation, the minimum steam ratio is much greater than the range we have investigated. This means that the chance of carbon formation during the reaction is possible. If the actual operations did not really reach equilibrium, the results should depend on the relative rate of the various reactions. Thus if reaction [3-6] is fast and reaction [3-7] is slow, carbon might form even with high steam ratios. Conversely, if reaction [3-7]

is fast, reactions [3-5] and [3-6] are reatively slow, operation might be possible at low steam ratios without the formation of carbon deposit. These effects are determined not only by reaction rates but also by the types of catalyst present.

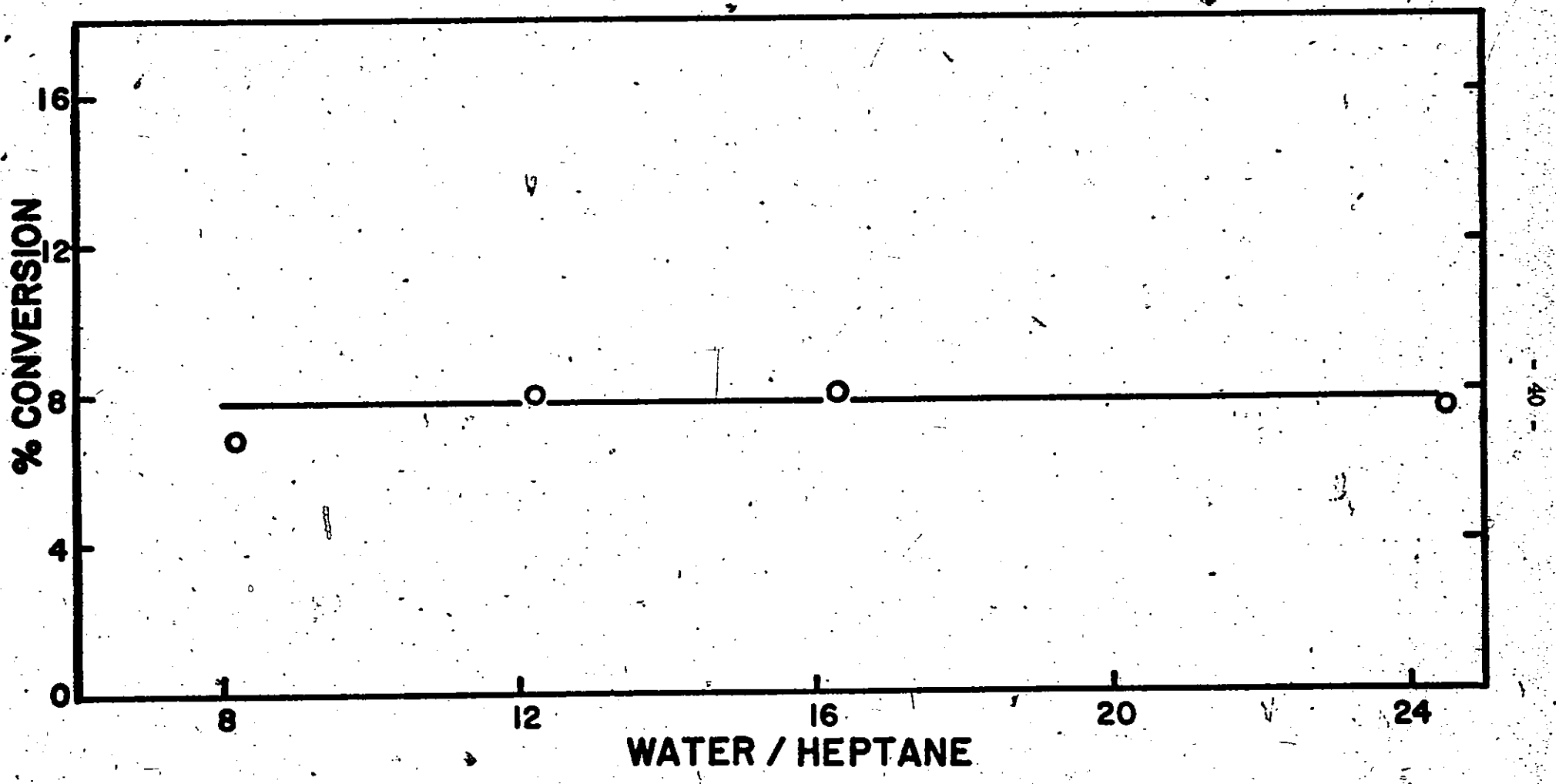


Figure 5-7 Effect of steam ratio on Conversion at 450°C and 200 psig.

Table 5-4

Dependance of Products Composition on Steam-Hydrocarbon Ratio

(T = 450°C, P = 200 psig, F = 0.0679 mole/hr)

Ratio C_7H_{16} : H_2O : N_2	Product Composition (dry basis) Vol. % CO_2	CO	CH_4	H_2	% Conversion
1 : 8.2 : 20.3	23.6	0.5	10.1	65.8	6.77
1 : 12.3 : 16.2	24.8	0.5	9.4	65.6	7.95
1 : 16.4 : 12.1	24.4	0.4	7.3	67.9	8.10
1 : 24.5 : 3.9	23.9	0.3	5.8	70.0	7.51

e) Deactivation of the Catalyst

Decline in activity of the catalyst might be the result of two factors. The first is the progressive sintering of the surface on the catalyst; the second is the coverage of active sites of the catalyst by carbonaceous deposits which would cause coke formation. From equation [3-7] which has been assumed to be a reaction for the removal of carbon;

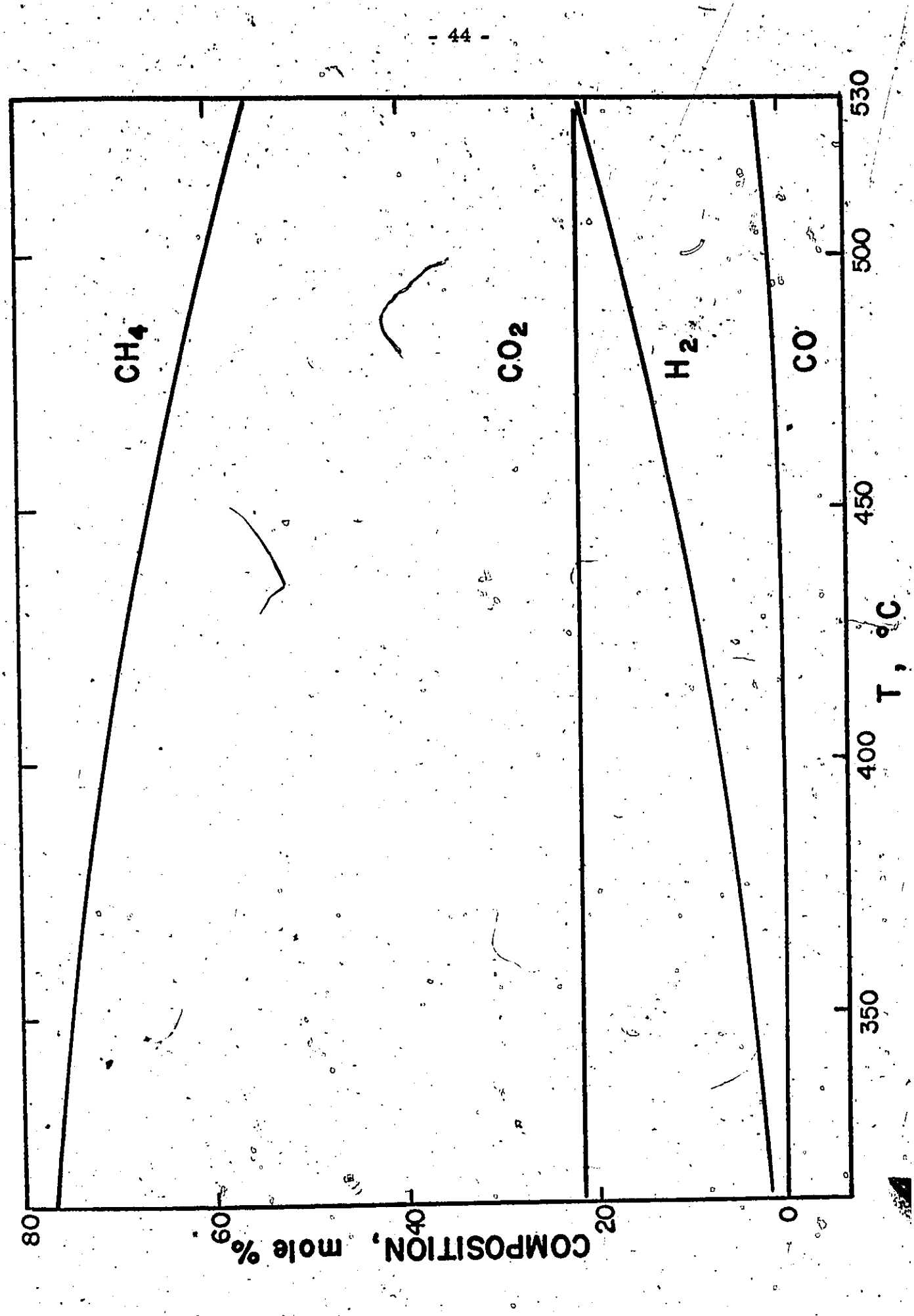
$$H_2O + C = CO + H_2 \qquad (3\text{-}7)$$

a high concentration of steam in the gas mixture will shift the reaction to the right. As a result the production of carbon is minimized.

We have found that when the reactant was fed in a low steam ratio (below 4), the chance of coke formation on the catalyst was much easier and faster. However, for the normal operations, the deposit of carbon was not found by visual observation of the spent catalyst.

f) Gas Composition at Equilibrium

The equilibrium gas composition for the n-butane-steam reaction has been studied by Rogers and Crooks[8]. The results of calculations of the combined equations [3-1] and [3-2] are given in Figure 5-8, 5-9 and 5-10. It will be seen that on a dry and heptane free basis, the volume percentage of methane decreases with increasing temperature and steam/heptane ratio, but increases with an increase of reactor pressure. Hydrogen behaves in an inverse manner. The carbon monoxide content, increases slightly with an increase in temperature but also falls slightly with an increase in pressure and steam/heptane ratio. However, carbon dioxide is the only gas whose yield is practically independent under all the conditions studied.


CH4
CO2
H2
CO
COMPOSITION, mole %
80
60
40
20
0
T, °C
530
500
450
400
350

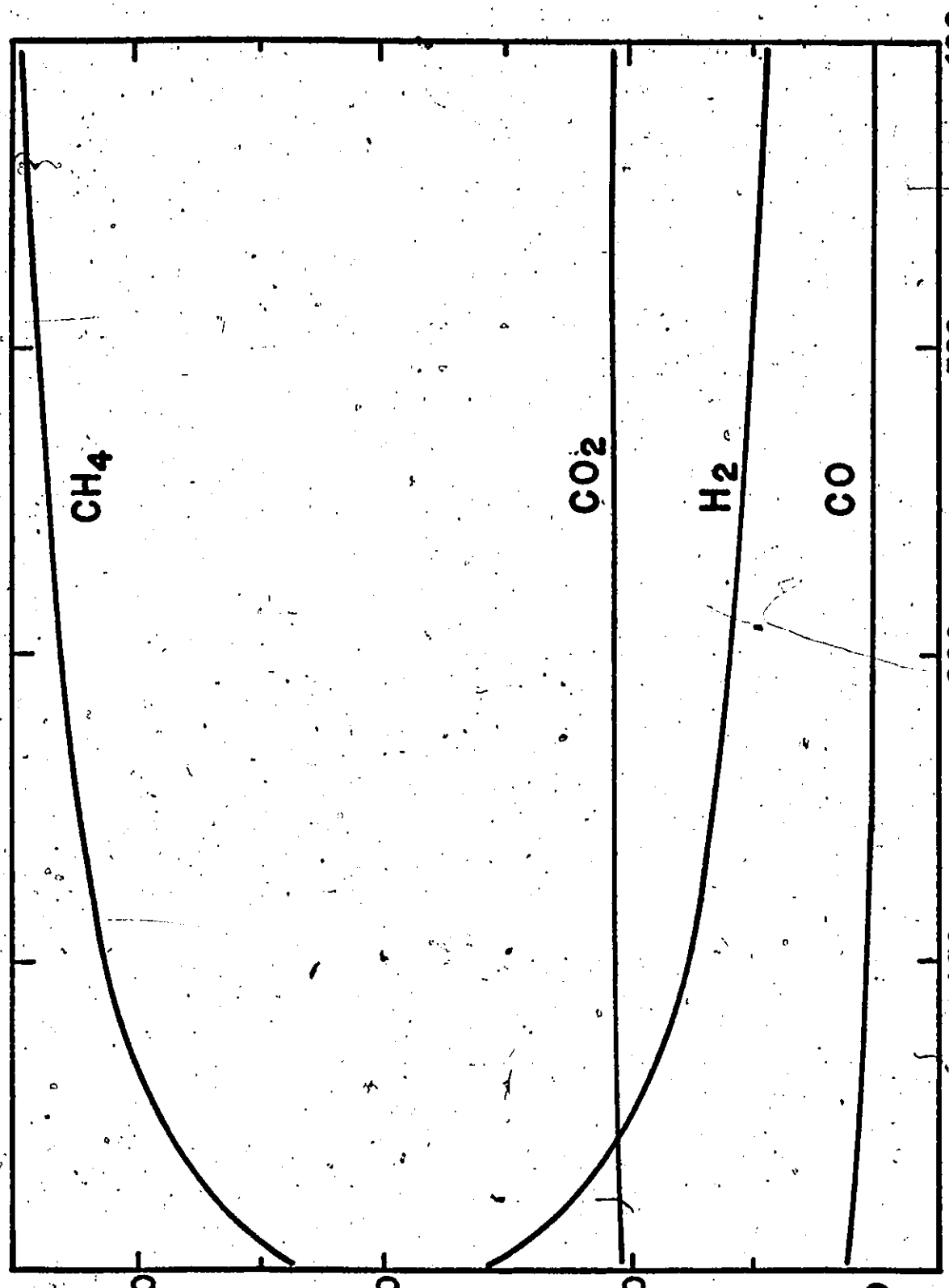
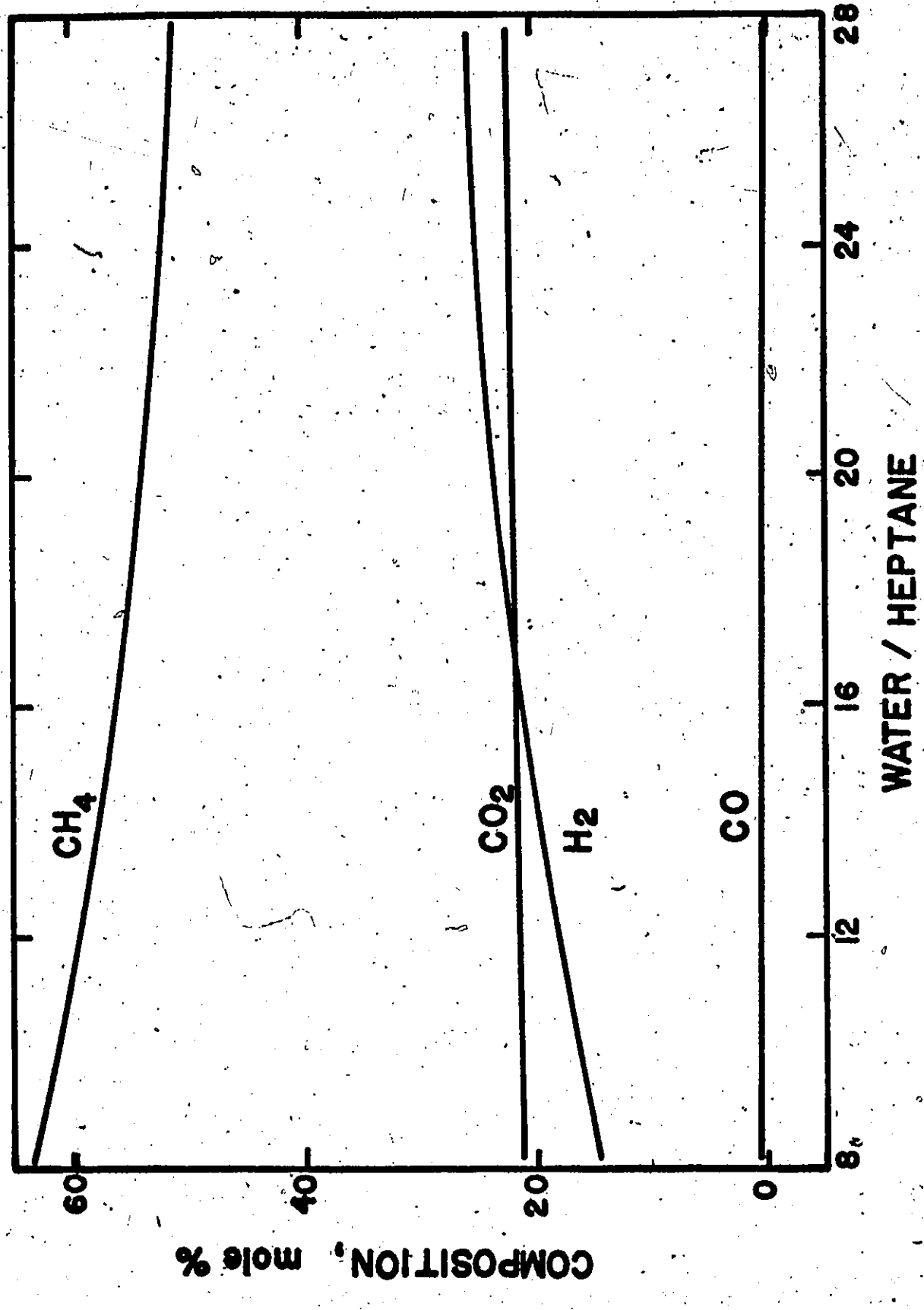


Figure 5-9 Pressure effect on the calculated equilibrium gas compositions on a dry basis.


CH4
CO2
H2
CO
0
20
40
60
8
12
16
20
24
28
COMPOSITION, mole %
WATER / HEPTANE

VI. CONCLUSION

With an operating condition of constant temperature, pressure and reactants ratio, the experimental results show that the gas products on a dry basis approach the theoretical composition, based on the assumption that the water-gas shift reactor and methanation reaction are at equilibrium. The results suggest that the initial products of decomposition are carbon monoxide and hydrogen. The content of methane is in good agreement with the theoretical equilibrium values at high stages of conversion.

The conversion of n-heptane is found to increase sharply with an increase of temperature especially for temperatures above 450°C, and to increase moderately with pressure below 300 psig. However it is independent of the partial pressure of steam within the steam-hydrocarbon ratio of 8 to 24.

The yield of hydrogen in the products decreases with an increase of pressure, a decrease of temperature and the steam-hydrocarbon ratio, but the yield of methane behaves in an opposite manner.

In order to reduce the possibility of carbon deposits during reactions, and to prolong the life of the catalyst, it would be necessary to use a high steam ratio in the feed together with a low reforming temperature. The experimental results indicate that for the production of a gas mixture rich in methane, it would be desirable to carry out the reforming reactions at pressures above 200 psig and temperatures below 600°C.

The analysis and the conclusions drawn from this work can be applied equally to the steam reforming of liquid hydrocarbons with approximately the same number of carbon atoms as n-heptane.

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VIII. APPENDIX

A. Economic Consideration

The cost of production of SNG is rather flexible, since it depends on many factors such as processing options, plant capacity, life of catalyst, grade of feedstocks and the market of raw meterials. The options may include the use of recycling to increase the hydrogen concentration in the gasification reactor; the adoption of partial oxidation process for the higher boiling point feedstock; the selection of the system for desulfurization; the requirement of a number of methanation stages and others factors. A report[5] based on a proprietary design shows the variations in production costs as they are affected by plant size and feedstock. The costs are listed in Table 8-1 with the unit of cents per million cubic feet. The type of feedstock used plays an important role in determining the cost of SNG. Since it affects the investment cost, operating cost and the price of raw material. A summary of estimated SNG production cost factors for various feedstocks are given in Table 8-2[26]. Table 8-2 is based on producing 250 million cu. ft./day of gas with a heating value of about 1,000 Btu/cu.ft. The comparative feedstock values to produce SNG at around $1/1000 cu. ft. are shown in this table. It should be noted that the investment cost increases sharply but the thermal efficiency decrease with the increase of heavier feedstocks.

From the above information the biggest single item in determing the cost of SNG is the feedstock. If a light liquid hydrocarbon is purchased for 75¢/million Btu (8.5¢/gal.), the cost of feedstock plus

fuel will contribute more than 80¢/M Btu. Capital recovery, operating and maintenance labor, supervision, maintenance supplied, etc., may average 15 to 30¢/million Btu. Finally, the cost of SNG before profit, federal tax, or gas distribution is about 95c to $1.10/million Btu. If the feedstock price were to increase to 95¢/million Btu (11¢/gal.), the cost of producting SNG, on the same basis would increase to perhaps $1.20 to $1.35/million Btu.

Table 8-1

Cost of SNG Production for Various Plant Sizes[5]

(¢/Msct)

	Plant size, M Mscfd		
	40	100	250
Operating expenses	4.9	3.7	2.8
Financial and Overhead	10.0	6.8	4.5
Catalyst	1.7	1.7	1.7
Fuel at 60/90¢/MM Btu	3.6/ 5.4	3.6/ 5.4	3.6/ 5.4
Total conversion	20.2/ 22.0	16.8/ 17.6	12.6/ 14.4
Feedstock at 60/90¢/ M M Btu	60.0/ 90.0	60.0/ 90.0	60.0/ 90.0
Total SNG	80.2/112.0	75.8/107.6	72.6/104.4

Basis : 350 days/year

Table 8-2

Cost of SNG Production for Various Feedstocks[26]

(c/Million Btu)

Feedstock	Light Naphtha	Kerosene/Lt. Gas Oil	Med./Hvy. Gas Oil	Crude
Utilities, catalysts, etc.	3.2	3.5	4.0	4.5
Labor & related overhead	1.1	1.3	2.0	3.0
Capital charges	13.8	23.0	33.7	41.4
Total non-feedstock Costs	18.1	27.8	39.7	48.9
Feedstock + Fuel	83.9	74.2	62.3	53.1
Fuel-gas price	102.0	102.0	102.0	102.0
Feedstock Cost				
c/gal	9.0	9.0	7.0	5.7
$/bbl	3.80	3.80	2.94	2.40
Thermal efficiency, %	91	90	84	79
Investment, $ million	40	70	105	130

Basis: Production 250 million std. Cu. ft./day, 330 days/year

The figures are presented for comparative purposes only.

B. Calibration of Equipment

1. Calibration of Gas Chromatographs

The calibration curves for the analysis of gas compositions of CO_2, CO_2, H_2, CH_4 and N_2 are given in Figures 8-1 to 8-4. During the analysis the temperature programming of -50°C to 120°C was employed. The graph shows that the calibration curve of hydrogen - carbon dioxide mixture is not a straight line. This is because helium and hydrogen have similar thermal conductivities. Consequently, the change in conductivity in the sample side of the detector will be small when hydrogen dilutes a helium carrier, and the analytical sensitivity of the G.C. for hydrogen is low. When hydrogen is determined using a helium carrier, the relationship between concentration and response is non-linear[27].

2. Calibration of Rotameter

The rotameter calibration curve for nitrogen at the pressure of 250 psig is plotted in Figure 8-5.

3. Calibration of Thermocouple

The calibration curve of temperature against millivolts is plotted in Figure 8-6.

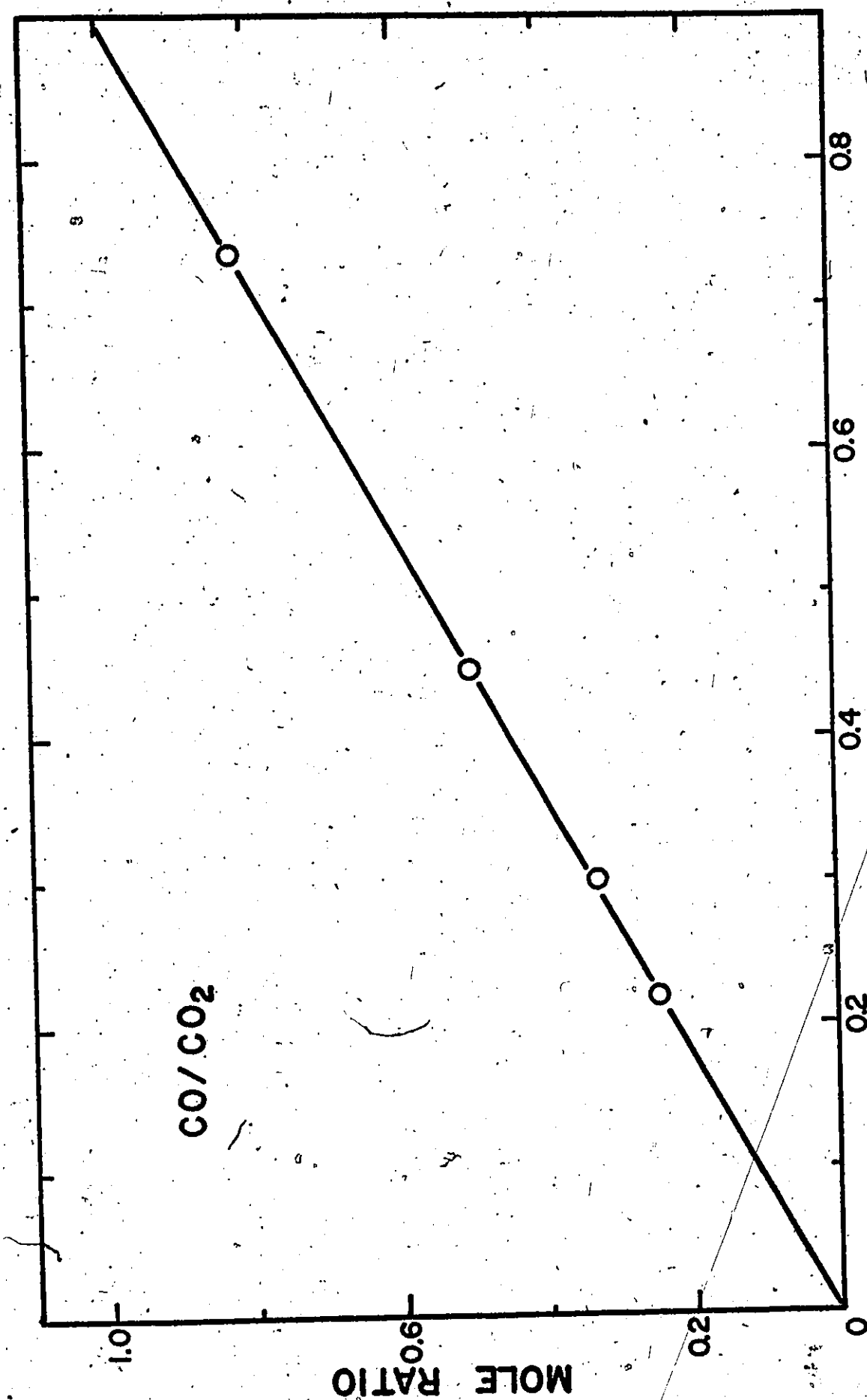

Figure 8-1 Calibration of G. C. for the mixture of carbon monoxide and carbon dioxide.

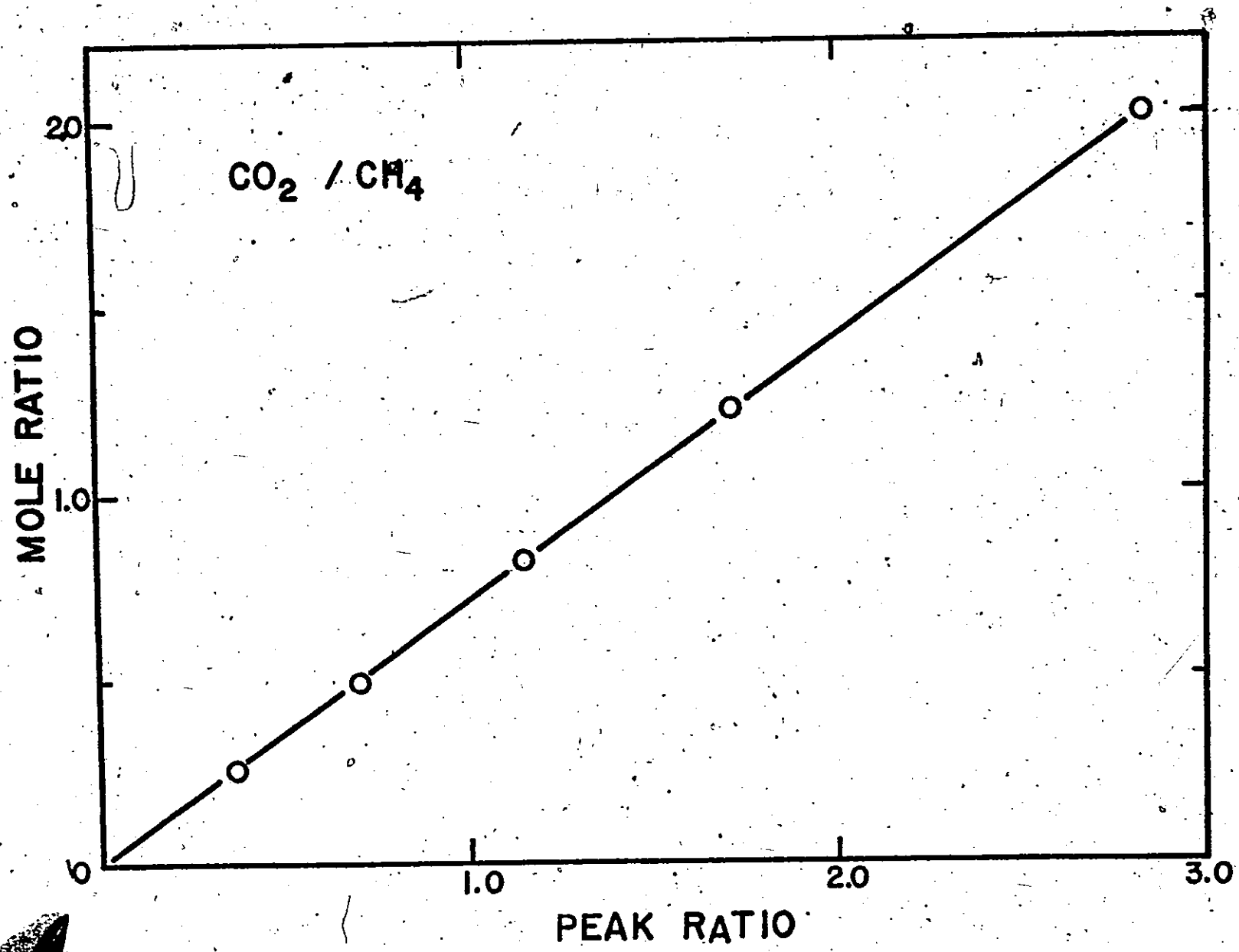

Figure 8-2 Calibration of G. C. for the mixture of carbon dioxide and methane

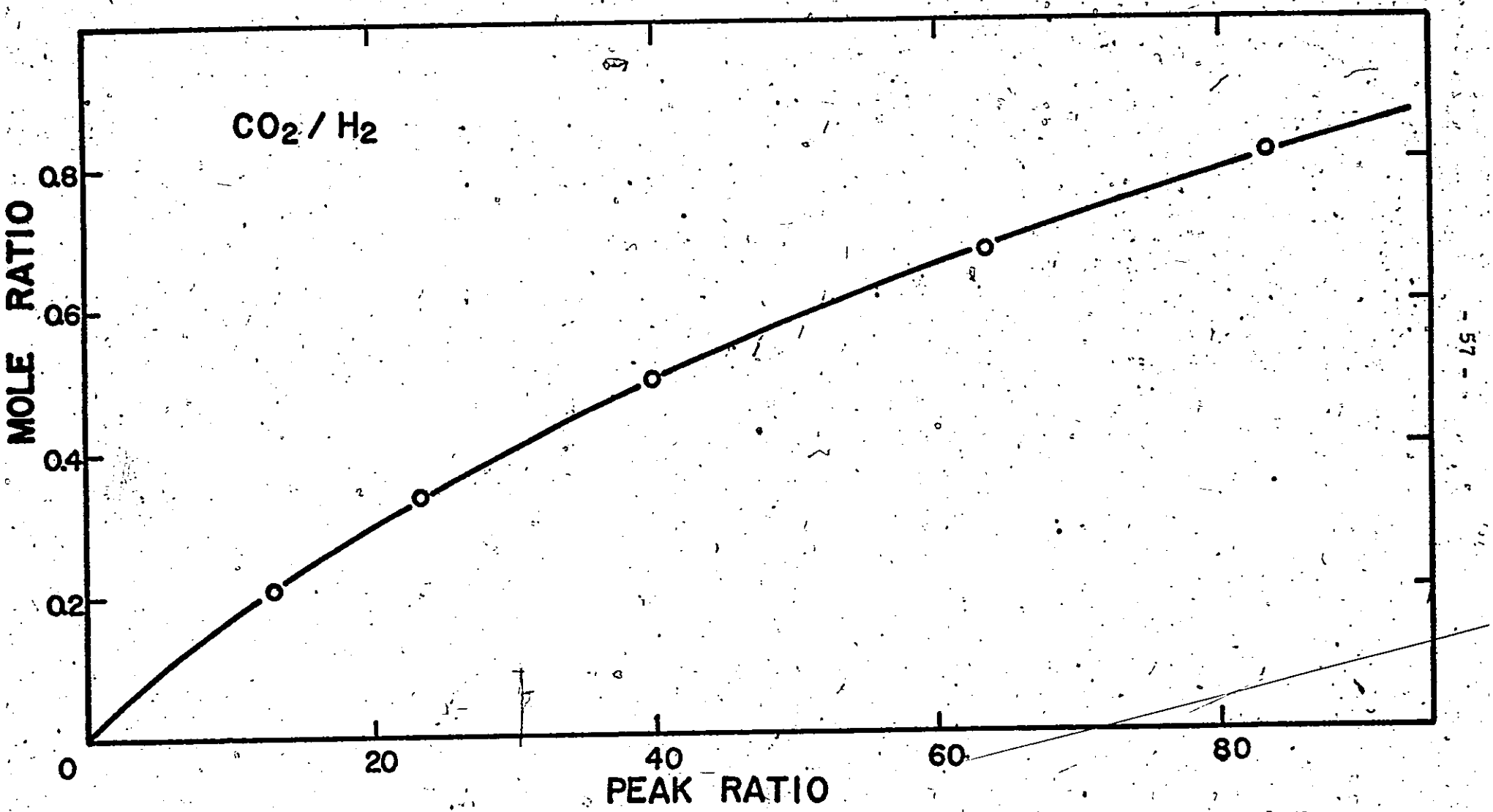

Figure 3-3 Calibration of G.C. for the mixture of carbon dioxide and hydrogen

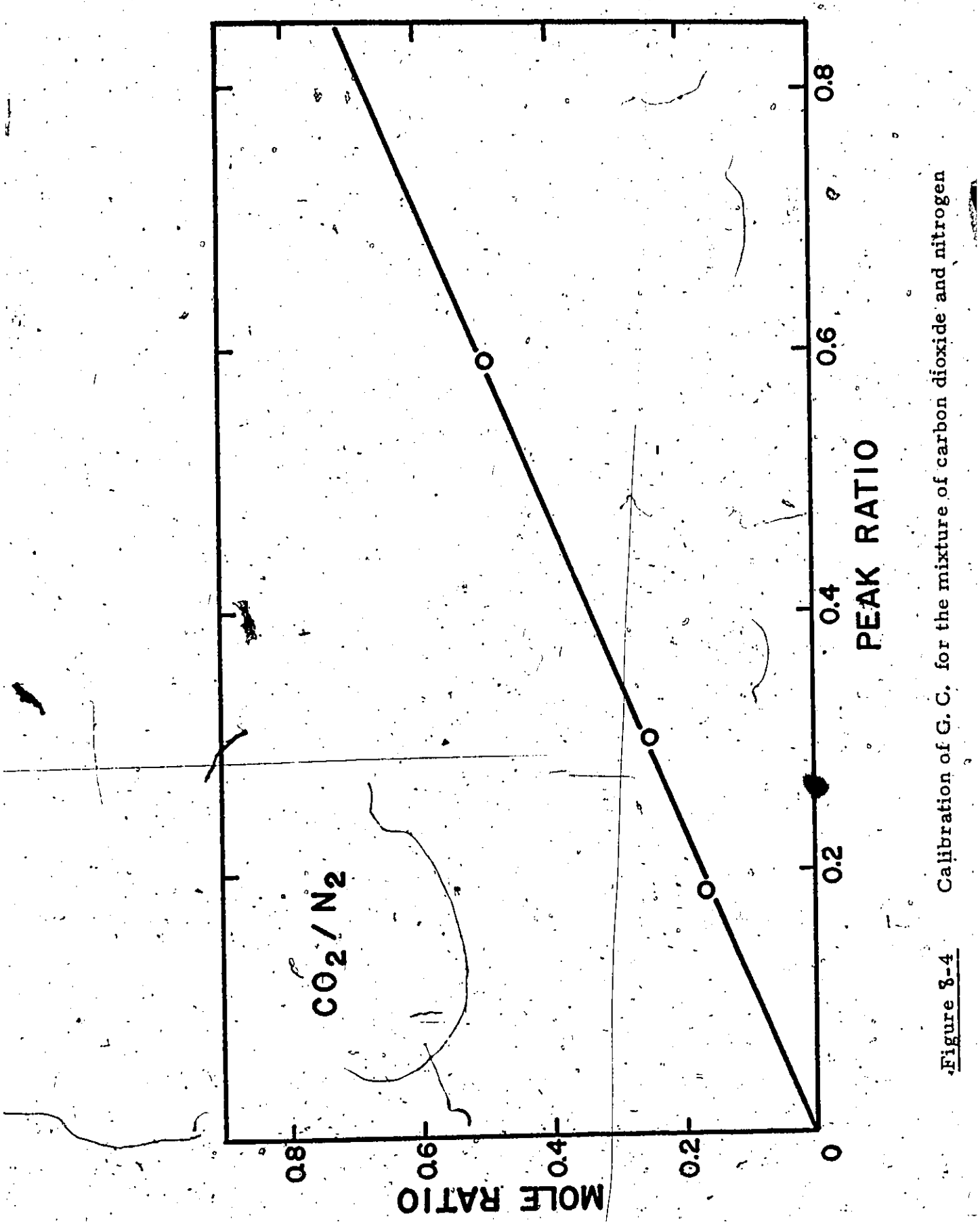

Figure 8-4 Calibration of G. C. for the mixture of carbon dioxide and nitrogen

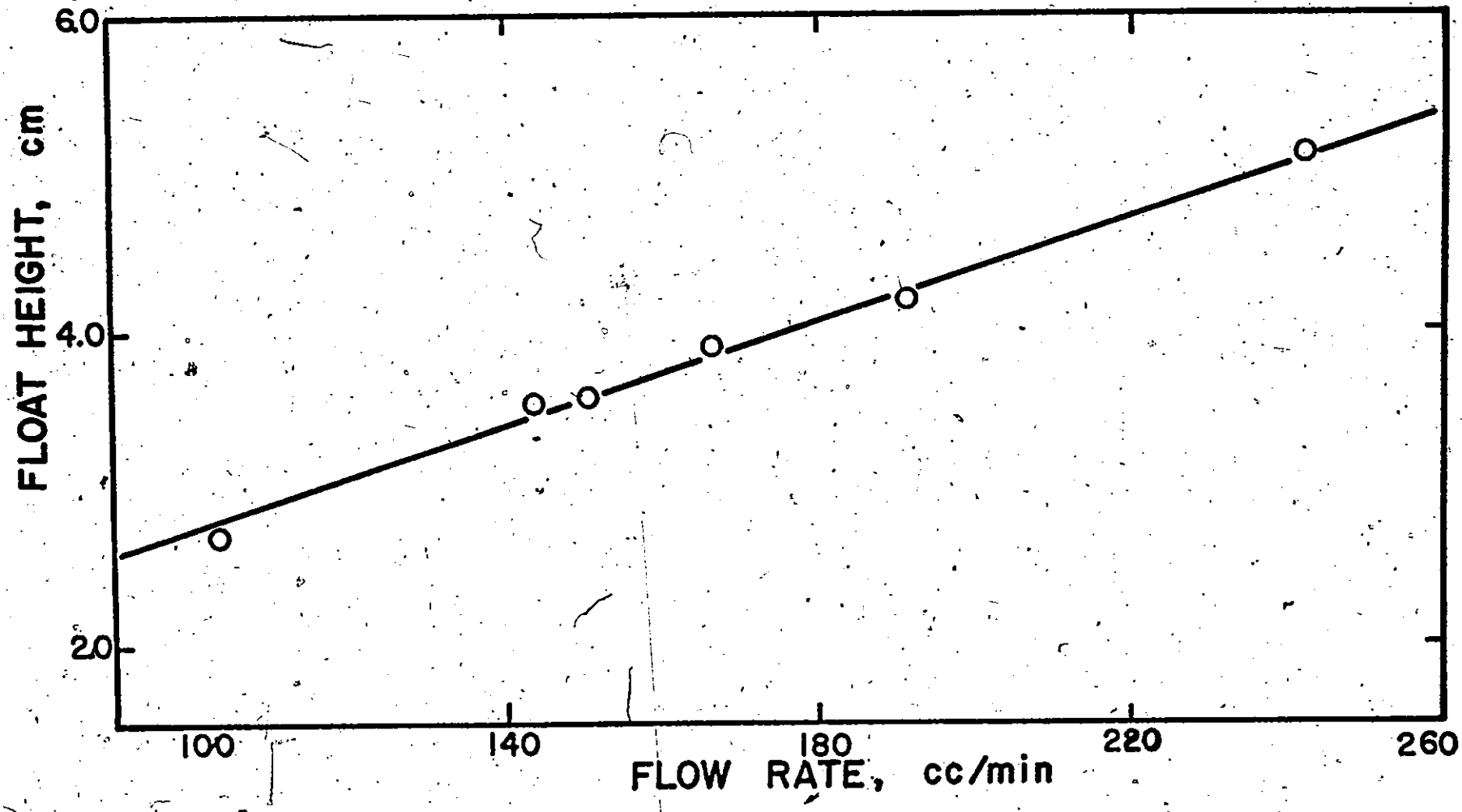

Figure 8-5 Calibration of rotameter for nitrogen at 200 psig

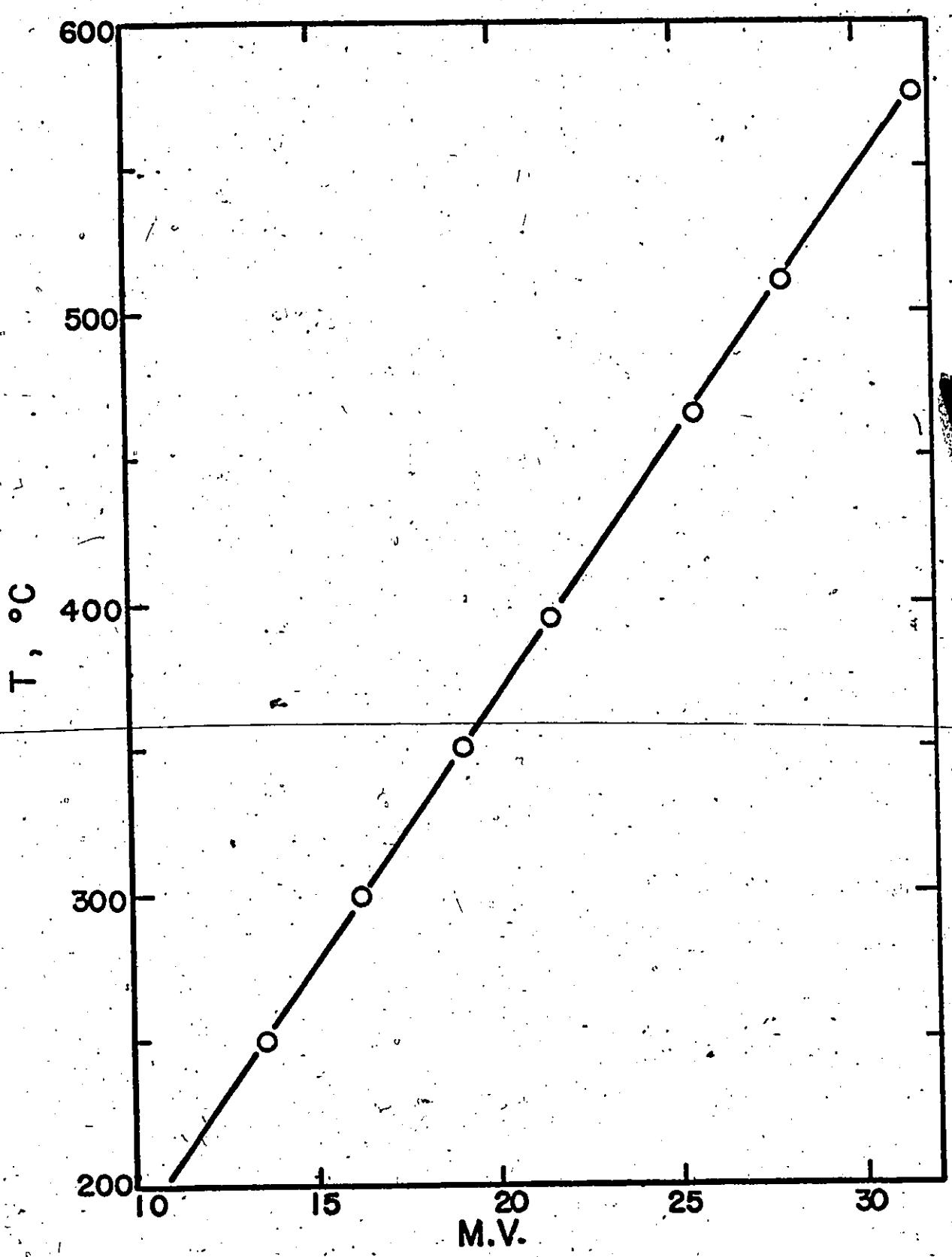

Figure 8-6 Calibration of the iron-construction thermocouple used in the reactor

C. Calculation of Equilibrium Constant and Concentration

The calculations are based on the assumption of following equilibrium reactions

$$CO + H_2O \rightleftharpoons H_2 + CO_2 \qquad (3\text{-}1)$$

$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O \qquad (3\text{-}2)$$

Standard heat of reactions:

Eq [3-1]

$$\Delta H^\circ_{298} = \Delta H^\circ_f (H_2) + \Delta H^\circ_f (CO_2) - \Delta H^\circ_f (CO) - \Delta H^\circ_f (H_2O)$$

$$= 0 + (-94052) - (-26416) - (-57798)$$

$$= -9838 \text{ cal/g-mole}$$

Eq [3-2]

$$\Delta H^\circ_{298} = \Delta H^\circ_f (CH_4) + \Delta H^\circ_f (H_2O) - \Delta H^\circ_f (CO) - \Delta H^\circ_f (3H_2)$$

$$= -17889 + (-57798) - (-26416) - 0$$

$$= -49271 \text{ cal/g-mole}$$

Standard free-energy change in reactions:

Eq [3-1]

$$\Delta G^\circ_{298} = \Delta G^\circ_f (H_2) + \Delta G^\circ_f (CO_2) - \Delta G^\circ_f (CO) - \Delta G^\circ_f (H_2O)$$

$$= 0 + (-94260) - (-32808) - (-54635)$$

$$= -6817 \text{ cal/g-mole}$$

Eq [3-2]

$$\Delta G^\circ_{298} = \Delta G^\circ_f (CH_4) + \Delta G^\circ_f (H_2O) - \Delta G^\circ_f (CO) - \Delta G^\circ_f (3H_2)$$

$$= -12140 + (-54635) - (-32808) - 0$$

$$= -33967 \text{ cal/g-mole}$$

Molal heat capacities[24] $C_p = \alpha + \beta T + \gamma T^2$

Compound	α	β	γ
CH_4	3.381	18.044×10^{-3}	-4.30×10^{-6}
CO	6.420	1.665×10^{-3}	-0.196×10^{-6}
CO_2	6.214	10.396×10^{-3}	-3.545×10^{-6}
H_2O	7.256	2.298×10^{-3}	0.283×10^{-6}
H_2	6.947	-0.2×10^{-3}	0.481×10^{-6}

Eq [3-1] $\Delta\alpha = -0.515$ $\Delta\beta = 6.233 \times 10^{-3}$ $\Delta\gamma = -3.151 \times 10^{-6}$

Eq [3-2] $\Delta\alpha = -16.624$ $\Delta\beta = 19.277 \times 10^{-3}$ $\Delta\gamma = -5.264 \times 10^{-6}$

Standard free-energy change at temperature T can be calculated by combining the following two equations:

$$\Delta H^\circ_T = \Delta H_o + \Delta\alpha T + 1/2\,\Delta\beta T^2 + 1/3\,\Delta\gamma T^3$$

$$\Delta G^\circ_T = \Delta H_o - \Delta\alpha T \ln T - 1/2\,\Delta\beta T^2 - 1/6\,\Delta\gamma T^3 + IT$$

Eq [3-I] $\Delta H_o = \Delta H^\circ_{298} + \Delta\alpha(298) + 1/2\,\Delta\beta(298)^2 + 1/3\,\Delta\gamma(298)^3$

$= -9934$ cal/g-mole

Eq [3-2] $\Delta H_o = -45125$ cal/g-mole

$$I(298) = \Delta G^\circ_{298} - \Delta H_o + \Delta\alpha(298) + 1/2\,\Delta\beta(298)^2 + 1/6\,\Delta\gamma(298)^3$$

Eq [3-1] $I = 8.40$

Eq [3-2] $I = -54.42$

At $T = 739°K$ (466°C)

Eq [3-1] $\Delta G^{\circ}_{739} = -2701$ cal/g-mole

Eq [3-2] $\Delta G^{\circ}_{739} = -9059$ cal/g-mole

Hence, the equilibrium constants are obtained from the following relationship:

$$\Delta G^{\circ}_{T} = -RT \ln K$$

$K_1 = 6.294$, $K_2 = 478$ at $T = 739°K$

Calculation of fugacity term:

At $T = 739°K$, $P = 14.6$ atm

	Tr	Pr	f/P (21)(22)
H_2	22.1922	1.1406	1.0036
CO_2	2.4309	0.2003	0.9999
CO	5.5564	0.4232	1.0043
CH_4	3.8691	0.3189	1.0034
H_{20}	1.1422	0.0670	0.9853

Eq [3-1] $$K_{\varphi_1} = \frac{(0.9999)(1.0036)}{(1.0043)(0.9853)} = 1.0141$$

Eq [3-2] $$K_{\varphi_2} = \frac{(1.0034)(0.9853)}{(1.0043)(1.0036)^3} = 0.9739$$

Calculation of concentration :

The concentration of gases at different fractions of conversion were calculated from equilibrium constant equations (3-8) and (3-9) by the try and error method. The results based on one mole of heptane feed were listed as below.

T=466℃ , P = 14.6 atm. $C_7H_{16} : H_2O : N_2 = 1 : 8.2 : 6$

Conversion	Gas Composition, moles				
	CO_2	CO	CH_4	H_2	H_2O
0.025	0.16143	0.00166	0.01191	0.50070	7.85078
0.05	0.25595	0.00396	0.09009	0.73568	7.65944
0.10	0.37250	0.00738	0.32013	0.91212	7.42292
0.15	0.46524	0.01028	0.57448	0.99179	7.23454
0.25	0.63030	0.01573	1.10397	1.06838	6.89897
0.50	1.00780	0.02967	2.46253	1.12022	6.13003
0.75	1.36860	0.04541	3.83599	1.11064	5.39269
1.00	1.72100	0.06387	5.21513	1.07560	4.66943

D. Sample Calculation

A simple calculation based on the experimental data of Run No. 115 is shown as below.

1) Feed Rate

C_7H_{16}

$$= \frac{10 \text{ cc/hr} \times 0.6803 \text{ g/cc}}{100.198 \text{ g/mole}} = 0.0679 \text{ moles/hr}$$

H_2O

$$= \frac{10 \text{ cc/hr} \times 1.0 \text{ g/cc}}{18.016 \text{ g/mole}} = 0.5551 \text{ moles/hr}$$

N_2

$$= \frac{9.96 \text{ l/hr} \times 273°K}{22.4 \text{ l/g mole} \times 298°K} = 0.4073 \text{ moles/hr}$$

2) Moles in Products

Peak area ratio:

$CO/CO_2 = 0.0233$

$CO_2/CH_4 = 0.5488$

$CO_2/H_2 = 96.8$

$CO_2/N_2 = 0.2678$

Mole ratio:

$R_1 = CO/CO_2 = \text{slope} \times 0.0233$

$= 1.117 \times 0.0233 = 0.0260$

$R_2 = CO_2/CH_4 = \text{slope} \times 0.5488$

$= 0.7077 \times 0.5488 = 0.3884$

$R_4 = CO_2/N_2 = \text{slope} \times 0.2678$

$= 0.8451 \times 0.2678 = 0.2263$

$R_3 = CO_2/H_2 = 0.88$ (from calibration curve)

Output gas:

$= 330$ cc/min $= 0.8098$ Moles/hr

$= N_{CO_2} + N_{CO} + N_{CH_4} + N_{H_2} + H_{N_2}$

$= N_{CO_2} + R_1 N_{CO_2} + N_{CO_2}/R_2 + N_{CO_2}/R_3 + N_{CO_2}/R_4$

$N_{CO_2} = 0.8098/ [1 + R_1 + 1/R_2 + 1/R_3 + 1/R_4]$

$= 0.0884$ moles/hr

$N_{CO} = N_{CO_2} \times R_1$

$= 0.0884 \times 0.0260 = 0.0023$ moles/hr

$$N_{CH_4} = N_{CO_2}/R_2$$

$$= 0.0884/0.3884 = 0.2276 \text{ moles/hr}$$

$$N_{H_2} = N_{CO_2}/R_3$$

$$= 0.0884/0.88 = 0.1005 \text{ moles/hr}$$

$$N_{N_2} = N_{CO_2}/R_4$$

$$= 0.0884/0.2263 = 0.3906 \text{ moles/hr}$$

3) Material Balance Based on Atomic element of Carbon

$$7 \times N_{C_7H_{16}}(\text{In}) = N_{CO} + N_{CO_2} + N_{CH_4} + 7 \times N_{C_7H_{16}}(\text{out})$$

$$N_{C_7H_{16}}(\text{out}) = [7 \times C_7H_{16}(\text{In}) - N_{CO} - N_{CO_2} - N_{CH_4}]/7$$

$$= (7 \times 0.0670 - 0.0023 - 0.0884 - 0.2276)/7$$

$$= 0.0224 \text{ moles/hr}$$

$$\%\text{Conversion} = \frac{N_{C_7H_{16}}(\text{In}) - N_{C_7H_{16}}(\text{Out})}{N_{C_7H_{16}}(\text{In})} \times 100$$

$$= \frac{0.0679 - 0.0224}{0.0679} \times 100$$

$$= 67.01$$

E. Estimation of Temperature Gradient Across the Bed

The estimation of the maximum temperature gradient of the catalyst bed in an isothermal condition based on the data of Run No. 226 which gives a highest conversion is described as below.

For the reaction at 530°C with 97.5% conversion,

$$(0.0662)C_7H_{16} + (0.2574)H_2O \rightarrow (0.1220)CO_2 + (0.0134)CO + (0.3280)CH_4 + (0.1374)H_2$$

Heat produced by the reaction :

$$\Delta H^\circ_T = \Delta H^\circ + \Delta\alpha T + 1/2\Delta\beta T^2 + 1/3\Delta\gamma T^3$$

$$\Delta\alpha = \sum_{\text{products}} n\alpha - \sum_{\text{reactants}} n\alpha = 0.570$$

$$\Delta\beta = \sum_{\text{products}} n\beta - \sum_{\text{reactants}} n\beta = -1.582 \times 10^{-3}$$

$$\Delta\gamma = \sum_{\text{products}} n\gamma - \sum_{\text{reactants}} n\gamma = 0.711 \times 10^{-6}$$

$$\Delta H^\circ_{298} = \sum_{\text{products}} n\Delta H^\circ_{298} - \sum_{\text{reactants}} n\Delta H^\circ_{298} = 158$$

$$\Delta H_o = -\Delta H^\circ_{298} - \Delta\alpha(298) - 1/2\,\Delta\beta\,(298)^2 - 1/3\,\Delta\gamma\,(298)^3$$
$$= 47 \text{ cal/hr}$$

$$\Delta H^\circ_{803} = 47 + \Delta\alpha\,(803) + 1/2\,\Delta\beta\,(803)^2 + 1/3\,\Delta\gamma\,(803)^3$$
$$= 117 \text{ cal/hr}$$

Heat removed by the products :

$$Q_p = C_{pm} \cdot W \cdot \Delta T$$
$$= 10.442 \times 0.6008\,\Delta T$$
$$= 6.274\,\Delta T \text{ cal/hr}$$

where C_{pm} is the heat capacity of gas mixture in cal/ mole product° C, $C_{pm} = \Sigma x_i C_{pi}$; W is the rate of products in mole products/hr ; ΔT is the temperature difference between inlet and outlet of the bed.

Heat lost through the wall :

$$Q_w = k\left\{\frac{A_2 - A_1}{\ln (A_2/A_1)}\right\}\frac{\Delta T'}{r_2 - r_1}$$

$$= 140 \times \frac{3.47 - 2.616}{\ln (3.47/2.616)} \times \frac{\Delta T}{2(1.30 - 0.98)}$$

$$= 661\ \Delta T \quad \text{cal/ hr}$$

where k is the thermal conductivity of stainless steel (type 316) in cal/cm hr °C ; A_1 is the inside area normal to the heat flow ; A_2 is the outside area normal to the heat flow ; The length of the stainless steel used in the calculation is the height of the catalyst bed, which is 0.425 cm ; r_1 and r_2 are the inside diameter and outside diameter of the reactor respectively ; $\Delta T'$ is the temperature difference between inside and outside of the wall, and is assumed to be 1/2 ΔT .

Energy balance in the reactor :

Heat produced by the reaction = Heat removed by the products + Heat lost through the wall

$$\Delta H = Q_p + Q_w$$

$$117 = 6.274\ \Delta T + 661\ \Delta T$$

$$\therefore \quad \Delta T = 0.18\ °C$$

It should be mentioned that the temperature gradient between the catalyst bed and the reactor wall has not been considered in the above calculation of Q_w. Consequently, the actual ΔT value could be much higher than 0.18°C.

F. Experimental Data

Table 8-3

Experimental Composition of the Gas Products

T = 466°C P = 200 psig C_7H_{16} : H_2O : N_2 = 1 : 8.2 : 6.0

Run No.	W gm.	Heptane Feed moles/hr	Products, moles/hr						% Conversion
			CO_2	CO	CH_4	H_2	H_2O	C_7H_{16}	
101	0.1	0.0679	0.0068	0.0000	0.0089	0.0208	0.5415	0.0668	1.62
102	0.25	0.0679	0.0144	0.0003	0.0042	0.0369	0.5260	0.0652	3.98
103	0.25	0.0679	0.0150	0.0004	0.0054	0.0417	0.5247	0.0649	4.42
104	0.5	0.0679	0.0361	0.0010	0.0338	0.0657	0.4819	0.0578	14.87
105	0.5	0.0679	0.0372	0.0012	0.0374	0.0650	0.4795	0.0571	15.91
106	0.75	0.0679	0.0468	0.0014	0.0598	0.0731	0.4601	0.0525	22.68
107	0.75	0.0679	0.0473	0.0015	0.0673	0.0709	0.4590	0.0513	24.45
108	1.0	0.0679	0.0503	0.0015	0.0723	0.0727	0.4530	0.0502	26.01
109	1.0	0.0679	0.0550	0.0021	0.0888	0.0828	0.4430	0.0471	30.63
110	1.5	0.0679	0.0658	0.0023	0.1344	0.0889	0.4212	0.0390	42.56
111	1.5	0.0679	0.0689	0.0024	0.1507	0.0907	0.4149	0.0362	46.69
112	2.0	0.0679	0.0716	0.0024	0.1640	0.0966	0.4095	0.0339	50.07
113	2.0	0.0679	0.0773	0.0025	0.1758	0.0992	0.3980	0.0314	53.76
114	4.0	0.0679	0.0842	0.0024	0.2110	0.0986	0.3843	0.0255	62.45

Table 8-3 (Cont'd)

Experimental Composition of the Gas Products

T = 466°C P = 200 psig C_7H_{16} : H_2O : N_2 = 1 : 8.2 : 6.0

Run No.	W gm	Heptane Feed moles/hr	Products, Moles/hr						% Conversion
			CO_2	CO	CH_4	H_2	H_2O	C_7H_{16}	
115	4.0	0.0679	0.0884	0.0023	0.2276	0.1005	0.3760	0.0224	67.01
116	4.0	0.0679	0.0894	0.0022	0.2395	0.0964	0.3741	0.0206	69.66
117	6.0	0.0679	0.0908	0.0025	0.2456	0.0913	0.3710	0.0195	71.28
118	7.0	0.0679	0.0970	0.0027	0.2684	0.0934	0.3584	0.0153	77.47

Table 8-4

Experimental Results for the Effect of Temperature on Conversion

P = 200 psig $C_7H_{16} : H_2O : N_2 = 1 : 8.2 : 6.0$

Run No.	W gm.	T °C	Heptane Feed moles/hr	Products, moles/hr						% Conversion
				CO_2	CO	CH_4	H_2	H_2O	C_7H_{16}	
201	0.25	350	0.0679	0.0031	0.0000	0.0002	0.0096	0.5489	0.0674	0.74
202	0.25	400	0.0679	0.0082	0.0000	0.0004	0.0256	0.5387	0.0667	1.77
203	0.25	450	0.0679	0.0186	0.0004	0.0071	0.0435	0.5175	0.0642	5.45
204	0.25	500	0.0679	0.0355	0.0018	0.0341	0.0640	0.4823	0.0577	15.02
205	0.25	530	0.0679	0.0546	0.0037	0.0534	0.1332	0.4422	0.0519	23.56
211	0.5	300	0.0679	0.0010	0.0000	0.0001	0.0038	0.5531	0.0677	0.29
212	0.5	350	0.0679	0.0032	0.0000	0.0004	0.0826	0.5487	0.0674	0.74
213	0.5	400	0.0679	0.0100	0.0000	0.0047	0.0282	0.5351	0.0668	3.09
214	0.5	450	0.0679	0.0270	0.0005	0.0187	0.5352	0.5006	0.0613	9.72
215	0.5	500	0.0679	0.0510	0.0028	0.0477	0.0761	0.4803	0.0534	21.35
216	0.5	530	0.0679	0.0710	0.0057	0.1153	0.1413	0.4074	0.0405	40.35
221	1.0	300	0.0679	0.0026	0.0000	0.0006	0.0093	0.5499	0.0674	0.74
222	1.0	350	0.0679	0.0076	0.0000	0.0040	0.0232	0.5399	0.0662	2.50
223	1.0	400	0.0679	0.0222	0.0006	0.0186	0.0331	0.5137	0.0620	8.69
224	1.0	450	0.0679	0.0472	0.0016	0.0720	0.0775	0.4591	0.0506	25.48
225	1.0	500	0.0679	0.0757	0.0043	0.1920	0.0935	0.3994	0.0290	57.30
226	1.0	530	0.0679	0.1220	0.0134	0.3280	0.1374	0.2977	0.0017	97.50

Table 8-5

Experimental Results for the Effect of Pressure on Conversion

F = 0.0679 moles/hr C_7H_{16} : H_2O : N_2 = 1 : 8.17 : 6.0 W = 0.5 gm.

Run No.	P psig	T °C	Products, moles/hr						% Conversion
			CO_2	CO	CH_4	H_2	H_2O	C_7H_{16}	
301	5	450	0.0176	0.0008	0.0003	0.0465	0.5191	0.0652	3.98
302	100	450	0.0231	0.0006	0.0053	0.0524	0.5083	0.0638	6.04
303	200	450	0.0248	0.0005	0.0145	0.0506	0.5050	0.0622	8.39
304	300	450	0.0270	0.0005	0.0174	0.0514	0.5276	0.0615	9.43
311	5	500	0.0421	0.0024	0.0317	0.1172	0.4685	0.0570	16.05
312	100	500	0.0437	0.0022	0.0463	0.1074	0.4655	0.0547	19.44
313	200	500	0.0431	0.0019	0.0513	0.0997	0.4670	0.0541	20.32
314	300	500	0.0419	0.0019	0.0554	0.0925	0.4694	0.0537	20.91

Table 8-6

Experimental Results for the Effect of Reactants Ration on Conversion

T = 450°C P = 200 psig W = 0.75 gm. Total Feed = 2.0 moles/hr

Run No.	Molal Ratio $C_7H_{16} : H_2O : N_2$	Heptane Feed moles/hr	Products, moles/hr CO_2	CO	CH_4	H_2	H_2O	C_7H_{16}	%Conversion
401	1 : 8.17 : 20.28	0.0679	0.0225	0.0005	0.0096	0.0629	0.5097	0.0633	6.77
402	1 : 12.26 : 16.19	0.0679	0.0271	0.0005	0.0101	0.0718	0.5004	0.0625	7.95
403	1 : 16.35 : 12.11	0.0679	0.0294	0.0005	0.0088	0.0819	0.4958	0.0624	8.10
404	1 : 24.52 : 3.93	0.0679	0.0285	0.0003	0.0069	0.0836	0.4978	0.0628	7.51