REACTIONS OF CARBON VAPOR WITH HYDROGEN AND WITH METHANE IN A HIGH INTENSITY ARC

by

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Massachusetts Institute of Technology
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May 10, 1963

Professor Phillip Franklin
Secretary of the Faculty
Massachusetts Institute of Technology
Cambridge 39, Massachusetts

Dear Sir:

The thesis entitled "Reactions of Carbon Vapor with Hydrogen and with Methane in a High Intensity Arc" is herewith submitted in partial fulfillment of the requirements for the degree of Doctor of Science.

Respectfully submitted,

Signature redacted

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MRL

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ABSTRACT

Reactions of Carbon Vapor with Hydrogen and with Methane in a High Intensity Arc

Jean L. Blanchet

Submitted to the Department of Chemical Engineering on May 10, 1963, in partial fulfillment of the requirements for the degree of Doctor of Science.

Thermodynamic equilibrium composition diagrams for the carbon-hydrogen system have been constructed for the temperature range 2,000 to 6,000°K at various total pressures and carbon to hydrogen ratios. Significant species in the high temperature region included C_2H, C_3H, and C_4H radicals.

Assuming that the C_2H radical serves as precursor to C_2H_2 formation, the maximum C_2H_2 concentration in the quenched gas has been calculated as a function of quenching temperatures and total pressures.

A mechanism for reacting carbon vapor with methane at high temperatures was postulated, whereby the available heat of reaction of carbon vapor with hydrogen provided the sensible heat to bring methane to reaction temperature and the heat required to crack methane to acetylene and hydrogen. A carbon vapor to methane ratio of 0.6 to 0.8 should produce between 40 and 47% C_2H_2 at temperatures of 2,000 to 4,000°K.

A high intensity carbon arc reactor was built to react carbon vapor with both hydrogen and methane as feed gases. The hot gases from the arc zone were quenched with a water-cooled sampling probe and then analysed by vapor chromatography.

At one atmosphere pressure, as high as 26% C_2H_2 was obtained for reactions of carbon with hydrogen and the data could be correlated by considering the quenching temperatures and the C/H_2 ratios. An acetylene concentration of 52% was reached with the carbon-methane system. These maximum concentrations are higher than any previously reported values in the literature for similar systems.

The energy required to make a given amount of acetylene by the present arc technique was found to be five to ten times higher than with the usual industrial processes. It was also found that only 20% of the vaporized carbon could be utilized to produce acetylene in the output gas. Methods are suggested for reducing

both these quantities, and it appears that the carbon-CH_4 system could produce very high acetylene concentrations at competitive power inputs.

Thesis Supervisor:

. . . .

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Introduction

Reliable thermodynamic data for C-H compounds at temperatures above 1500°K are almost nonexistent in the literature. Techniques used nowadays for estimating high temperature thermodynamic properties are based on estimates of interatomic distances and vibrational energies of the molecules[3]. Spectroscopic data taken at high temperatures in order to provide more reliable values[11] are still needed.

This thesis was undertaken to study thoroughly the carbon-hydrogen and carbon-methane system at temperatures between 2,000 and 6,000°K in a high intensity arc. The determination of acetylene yields that can be expected from such systems was another objective considered. In contrast with previous work[2], this thesis was aimed at studying the homogeneous region, where carbon exists in the gas phase only.

Procedure

A high temperature carbon arc reactor, shown schematically in Fig. 7, was built in order to carry out reactions of carbon with hydrogen and with methane. The gases from the arc reaction zone were sampled with a water-cooled sampling probe, under fast quenching conditions, and analyzed by gas chromatography. The arc characteristics were determined for anode sizes of 1/4 in. and 3/8 in. and the effects of arc power input, C/H_2 ratio

and gas flow rates upon C_2H_2 content of the quenched gas were studied at a pressure of 1.0 atmosphere.

Results and Conclusions

Thermodynamic equilibrium composition diagrams were determined for the carbon-hydrogen system in the temperature range 2,000 - 6,000°K. Several total pressures and carbon to hydrogen ratios were considered, since previous studies failed to consider these conditions (2,19). Species that were assumed to exist in the high temperature region included C_1, C_2, C_3, C_2H_2, C_2H, C_3H, C_4H, H_2, H, CH, CH_2, and C_4H_2. Figs. 11 to 16 show some of the diagrams obtained for a pressure of 1.0 atm. Actual calculations were performed by means of the IBM 7090 computer of the M.I.T. Computation Center.

Assuming that the C_2H radical serves as precursor to C_2H_2 formation (2,26), i.e.,

$$C_2H + H \longrightarrow C_2H_2$$

the maximum C_2H_2 concentration obtainable under optimum quenching conditions was computed. Fig. 20 shows the dependence of the % C_2H_2 in the quenched gas on the C/H_2 ratio and the temperature. A rather narrow temperature band between 3,700 and 4,500°K for $C/H_2 \approx 5.0$ would exhibit optimum C_2H_2 concentration in the product gas.

The following mechanism was postulated for the reaction of methane with carbon vapor:

2?

$$C_1 + H_2 \longrightarrow C_2H_2 \quad \text{(at T)} \tag{1}$$

$$2\ CH_4\ _{(298°K)} \longrightarrow 2\ CH_4 \quad \text{(at T)} \tag{2}$$

$$2\ CH_4 \longrightarrow C_2H_2 + 3\ H_2 \quad \text{(at T)} \tag{3}$$

The heat released by reaction (1) is used to raise CH_4 to reaction temperature by reaction (2) and to crack methane to acetylene by reaction (3). The overall reaction can be represented by

$$C_1 + CH_4 \longrightarrow C_2H_2 + H_2 \tag{4}$$

Carbon vapor requirement and theoretical C_2H_2 content for a null reaction heat of reaction (4) are plotted in Fig. 25. At temperatures 2,000 - 4,000°K, as much as 40-47% C_2H_2 at C/H_2 ratio of 0.8 to 0.9 could be obtained according to this reaction scheme.

Experimental results show that a maximum of 26% C_2H_2 was obtained for reaction of carbon with hydrogen at one atmosphere, as seen in Fig. 32, and that the data could be correlated with the theoretical calculations, if sampling was assumed to take place along an isotherm. This value of C_2H_2 concentration is higher than any previously reported in the literature for reaction between the elements. By comparison with theory it was deduced that sampling was performed at excessively high temperatures, but limitations of the reactor design prevented reaching the higher possible yields of C_2H_2. Acetylene output was found to be also a function of both quenching temperatures and C/H_2 ratios.

An acetylene concentration equal to 52% was reached with the carbon-methane system. This is higher than the 25% theoretically attainable by the cracking reaction of methane[1] alone (Eq. 3) or the 12% claimed by Weir's patent[35] for a similar case. The results of Fig. 36 are, however, far from the predicted values of Fig. 25.

Economic considerations for these two systems revealed that, for the conditions studied, the energy required to produce a given output of acetylene was five to ten times higher than that of usual industrial processes for making acetylene. This is presented in Figs. 33 and 37. The carbon-methane system has, however, a potential of lower energy requirements, since a trend opposite to that of the carbon-hydrogen system is experienced.

In Fig. 38, it is shown that the efficiency of carbon utilization for acetylene production did not reach more than about 20% with both systems. More carbon was found, however, in the product gases with the carbon-methane system and the efficiency increased with increasing flow rates of gas fed to the reactor.

II. INTRODUCTION

Newly developed devices have made available sources of gas at temperatures between 3,000°K and 50,000°K. During the past decade, electric arcs have been used in various ways to create high energy environments. In particular, plasma jets, low intensity arcs and high intensity arcs have been studied extensively for high temperature operation in the range of about 3,000 to 20,000°K. The use of such devices seems attractive for carrying out chemical reactions of potential industrial importance.

Chemical reactions may benefit from high temperature environments in those cases where the formation of a particular substance would not be otherwise possible, or where a state of equilibrium not limited by chemical kinetics or a very rapid reaction rate is sought. Certain recombination reactions may also favor the formation of a desired product upon proper quenching of a gas mixture from a high temperature region. Other uses of high temperatures may include studies of chemical equilibrium under extreme conditions, radical and ion formation or reaction mechanisms.

Research at temperatures above 2,500°K is hindered, however, by two factors that are closely related: first, reliable thermodynamic data are scarce, and, second, it is very difficult to verify experimentally these data, as special techniques and apparatus are required which are still in the development stage. One extraneous but important factor that does not help the gathering of new data is the limitation imposed by materials of construction which are subjected to extreme conditions. Up to about four or five years ago, there were only a few works published on this type of research; however, due to the increased interest aroused mostly by space research and technology, and the understanding of highly reactive media, it is hoped to close the gaps created by an extended range of operating conditions and to ascertain experimentally many of the assumptions involved in extrapolating properties of atoms and molecules to high temperature systems.

Objects of the Thesis

This thesis was undertaken as a continuation of Iwasyk's work[(16)] on the carbon-hydrogen system at temperatures above 2,500°K. A high intensity arc reactor was used to react carbon with hydrogen, and the major product obtained was acetylene, up to 18% at one atmosphere pressure. Due to limitations in available thermodynamic data at that time and in design of the original reactor, only the heterogeneous region where carbon exists in the solid phase, was investigated.

The present study was aimed at

(1) a more thorough analysis of the equilibrium compositions of the carbon-hydrogen system, especially in the homogeneous phase, with emphasis given to the effects of carbon to hydrogen ratios and radicals expected to be present in the high temperature region,

(2) a determination of acetylene yields that may be expected from such equilibrium diagrams according to a simple quenching

mechanism,

(3) the construction and operation of a high intensity arc reactor for reacting carbon vapor and hydrogen at temperatures up to 7,000°K, and the determination of the important variables that control the output of acetylene in the reaction products,

(4) an extension of the above study to the carbon-methane system for the high temperature production of acetylene using arc techniques also.

Literature Survey

With these goals in mind, the literature survey was directed toward the review of works dealing with

(1) high temperature chemistry in general and means of generating high temperatures by the electric arc; measurements of high temperatures were also investigated;

(2) acetylene formation from the elements and from hydrocarbons, methane in particular.

High Temperatures

The term "high temperatures" is certainly a relative one. In combustion furnaces, temperatures were limited by the amount of energy of the chemical bond of fuels and the conditions under which the energy released was affected. The temperature range was increased to an upper limit of about 5,500°K, with the development of electric furnaces, solar furnaces, and special cutting flames.

With plasmas the temperature range has been expanded to still higher limits.

Above 6,000°K, all elements are in the gaseous phase at atmospheric pressure. At this temperature hydrogen H_2, for example, consists almost entirely of free atoms, i.e., in the dissociated state of H. Above 6,000°K hydrogen atoms begin to ionize and exist as a mixture of ions, electrons and free atoms. At 30,000°K hydrogen would be completely ionized. This is shown in Figure 1, where the dissociation portion was calculated by means of the equilibrium constants[(28)] of the dissociation reaction of hydrogen

$$H_2 \rightleftharpoons 2H$$

and where the ionization curve was computed according to the Saha equation[(7)] related to thermal ionization

$$H \rightleftharpoons H^+ + e - U_i$$

Thermal ionization is a general term applied to the ionizing action of molecular collisions, radiation, and electron collisions occurring in gases at high temperatures. Saha, on the basis of thermodynamic reasoning, assumed that the process of ionization is a completely reversible reaction defined by the equation

$$A \rightleftharpoons A^+ + e - U_i$$

where A represents a neutral atom, A^+ a singly ionized atom, e the electron removed from the atom, and U_i the ionization energy.

The concentrations of neutral atoms, n_n, of singly ionized atoms, n_i, and of the electrons, n_e, are assumed to be in complete thermal equilibrium, that is, they all have the energy of excitation corresponding to the temperature T. The concentrations are further assumed to follow Dalton's law of partial pressures for gas mixtures

$$\pi = p_n + p_i + p_e$$

Defining n as the original concentration of atoms in the gas, $n = n_n + n_i$ and the fraction of ionized atoms is $x = n_i/n = n_e/n$ since there are as many ions present in the gas as electrons. The relation developed is

$$\frac{x^2}{1-x^2}\pi = 3.16 \times 10^{-7} T^{2.5} \varepsilon^{-\frac{eV_i}{T}} \quad (1)$$

where π is the total pressure in atmospheres, T the gas temperature in degrees Kelvin, eV_i is the ionization energy in ergs, and K is the Boltzmann's constant. A more convenient form is

$$\log\left(\frac{x^2}{1-x^2}\pi\right) = \frac{-5{,}050\ V_i}{T} + 2.5 \log T - 6.5 \quad (2)$$

where V_i is in volts.

The relative concentration of positive ions and electrons may be altered however, for example, by the superposition of an electric or magnetic field; thus it might not be safe to assume $n_e = n_i$ in the use of the Saha equation. In this case, the following form should be used:

$$\log \frac{n_e n_i}{n_n} = \frac{-5{,}050\ V_i}{T} + 1.5 \log T + 15.385 \qquad (3)$$

The ionization potential corresponding to the energy required to remove completely the outer electron from its normal state in a neutral atom to a distance beyond the sphere of influence of the nucleus, is 13.6 volts and for H atoms[7] this value was used in Equation 2 for computing the concentration of atoms in a partially ionized gas up to 30,000°K at one atmosphere pressure. Also shown on Figure 1 is the partial pressure of H_2 molecules from 2,000 to 6,000°K and the partial pressures of H^+ and electrons (set equal in the present case) from 6,000 to 30,000°K. Ionization is very small below 6,000°K, the fraction of ionized atoms being only 5×10^{-5} at this temperature, reading 0.99 at 25,000°K and complete ionization near 30,000°K where the gas would comprise an equal concentration of H^+ and electrons. Results of the calculations appear in Table I.

The above analysis has certain limitations: first, the ideal gas state was assumed in this derivation whereas actual conditions at high temperatures may depart widely from this behavior; second, processes of multiple or cumulative ionization may also take place, as for instance ionization by contact with excited atoms, the so-called collisions of the second kind; third, the gas is assumed homogeneous, but flames and arcs usually burn in mixtures of gases and vapors whose ionization potentials may vary considerably: the gas having the lowest ionization potential in a mixture will be the most ionized and the gas with the highest, the least.

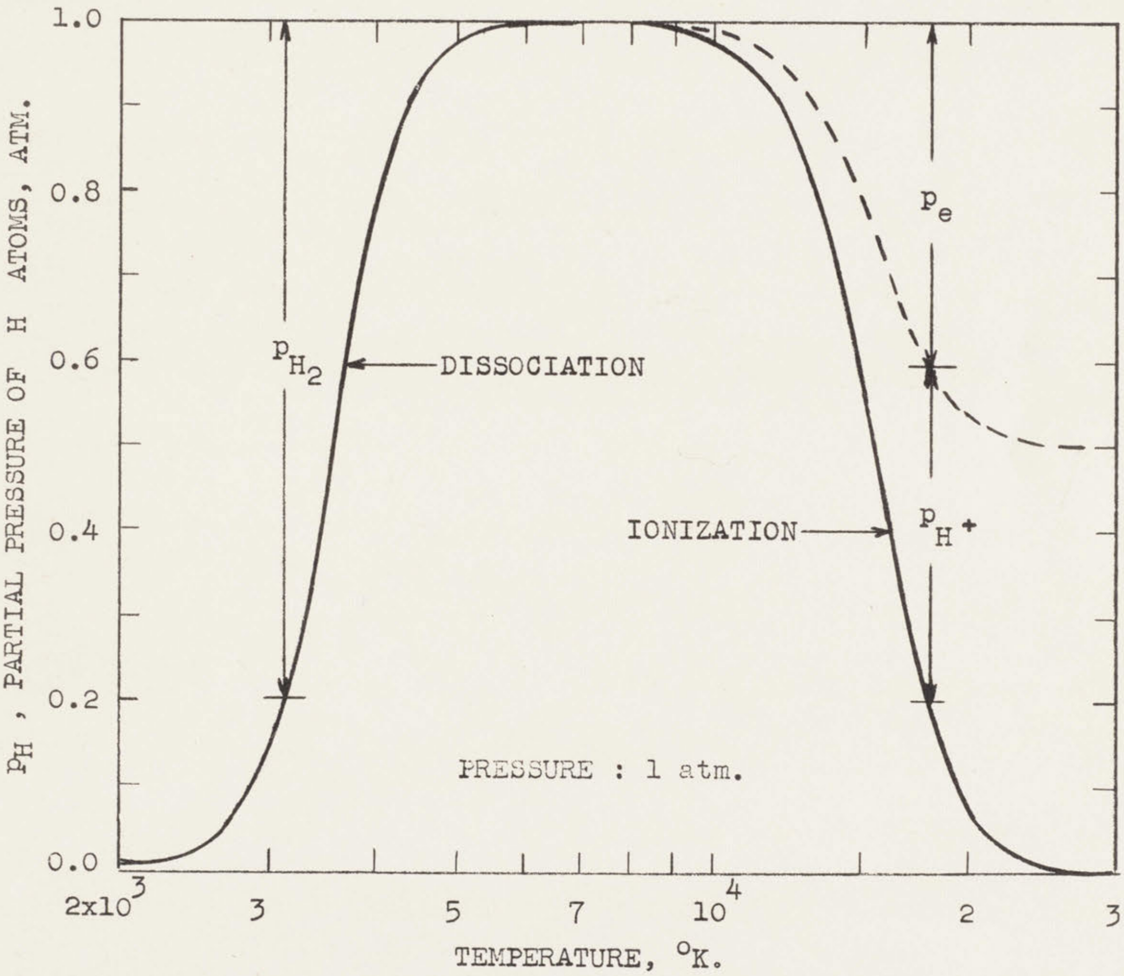


FIG. 1 . Effect of Temperature on Hydrogen Gas.

Table I

Ionization of H Atoms at One Atm.

(according to Saha's equation (Eq. 2))

T, °K	x	p_H
6,000	5.75×10^{-5}	1.00
8,000	2.17×10^{-3}	.998
10,000	0.02	.979
12,000	0.0930	.907
14,000	0.288	.712
16,000	0.585	.415
18,000	0.820	.180
20,000	0.930	.070
22,000	0.970	.030
25,000	0.992	.008
30,000	0.999	.000

A gas that is completely ionized is known as a "plasma", but the term has been extended to include also partially ionized gases. Thus a plasma is a mixture of molecules, free atoms, ions and electrons where the ionic charge is numerically equal to the number of electrons in a finite volume of gas, i.e., electrical neutrality is a basic property of plasmas.

Because chemical engineers are used to associate rates of heat transfer with temperature, the statement relating greater heat transfer rates with higher temperatures no longer holds at very high gas temperatures. The usual concept of temperature cannot be defined on this basis, because now we must consider the heat content of a gas as well as its temperature. It is common knowledge that a diatomic gas is much more suitable for heating than a monatomic gas.

If we assume a nearly constant specific heat, then a monatomic gas exhibits a linear enthalpy increase with rising temperature. When the gas begins to ionize at still higher temperatures, the enthalpy increases more rapidly for a given temperature rise.

A similar process occurs for a diatomic gas, except there is one more step that brings the heat content to a higher value: a diatomic molecule begins to dissociate around 2,000°K and for most gases, dissociation is complete at 7,000°K. The energy required for dissociation allows the gas to have a larger heat content at lower temperatures than a monatomic gas. When a dissociated gas is cooled down through the dissociation range, large amounts of heat are released per unit temperature drop, making the gas more suitable for heat transfer application than a monatomic gas. The effect of temperature on the heat content of hydrogen has been discussed by Anderson and Case [(1)] where is shown the sharp enthalpy rise over the dissociation range which levels off when dissociation is completed.

If higher temperatures are reached, another increase in enthalpy will occur over the ionization range, and depending on the gas there may be several plateaus depending upon the ionization level.

There exists, however, a limit to heat transfer rates, since at these plateaus, heat content is almost constant over a wide temperature range, and heat transfer can no longer be associated with temperature, according to the usual concept.

Temperature can be defined at these extreme conditions on the bases of the energy distribution over all particles: molecules, atoms, ions and electrons. Four different kinds of temperature describe average energy of the particles in ionized media: the electron temperature which gives the kinetic energy of the electrons, the gas temperature which provides the number of atoms per cm^3, the concentration temperature which determines the population of the excited states and the ionization temperature which gives the ion density. At thermal equilibrium, the four temperatures will be the same. The gas pressure is the other condition necessary to describe completely a plasma. At low pressures, the electron and gas temperatures differ by as much as several orders of magnitude.

At high pressures, above say 20 mm Hg, the ions, electrons and gas atoms are in thermal equilibrium, thus bringing the temperatures to the same value. This behavior is shown by Cobine[7] and Iwasyk[16] when describing the general properties of plasma produced in arcs.

Temperature equilibrium for a plasma implies that the number of excitations of atoms by electrons is equal to the number of collisions of the second kind; that events of ionization by collision are equal to the events of recombination by all mechanisms of collision (third body collisions); that the radiation emitted is equal to the radiation absorbed; and that dissociation of molecules to secondary products of ionization by collisions is equal to the association into molecules. In plasma generators with plasma temperatures of the order of 10,000°K, instead of such a state of equilibrium, there can only exist some sort of stationary state where a supply of energy balances the inevitable losses by radiation, by convection and by diffusion.

Of course, the field of plasmas is relatively new and most of the research in this area has been published only in technical reports, and the like. A survey of the research of ionized media has been thoroughly made by Jackson[17], mostly directed toward the dynamical or equilibrium properties of ionized media. Various designs of plasma generators, properties of arc plasmas including composition, viscosity, temperature, electrical conductivity and plasma instabilities and various uses of plasma jet generators have been discussed also in greater details by Turner[33], Iwasyk[16], Cobine[7], and Dow[9], while an advanced kinetic theory of plasma behavior has been developed quite extensively by Kaepeller[18]. In this latter report, a trial has been made to establish a stochastic theory of transport phenomena occurring in plasmas at very high temperatures by considering both mathematical and physical models. The temperature range treated was extended to 10^6°K.

Problems of heat transfer and diffusion associated with ionized gas have also been studied by Grey[13]. Average temperatures up to 15,000°K were determined by considering the enthalpy of an argon plasma jet.

However, properties of the plasma are not the primary concern of this thesis. The above discussion was intended to point out the different phenomena that are known to exist at elevated temperatures. Since the temperature range covered in the present work was believed to be between 4,000 and 7,000°K, the plasma consisted mostly of partially ionized gas, containing many dissociation products. As the source of high temperatures for plasma production is a form of gaseous discharge, usually established by an applied electric field, a further look into gaseous discharge theory is warranted, especially because an electric arc was used in the present work to create a high energy environment.

Gaseous Discharge Theory

An arc has been defined as "a discharge of electricity between electrodes in a gas or vapor, which has a voltage drop at the cathode of the order of the minimum ionizing or minimum exciting potential of the gas or vapor"(7). It is a self-sustained discharge having a low voltage drop and capable of supporting large currents.

It is customary to distinguish between three forms of steady-state gaseous discharge; Figure 2 shows the typical volt-ampere characteristics of various discharges. These characteristics are obtained for a discharge tube in series with a battery of voltage V and a resistance R, and can be determined by increasing the battery voltage, from V_1 to V_2, with constant resistance, or by decreasing the resistance, from R_1 to R_2, at constant battery voltage. In order of increasing current magnitude, discharges between two electrodes may be described in terms of:

(a) Townsend currents, usually measured in micro-amperes, $I_A \approx 10^{-6}$ amp. Voltage may range from about 25 to 50 volts, and the current in this region can be increased only by increasing the voltage. As the applied voltage reaches a point S at a current of 10^{-5} amp., there appears a glow discharge or a spark or an arc. These currents are prerequisite for starting electric arcs.

(b) Glow discharge currents, usually measured in milliamperes, $I_B \approx 10^{-3}$ amp. The region between S and B is a "normal" glow discharge which exhibits a voltage drop nearly independent of the current. The transition from the Townsend to the glow discharge

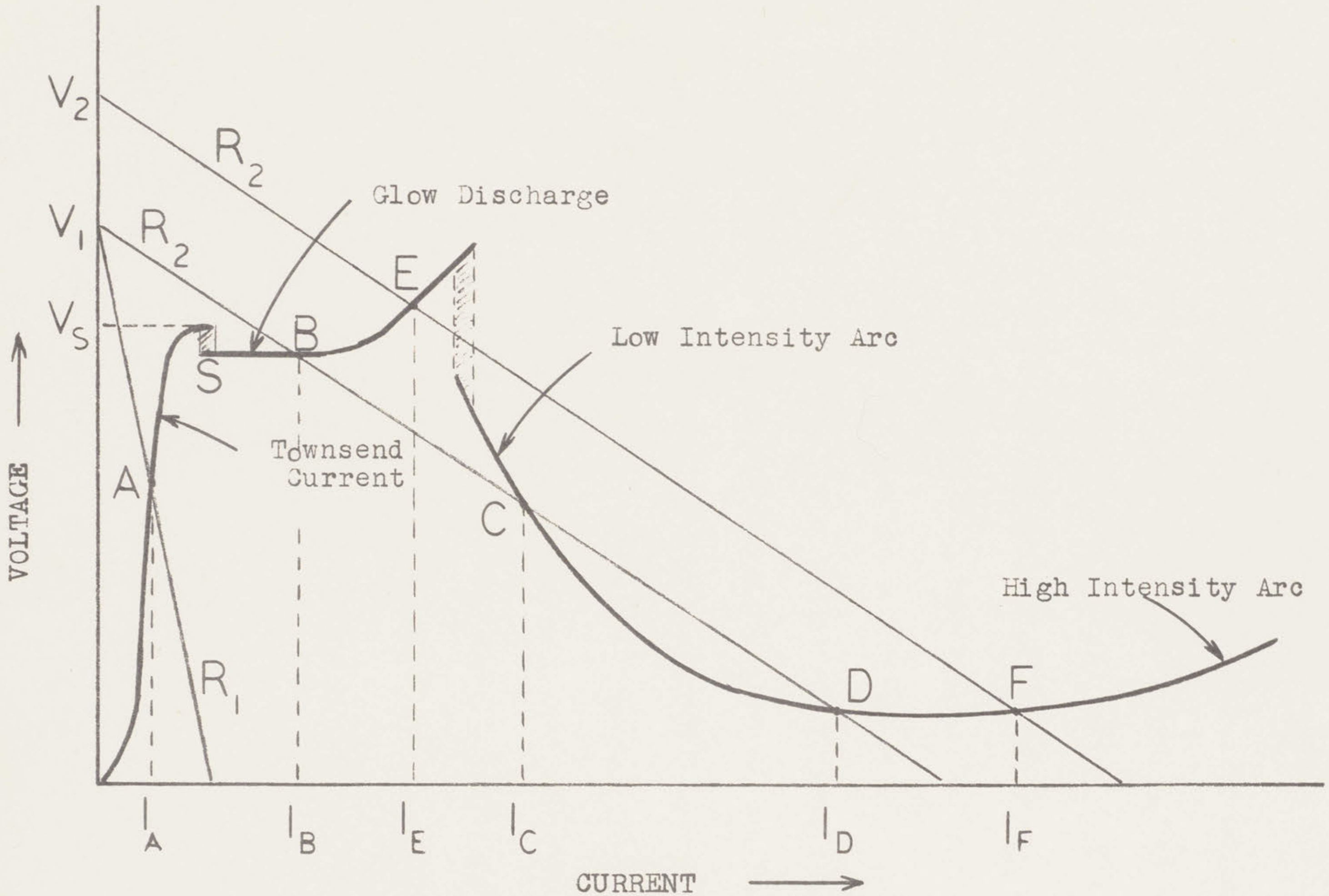


FIG. 2. Voltage-Current Characteristics for Gaseous Discharges.

is usually characterized by a drop in voltage, as shown in Figure 2. A region termed "abnormal" glow extends from about 10^{-2} to 10^{-1} amp. where the voltage increases with current up to a point where a sudden transition to a low intensity arc takes place.

(c) Electric arc currents, occurring at much higher amperage (0.1 to 1000 amp.) and relatively low voltage (usually below 100 volts), $I_c \approx$ 1 amp. There exists no upper limit to the current carried by an electric arc, provided the surroundings can withstand the charge. While low intensity arcs appear in the negative slope region as indicated in Figure 2, the high intensity region shows a rising voltage-rising current behavior and yields much higher temperatures than the low intensity region.

In the arc regions, the discharge is made of

(1) a main current-carrying discharge, named the plasma, which contains, as explained previously, gas particles, electrons and positive ions in equal concentration, hence giving no space charge. If a moderate potential is applied to the plasma, a considerable drift current of electrons will be driven through, accounting for the observed current flow.

(2) plasma boundary regions through which current also passes, the anode and cathode fall regions.

In the cathode fall region of the low intensity arc positive ions move toward the negative electrode, accelerated by a cathode voltage drop of about 10% of the total arc voltage, strike the cathode, and heat it to a temperature of 3,200 - 3,600°K. Electrons are then emitted and they ionize neutral atoms in the cathode fall region.

At the anode, electrons are accelerated by a voltage drop of about 10 to 30% of the total. They strike the anode and heat it to a temperature of the order of 3,600°K. The temperature is hotter at the anode because of the cooling effect of electron emission, conduction and radiation taking place at the cathode. At the anode surface, electrons convene together and form a "space charge" that tends to repel further electrons from entering the anode, unless this barrier is overcome by an additional amount of energy given to the electrons. For attaining steady-state discharge, enough potential drop must be established across this region in order to force additional electrons through the anode fall space. As positive ions also are present near the anode, the negative "space charge" is somewhat neutralized, thus lowering and reducing the high potential drop that would have been necessary, were it not for these ions.

The anode and cathode fall regions extend only a tiny fraction of the distance between the electrodes, the plasma, also termed "positive column" forming the major portion of the arc. It is probable, according to Cobine[(7)] that the cathode-drop thickness is of the order of an electron mean free path, and the potential drop in this region is of the order of the least ionization potential of the gas or vapor in which the arc burns. For carbon cathodes, for which the temperatures are very high under normal operation, the most obvious mechanism for maintaining the current at the arc cathode is thermionic emission of electrons. The high temperature is produced by the energy released by the impinging positive ions which may come from the positive column but probably are produced in the cathode fall region.

Now consider what happens when the current in a low intensity arc is increased to the high intensity region, i.e., when the energy barrier, as explained above, is overcome by a progressive supply of electrical energy. This effect on the appearance of an ordinary carbon arc has been shown by Iwasyk[16] and a good description of anode and cathode is given also in Cobine[7].

In the low intensity arc, the current is such that the arc forms a characteristic crater that just covers the central portion of the anode tip. By increasing the current, the arc crater will now expand over the entire area. A further increase of current will cause the crater to spill over onto the sides of the anode. At this point, radiation and conduction can no more handle the energy losses; this condition corresponds to the transition from the low intensity region and the high intensity region, depicted as point D in Figure 2. The current density goes up, the temperature of the anode tip rises up to a point where disintegration of the anode material may begin. If, for instance, the electrodes are made of carbon, the sublimation point of carbon will be reached (as the anode temperature is limited to the boiling point of the material), and the vaporization rate of the carbon anode will increase notably with the current. This high intensity effect causes a tail flame to appear with an increased intrinsic brillancy. This is due to radiation from vapors at the base of the tail flame and indicates that superheated vapors exist also near the anode.

A main fraction of the arc power input is now being transferred directly to the anode. This intense concentration of energy can heat carbon electrodes so rapidly that they will vaporize instantaneously and the vapors produced will stream away from the surface at high speed. It is not uncommon for this tail flame to extend outward as much as several inches, even though the spacing between the electrodes is of the order of a fraction of an inch. The arc core is a region of intense chemical activity and the temperature is so high that all gases coming through it are mainly dissociated. Suits[(31)], for instance, reports a temperature of 7,400°K at one atmosphere for H_2 gas passed between two carbon electrodes for a current of 10 amp. The temperature also is seen to increase with both current and pressure.

The plasma column of the high intensity arc has, in most cases, a well-defined boundary. The surrounding cold gas acts as a wall to receive diffusing ions and electrons for recombination. It has been found[(31)] that the temperature of the surrounding gas departs very little from the ambient value up to a distance only a few millimeters from the luminous region. Thus, a temperature gradient of the order of several thousand degrees per inch exists in the region immediately surrounding the arc core. A high-temperature gradient is evidently necessary from the Fourier heat-flow equation, for thermal conductivity k and area A

$$\frac{\partial H}{\partial t} = - k\, A \,\frac{\partial T}{\partial r} \qquad (4)$$

because the temperature gradient must be large enough for the outward flow of heat, $\partial H/\partial t$, to be equal to the total electrical energy supplied to the arc.

Heat is lost from the electrodes by conduction through the electrode supports, by convection to the surrounding gas, and by radiation. If the material constituting the electrodes is a relatively poor heat conductor, as carbon, conduction of heat through the solid can be neglected. If in addition the convection loss to the gas is neglected, the entire heat loss per unit area is by radiation, according to the Stefan-Boltzmann law:

$$\text{Heat losses} = \alpha \sigma T^4 \qquad (5)$$

where α is the emissivity of the electrode material relative to a black body (about 0.75), σ is the radiation constant (5.77×10^{-12} watts/(cm)^2(deg)^4, and T is the absolute temperature in °K. Estimates of heat transfer rates to probes placed in plasmas(13) reveal that at least 75% of heat losses are due to radiation.

The temperature of the arc column at atmospheric pressure is sufficiently high for thermal ionization to become an important factor in the maintenance of ionization, according to the Saha equation (Eq. 2). The thermal ionization that maintains the arc column is established by virtue of the high gas temperature, which in turn is established and maintained by the energy given up by the ions and electrons in collision with the gas particles. Of course, the energy of the ions and electrons comes directly from the electric field, or the arc power input. Thus, although the maintenance of the arc column is by thermal ionization, this is only an intermediate process whereby electrical energy is converted into heat.

Operation of the High Intensity Arc

The stability of a high intensity arc depends on a few factors which will be discussed briefly. The type of discharge that results upon spark breakdown of a gap depends upon the shape of the electrodes, the gap, the gas pressure, and the nature of the external circuit. A self-sustained discharge is established only when the conditions of field, pressure, and gap are such that each electron leaving the cathode establishes secondary processes whereby it is replaced by a new electron leaving the cathode.

For a given gas at a fixed pressure and for any given arc length, the conditions of the external circuit establish the voltage and current of the burning arc. The requirement of constant arc length is often hard to fulfill: if an arc burns horizontally, the buoyant forces due to the hot gases will cause the column to arch and thus increase the actual length of the column even though the electrode separation is unchanged. If the arc is struck between vertical electrodes, the hot gas may alter the phenomena at the upper electrode.

A sudden increase in arc voltage due to an increase in arc length may cause the current to decrease to a value less than that necessary for stable operation for so long a period that the arc will be extinguished.

The stability of an arc can be increased by the superimposition of a high-frequency voltage. For welding arcs, using carbon electrodes, a magnetic field produced by a solenoid coaxial to the carbon electrode is sometimes used to stabilize the arc and produce a stirring action in the molten metal which is carrying the welding current.

Measurement of High Temperatures

At present none of the usual temperature measuring devices can withstand temperatures at extreme conditions (7,000°K); investigators had to look for some other ways to find temperatures encountered in plasmas. Although the methods used are somewhat refined, good reliability is claimed with regard to the assumptions involved.

One method relies on equilibrium composition of gases at elevated temperatures. Mollier diagrams for enthalpy-entropy have been issued for a few gases, and they are used to compute the plasma temperature, for argon plasmas for instance[13]. On the other hand, if the equilibrium diagram for a gas or mixture can be calculated reliably as a function of temperatures, then the composition of the gas determines the temperature.

The velocity of propagation of acoustic waves in gases is another way of determining temperatures[34]. Thermodynamic and fluid flow theories are then applied in these cases. The effects of vibrational, dissociative, and radiative relaxation and absorption on the propagation of sound waves provide a means of computing the temperature of a gas. The applicability of acoustic methods is unfortunately limited to special apparatus.

The determination by Dickermann[8] of the equilibrium temperature of a plasma has been obtained by the analysis of the Bolmer series lines in hydrogen. According to the line broadening theory, the plasma temperature is directly related to the spectral line width. The use of Holtsmark theory together with the Saha equation discussed previously provides the necessary relationships to express ion and atom concentrations as a function of temperature.

Assuming that the plasma has no net charge, the excitation energy E_o is related to the number of electrons, n_e (equal to the number of positive ions) by

$$E_o = 2.61\, e\, (n_e\, T)^{2/3} \qquad (6)$$

where e is the ionic charge. Wave lengths and relative intensities of the H_2 Balmer lines are measured, and by choosing a value of E_o that provides for the best fit of experimental and theoretical curves, a temperature is directly matched from the broadening of the Balmer lines.

Results are claimed to be consistent in the temperature range 10,000 to 18,000°K with an accuracy of five percent. This method is applicable to plasmas largely made up of hydrogen, but it is claimed to be suitable for plasmas in which hydrogen amounts to only one percent. Consistent results are expected, provided the total pressure is sufficient to assure a close approach to thermal equilibrium (20 cm Hg or higher).

Spectral methods of broader applications can also be applied to determine temperatures in the range 5,000 to 15,000°K, using the intensities of the atomic lines or of the ionic lines. The latter depends, however, on a shape factor and the work of Pearce[25] should be very useful in that respect, since it lists several tables relating wavelengths and excitation energies to various shape factors for several substances. The spectral methods require again very elaborate apparatus.

In studying high temperature systems by means of the high intensity arc, none of the discussed methods seem practical for temperature measurements, unless temperature determinations are specifically involved. Unfortunately also, the usual thermocouples are unsuitable, even for heat transfer study, because the intense electric field generated by the arc renders such devices useless.

Acetylene Production from Hydrogen and from Methane at High Temperatures

Gas mixtures made up essentially of carbon and hydrogen have been the object of several investigations at high temperatures. Thermodynamics shows that the formation of acetylene, C_2H_2, is favorable at elevated temperatures; the energy to form acetylene thermally from hydrocarbons or carbon and hydrogen must be supplied at high enough temperatures so that the free energy is favorable, as shown in Figure 3 where free energies of formation[(28)] per carbon atom for several hydrocarbons are plotted against temperature [(14, 16)]. The temperature required for acetylene formation decreases as the molecular weight of paraffinic hydrocarbons is increased, though in general it will be above 1,200°K for all hydrocarbons.

To convert any hydrocarbon to acetylene also requires a relatively large amount of energy as indicated in Figure 4 which shows the heats of formation[(28)] of several hydrocarbons[(14, 4)]. Of all hydrocarbons, methane requires the largest amount of energy in order to be converted to acetylene. Under extreme conditions, acetylene production is thus possible.

Arc processes used to react gases formed of carbon and hydrogen date back to 1862 when Berthelot first studied qualitatively the C + H_2 reaction. Bone and Jordan[(5)] reviewed more quantitatively Berthelot's work. They operated a low intensity arc (40 - 60 amp., 160 volts) with two carbon electrodes, using atmospheres of (1) hydrogen, (2) either methane or acetylene, (3) methane and acetylene. When H_2 was used alone, a state of

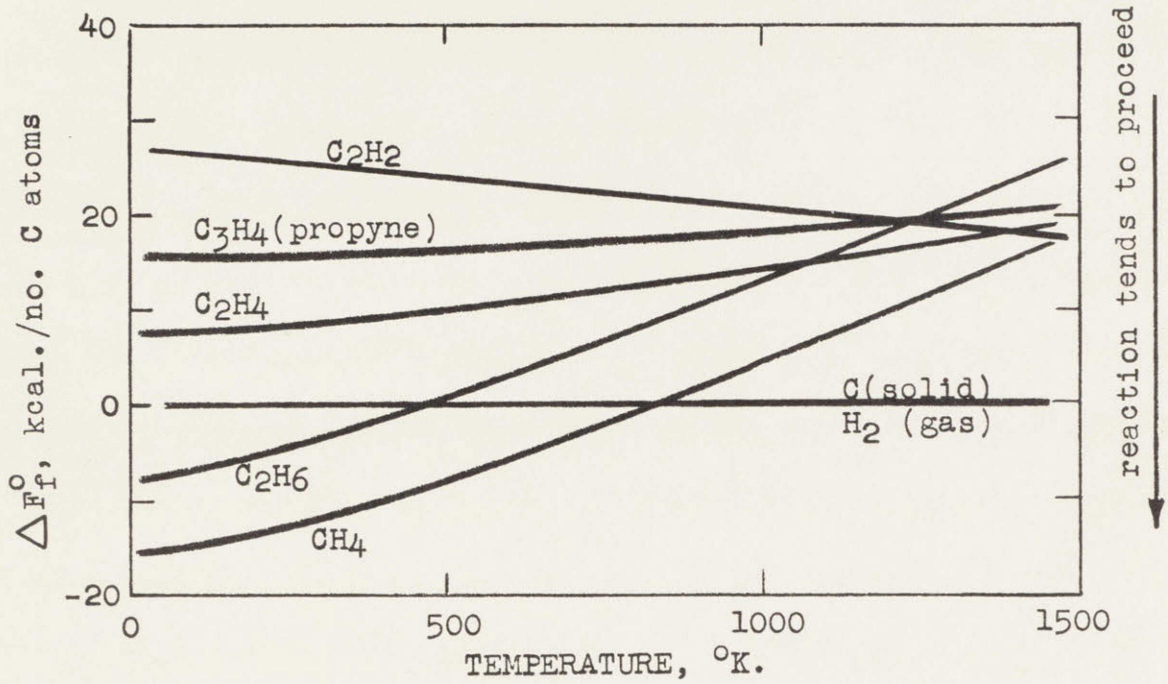


FIG. 3 . Free Energies of Several Hydrocarbons.

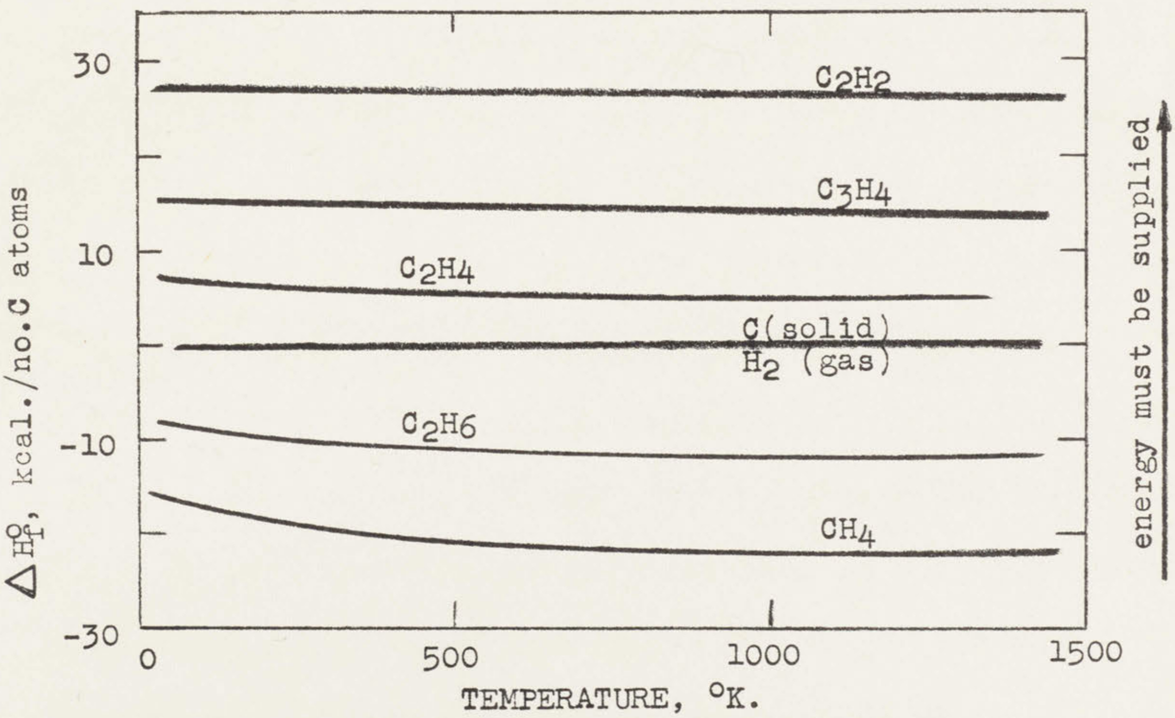


FIG. 4 . Heats of Formation of Several Hydrocarbons.

equilibrium was established between the unconverted H_2 and the CH_4 and C_2H_2 formed; the same state of equilibrium was also reached when either CH_4 and/or C_2H_2 was used under the same conditions. The product gases contained typically about 10% of C_2H_2 and 3% CH_4.

The first successful commercial plant for the production of acetylene by thermal cracking of low molecular weight hydrocarbons was probably the electric arc process of the I.G. Farbenindustrie of the Chemische Werke plant at Huels in Germany. The plant produced about 200 metric tons/day of a 97% acetylene, first from C_2 and C_3 hydrocarbons and later from natural gas. Detailed information on the design and operation of this plant is available as the plant was found to be virtually undamaged after the war. In this process, the product gas from the arc zone qas quenched several feet away by a water spray and contained 16 to 17% C_2H_2.

The synthesis of C_2H_2 directly from C and H_2 has been studied[(32)] at temperatures up to 2,600°C in resistance heated furances, but in this case the acetylene produced did not amount to over 5%. It is also noted in this work that methane formation predominates in the temperature range 1,450 to 2,000°C due to CH, CH_2 and CH_3 radicals forming and recombining to methane, while at temperatures above 2,000°C the amount of C_2H_2 increases upon quenching of the reaction products due primarily to the same radicals which recombine to yield C_2H_2 rather than CH_4.

Plooster and Reed[(26)] have also investigated the carbon-hydrogen system in resistance heated furnaces up to 2,500°C and found good agreement between experimental and thermodynamical equilibrium concentrations of acetylene based on the following mechanism. They postulated acetylene dissociation to go to C, H, CH, C_2 and C_2H radicals; the C_2H radical was explained on the reasoning that the rupture of a carbon triple bond or of two separate double bonds is quite improbable until even higher temperatures are reached, but the rupture of one C-H bond to give $C_2H + H$ should be most likely.

At temperatures of the order of 3,000°K, the following dissociation reactions were postulated:

$$\text{I)}\quad H_2 \rightleftharpoons 2H, \qquad K_1 = p_H^2/p_{H_2} \tag{7}$$

$$\text{II)}\quad 2C + H_2 \rightleftharpoons C_2H_2, \qquad K_2 = p_{C_2H_2}/p_{H_2} \tag{8}$$

$$\text{III)}\quad C_2H_2 \rightleftharpoons C_2H + H, \qquad K_3 = p_H p_{C_2H}/p_{C_2H_2} \tag{9}$$

The partial pressures of the species are then related to the total pressure by Dalton's law

$$P = p_{H_2} + p_H + p_{C_2H_2} + p_{C_2H} \tag{10}$$

Three possible recombination reactions are assumed to occur upon quenching:

$$\text{IV)}\quad H + H \longrightarrow H_2 \tag{11}$$

$$\text{V)}\quad C_2H + H \longrightarrow C_2H_2 \tag{12}$$

$$\text{VI)}\quad C_2H + C_2H \longrightarrow C_4H_2 \text{ (diacetylene)} \tag{13}$$

but, according to kinetics, diacetylene formation should be very small.

The free energies of formation of the C_2H radical were theoretically calculated up to 3,500°K, taking into account estimation of interatomic bond to bond distance and frequencies of vibration of the molecule.

Experiments carried out up to 3,000°K seem to verify this assumption regarding the C_2H radical, but the evidence is not clear cut since the maximum acetylene concentrations found were of the order of 5 or 6% and the data were widely scattered.

Following Plooster and Reed's theory concerning the C_2H radical and quenching mechanism, Iwasyk[(16)] calculated the thermodynamic equilibrium diagram of the $C + H_2$ system from 2,500 to 4,500°K. At one atmosphere pressure and for a carbon to hydrogen ratio of unity, his calculations showed that a maximum concentration of C_2H_2 equal to 34% could be obtained at the sublimation point of carbon determined as 3,750°K. However, if the radical C_2H was not taken into account, only 14% C_2H_2 could be obtained. Among the species assumed to be present in the high temperature region were C_1, C_2, C_3, C_2H, C_2H_2, H_2, and H.

Figure 5 shows the results of calculations based on the scheme used by Iwasyk to evaluate the composition of the carbon-hydrogen system. Note that two values of ΔH°_{of} for C_2H were used, since at the time, this was a major element of uncertainty, as pointed out by Plooster and Reed.

Figure 6 indicates the maximum concentration of acetylene that

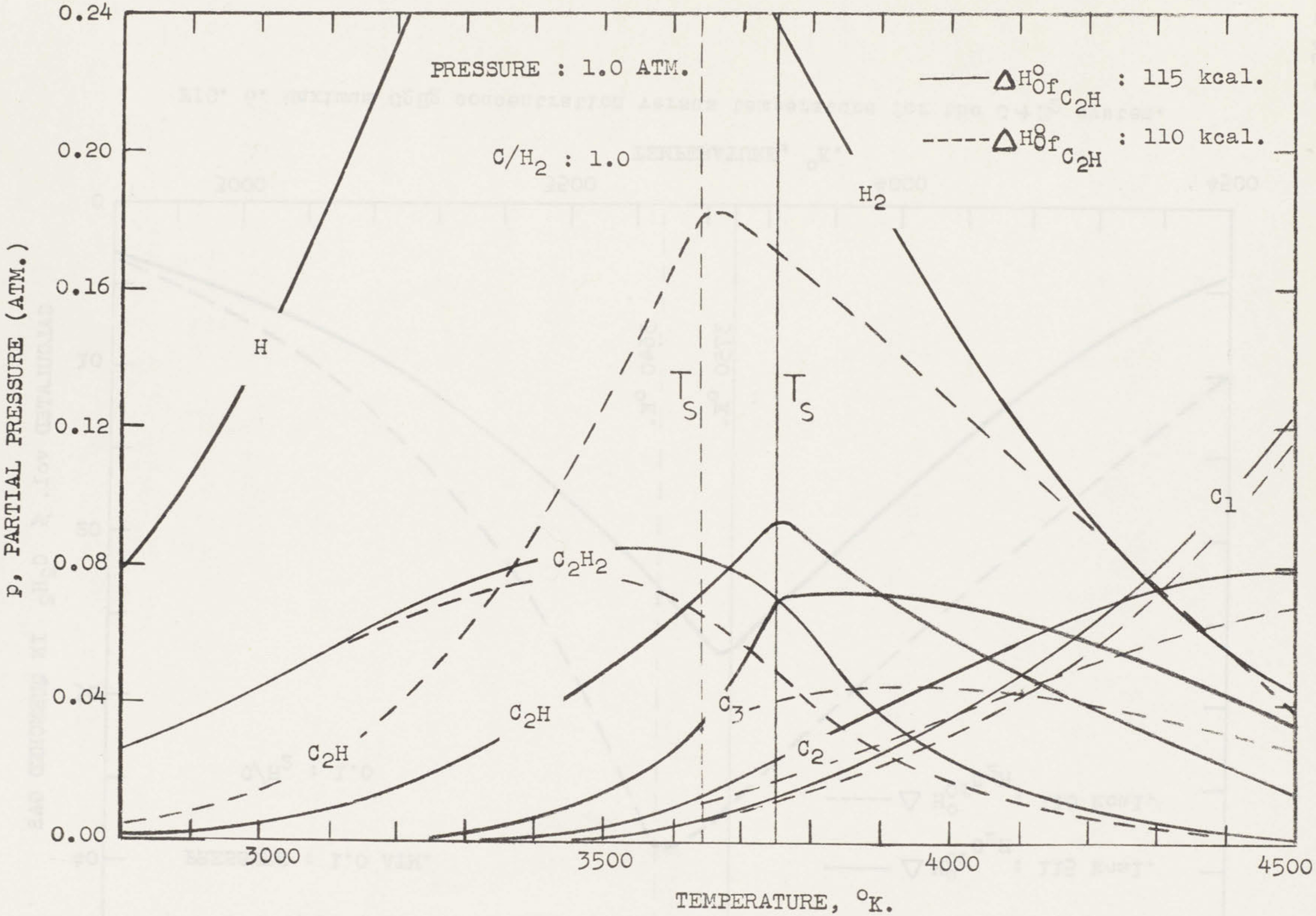


FIG. 5. Equilibrium Composition of the C + H_2 System, C_2H considered.

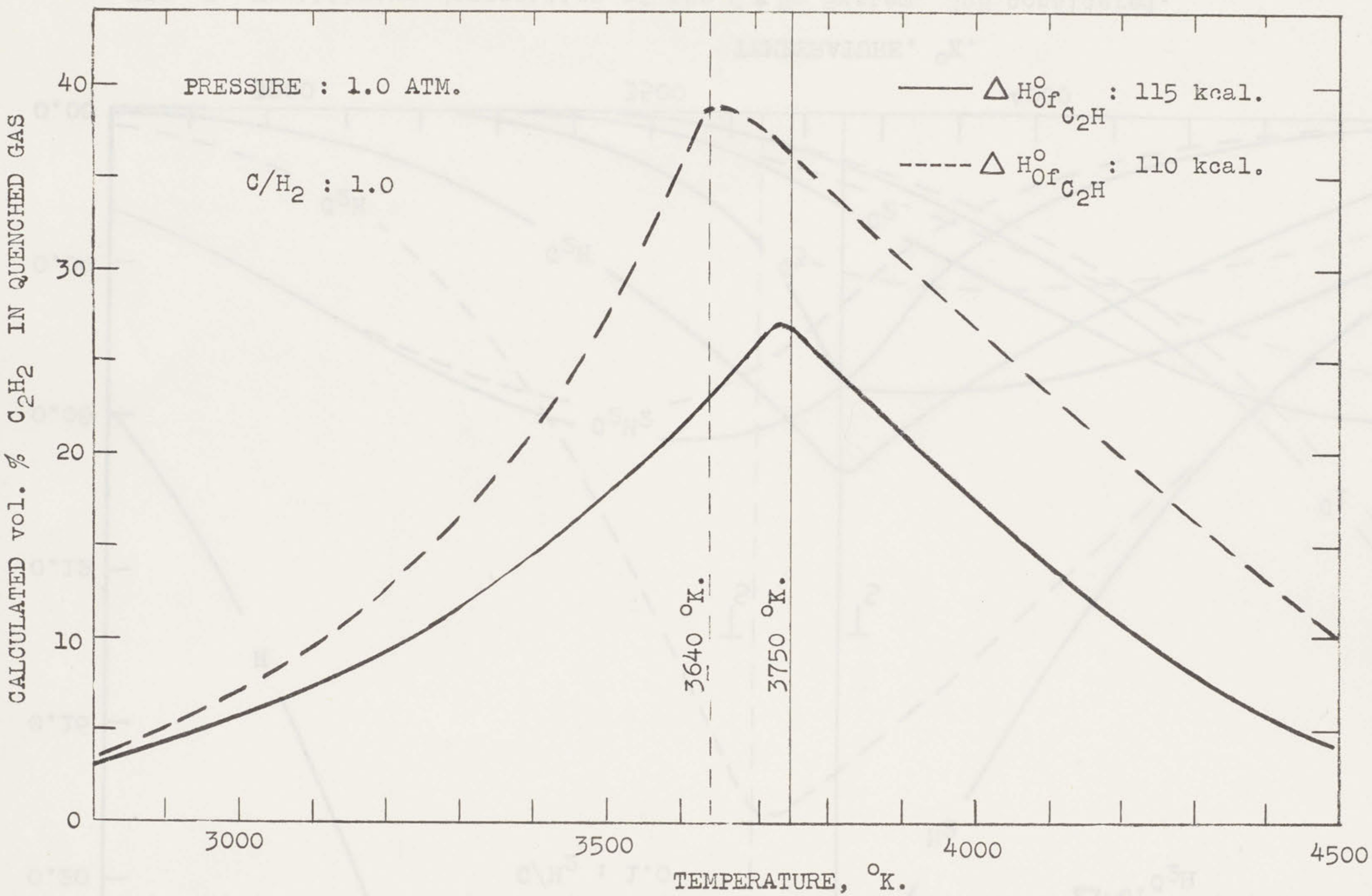


FIG. 6. Maximum C_2H_2 concentration versus temperature for the $C + H_2$ system.

can be obtained at various temperatures following a perfect quench of the high temperature gas and assuming the gas to yield only C_2H_2 and H_2. Calculated values related to these two graphs appear in Tables A-1 and A-2 of Appendix A. The equilibrium diagram and the quenched C_2H_2 concentration are largely dependent on the value assigned to the heat of formation of the C_2H radical, as indicated in the two graphs. Also the calculated sublimation point of carbon is different for both values used in the calculations, the heterogeneous region lying at the left of the sublimation point and the homogeneous region at the right.

The above equilibrium determinations are nevertheless limited in that they consider only one carbon to hydrogen ratio, $C/H_2 = 1.0$, whereas it is not only probable but also very likely to take lesser or greater ratios.

However experiments directed to C_2H_2 production and carried out in a high intensity d.c. arc added evidence to the formation of C_2H radicals and to the quenching mechanism of Eqs. 11 and 12, since as high as 18.6% C_2H_2 was obtained at one atmosphere and 23.8% with 66.7% helium diluent. These results are two or three times higher than any previously reported in the literature for reactions between the elements.

In a recent paper, Eremin et al.[(12)] report the results of their study on the electrocracking of methane in a low intensity a.c. arc to produce acetylene. It was shown that the quantity of methane reacted per unit of energy consumption in the initial period of the reaction was practically independent of the geometric dimension of the discharge, of the current density, of the power and of the amount of dilution of the initial CH_4 with H_2, but it was found to be influenced by pressure, decreasing with an increase of pressure. However, the final concentration of acetylene in the output gas did not reach more than 17% for power input ranging from 0.5 to 4 kw in a high voltage (2,000 volts) arc. The kinetics of methane reaction to yield $C_2H_2 + H_2$ and simultaneously to degrade to $C + H_2$ were also analysed as a function of methane flow rate and power requirement of the cracking reaction.

In a patent issued to H. M. Weir[35], a process is disclosed for making acetylene in an electric arc and data for treating each of the four simplest aliphatic hydrocarbons in order to yield product gases with 12% C_2H_2 by volume arc presented. The invention is also related to the case where carbon particles are passed repeatedly through an arc and present a relatively large surface for reaction with hydrogen coming from either pure gas or excess H_2 by cracking of hydrocarbons.

Molecular fragments likely to occur upon treatment of hydrocarbons such as methane were assumed to be CH, CH_2, CH_3, C, and H. Acetylene is said to result only from breakdown to C, H, and CH, and when the high temperature zone of the arc is increased by high temperature heat transport by solid particles this drastic breakdown of the original molecules is sensibly increased. The end result would be a greater production of C_2H_2 with the same input of electrical energy. Also with the addition of solid carbon particles, forming extended surfaces of reactive material and contacting the atomic hydrogen derived from the feed, acetylene is formed in amounts substantially exceeding those theoretically possible only by cracking of hydrocarbons where no carbon other than that from the gas is available.

The main products of the process consist chiefly of H_2, unreacted feed gas and C_2H_2, whereas side reaction products such as methyl acetylene, vinyl acetylene and diacetylene are also found.

Processes using carbon electrodes, C_2H_2 manufacture from H_2 and from mixtures of H_2 and hydrocarbons with recycling of H_2 are also disclosed in the patent. It is stated, however, that the net yield of C_2H_2 from any arc process depends critically on the effectiveness and speed of cooling the product gas stream to temperatures well below the range of rapid decomposition. No C_2H_2 concentration larger than 12% is nonetheless disclosed.

In a recent study of plasma yet, Leutner and Stokes [(22)] mixed carbon powder to the high temperature stream of an H_2 plasma jet; considerable soot formation was experienced and it was argued that the quench was not fast enough to prevent decomposition of the acetylene formed to carbon and hydrogen. Another experiment using an argon plasma jet was successful in bringing about 80% yield of C_2H_2 when CH_4 was fed into the flame of the jet and contained in a graphite insert. The limit of C_2H_2 concentration was only 20%.

Anderson and Case[1] made a detailed study of the cracking of methane at temperatures of the order of 1,000 to 2,000°K. Theoretically, they applied thermodynamic and kinetic data to predict quantitatively the results that could be obtained by mixing the hot hydrogen from a plasma torch with cold methane and subsequently quenching the mixture. Experiments which were found to agree very well with the theory showed that a mixture providing a temperature between 1,700 and 2,000°K could produce 80 to 90% yield with minimum energy requirement. It was also found that mixing (not instantaneous) and the speed of quenching were not important for the cases considered. Acetylene concentration greater than 22% were not obtained; the optimal experimental values of C_2H_2 yield, C_2H_2 concentration and energy requirement were 76%, 15%, and 370,000 B.t.u./lb. mole C_2H_2 respectively.

The latest developments regarding acetylene production at high temperatures involve processes using hydrogen dilution[20] which yield approximately 7% C_2H_2 at a reactor temperature of 1,700°K and processes using partial oxidation[14] which provide the heat necessary to crack unreacted hydrocarbons with C_2H_2 output of about 6.5%. An analysis of the kinetics of the partial oxidation process has been reviewed extensively by Leroux and Mathieu[21]. According to their study it is possible to calculate with a fair accuracy the performances of a partial oxidation burner using basic kinetic data, assuming that the cracking process follows the combustion process and that the combustion leads to equimolar quantities of CO and H_2O. The mechanisms of methane pyrolysis, ethane, ethylene, and acetylene formation, acetylene polymerization and oxidation by water vapor are set forth and the velocity constants are calculated from the results of experiments. However, a C_2H_2 concentration of only 15% seems possible from these processes.

From an economic standpoint, a summary of costs for producing acetylene by the electric arc, direct pyrolysis and partial oxidation processes has been prepared recently by Lobo[(23)].

III. APPARATUS AND PROCEDURE

In order to carry out the reactions of carbon vapors with hydrogen and with methane, a special reactor was built. A modification of the basic design originated by Iwasyk[2, 16] was used. The reactor consisted of four parts as pictured in Figure 7.

(a) The anode holder section and the screw drive mechanism (not shown) for the anode feed have been left unchanged from Iwasyk's reactor. The plunger assembly was machined at one end to receive threaded carbon anodes and thus provide good electrical contact. Three O rings made a good seal between the inside walls of the anode holder pipe and the plunger assembly. Reactant gas could be fed through either the anode holder flange or through hollow anodes.

(b) The main reactor shell was made of a 3 1/2 in. i.d. steel pipe with 1/4 in. walls and it was cooled by water flowing through three copper coils wrapped around the outside walls; a rectangular window covered with a Vycor glass plate and a dark blue glass plate was cut in the main shell to allow observation of the arc and to permit visual control of the anode feed. Radiation shields made of graphite were placed around the arc zone and in the window cut-out to reduce heat losses to the reactor walls and internal stresses to the Vycor glass. The main reactor shell contained anode and cathode, and also the sampling probe as seen in Figure 7.

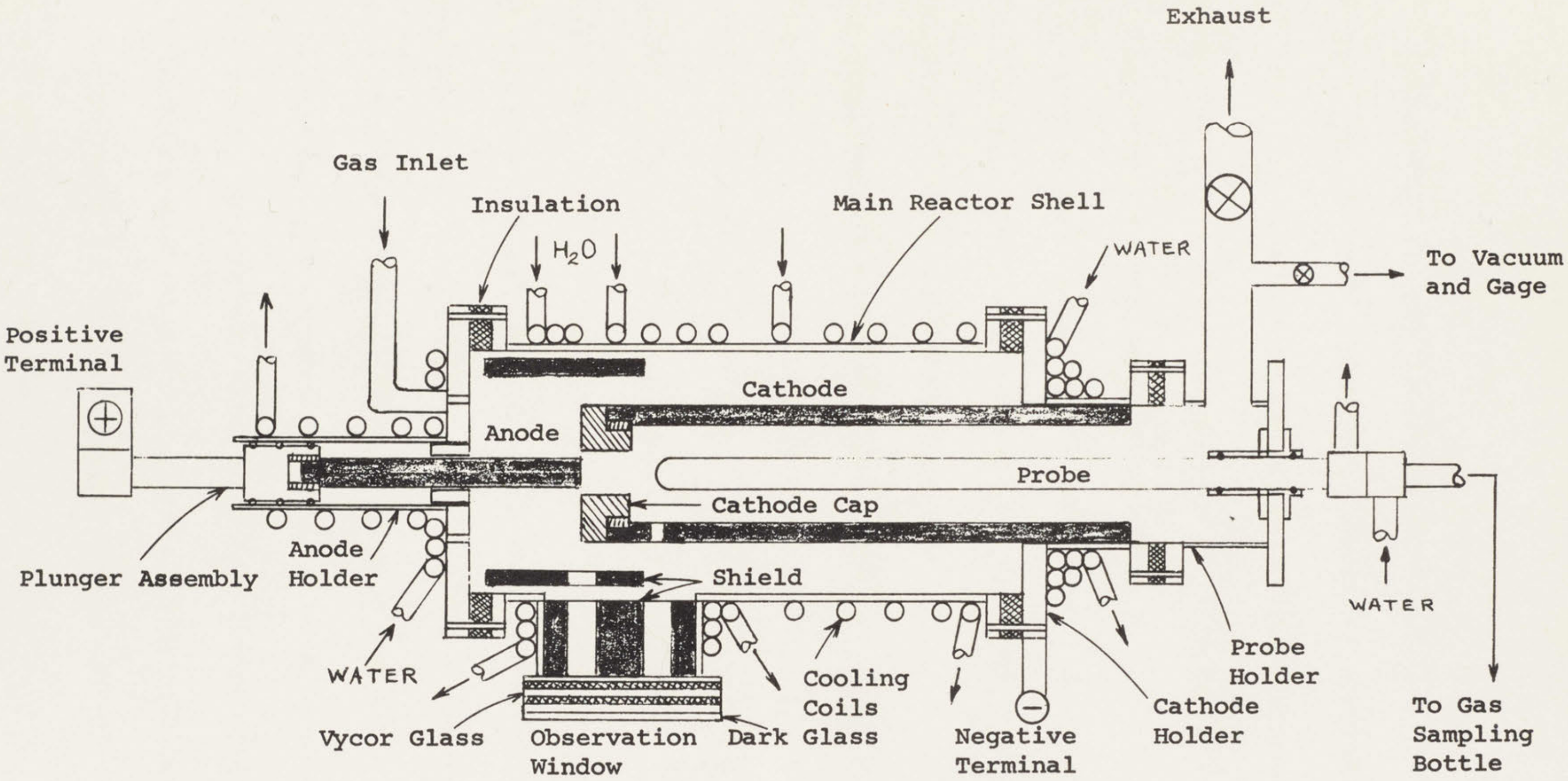


FIG. 7. Details of the Experimental High Temperature Arc Reactor

(c) The cathode holder section was also made of a single brass pipe 2 1/2 in. o.d. with one cooling coil wrapped closely around the exterior. The cathode was forced in the inside cylindrical chamber to provide good electrical contact through the holder material.

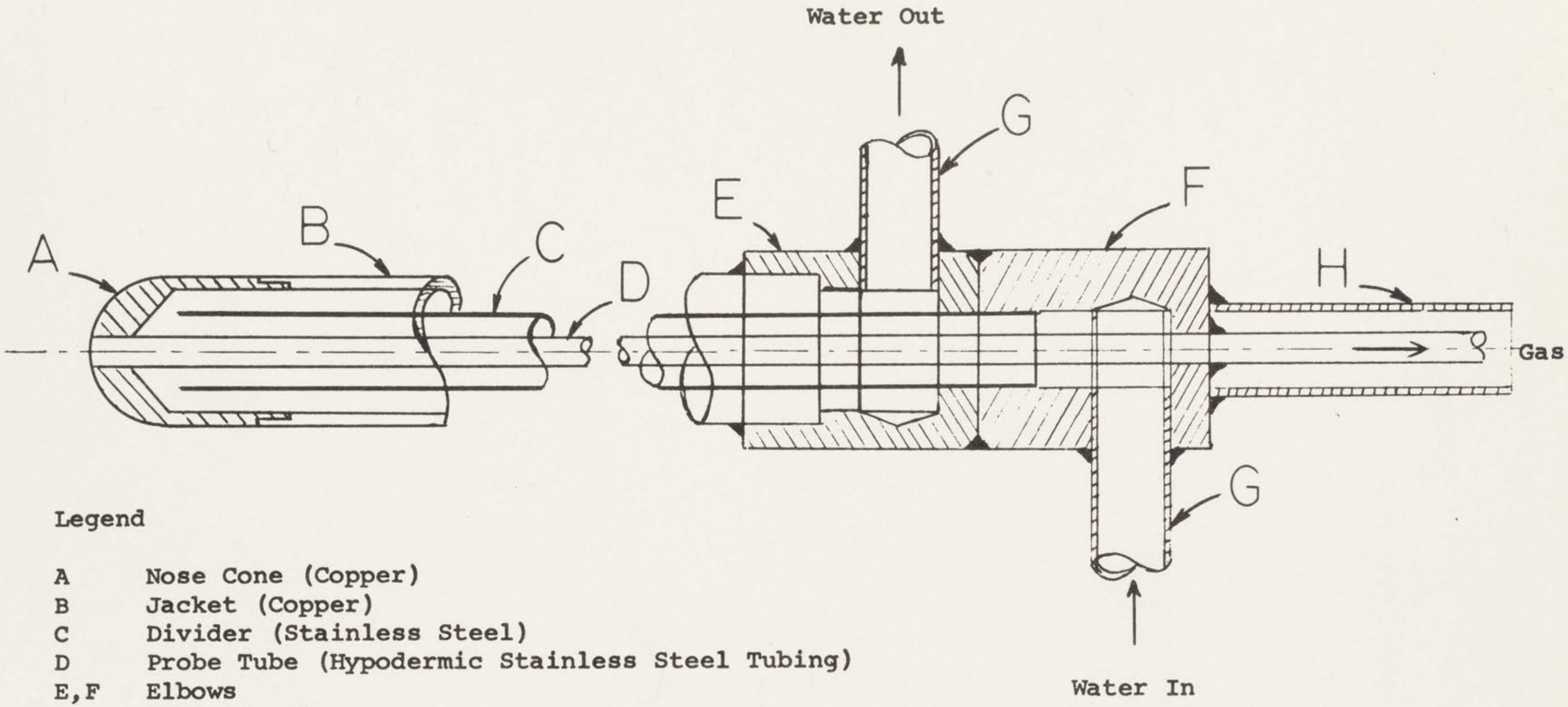
(d) A probe holder section was added at the back of the cathode holder to isolate electrically the probe from the cathode section and thus prevent arcing between the anode and the probe, should the probe have been positioned too close to the arc zone. This section also contained the exhaust line from the reactor and an inlet for vacuum and pressure gage.

The reactor was placed in an area containing two blow windows and surrounded by a barricade made of steel plate. Operation of the reactor was made by remote controls.

Anodes were 1/4 and 3/8 in. o.d. graphite electrodes; cathodes were made from a 1 1/2 in. to 2 in. o.d. solid graphite rod through which a one in. center hole was bored. One end was threaded in order to accept screwed-on graphite caps and this feature allowed quick and easy replacement of the cathode part which became partially blocked with carbon deposits after a run.

Electrical insulation was provided by means of thick Teflon and rubber gaskets with plastic washers for preventing electrical contact between any two parts of the reactor through the screws that held them together.

The probe was inserted through a special fitting containing two rubber O rings that made a good seal and permitted easy sliding



Legend

A	Nose Cone (Copper)
B	Jacket (Copper)
C	Divider (Stainless Steel)
D	Probe Tube (Hypodermic Stainless Steel Tubing)
E,F	Elbows
G	Water Supply
H	Protector Tube

FIG. 8. Details of the Sampling Probe

of the probe for proper positioning before each run. In most of the runs the probe was kept close to the arc reaction zone, the closest practical distance without experiencing probe failure being one-half in. The sampling probes were made of three concentric tubes. Details of construction may be seen in Figure 8. The inner tube consisted of a stainless steel hypodermic needle with inside diameter varying from 0.043 to 0.135 in. where the hot gases from the arc zone were quenched in a few milliseconds[(16)]. A middle tube, made of copper or stainless steel, divided the water flow. The outside shell was made of a copper tube, either 5/16 or 3/8 in. in outside diameter. Two special elbows directed the water flow in and out the probe. All parts were silver soldered for resistance to high temperatures.

A 5 h.p. pump provided cooling water to the three coils wrapped around the main reactor shell and to the coil encircling the cathode holder; the four parallel combination circulated 7 gpm at 200 psi while an independent 1 h.p. pump forced water through the probes at a rate of 0.3 to 1.5 gpm under 125 psi.

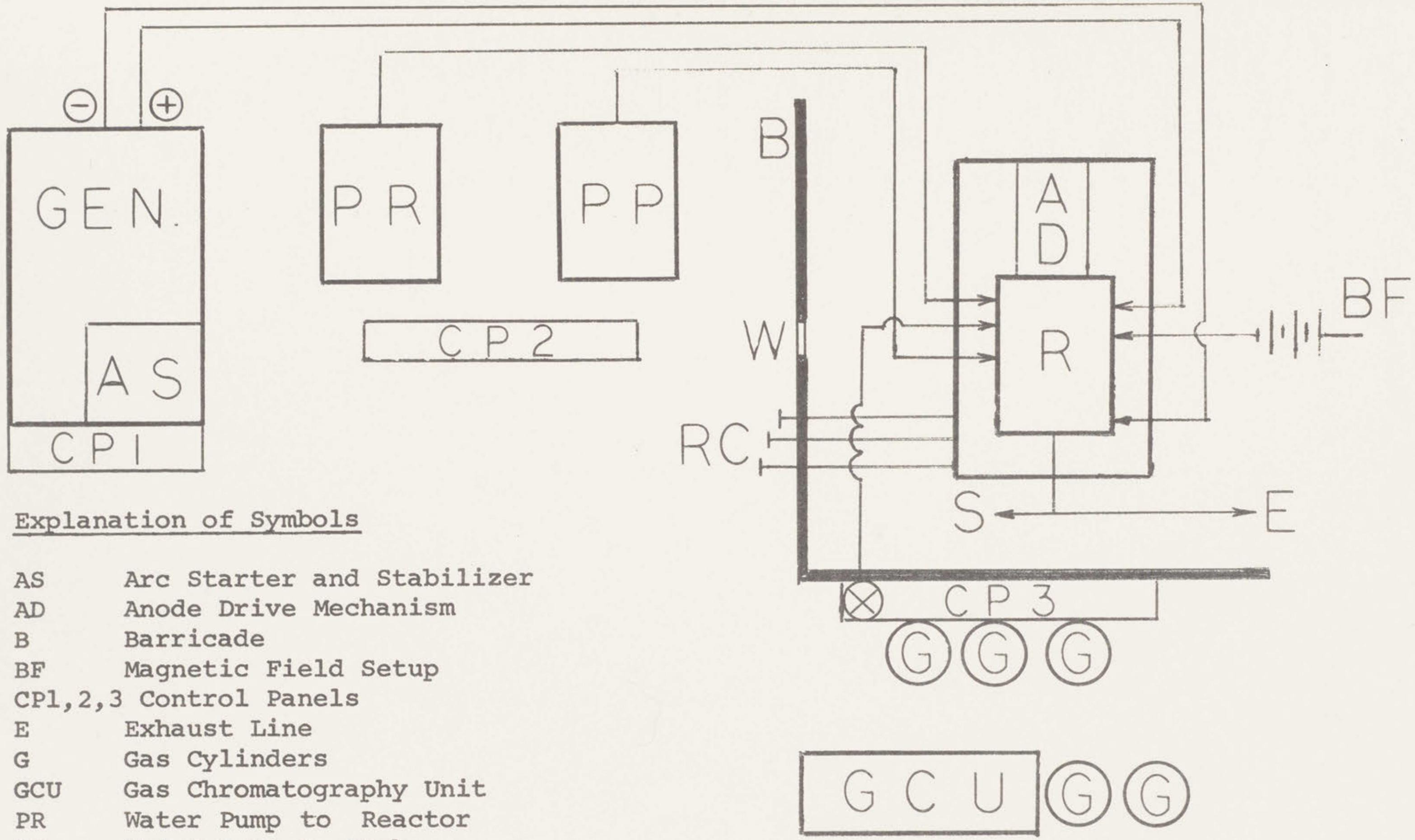
A coil of No. 24 enameled copper wire was also wrapped around the reactor over a 1 in. portion at the reaction zone. Direct current passing though this coil generated a magnetic field at a right angle to the electron path, providing a swirling action for mixing the hot gases. The magnetic strength was about 70 gauss. Considerations regarding the choice of this value are discussed in details in Appendix F. Power for this circuit was furnished first by four 6 volt batteries in parallel which were changed later on to a regulated d.c. power supply.

Power to the arc was provided by two Lincoln welding generators hooked in series and capable of delivering 30 kw to the electrodes. A Miller arc starter and stabilizer was used in series with the generators.

A gas collecting system completed the experimental set-up. It consisted of 125 ml gas sampling bottle connected to either a vacuum or the sampling probe by means of a three-way stopcock. Gas analyses were performed with a Perkin Elmer gas chromatography unit model 154. Calibrations of the chromatograph are shown in Appendix G. The layout of high temperature facilities is presented in Figure 9.

To perform an experiment, the procedure consisted in assembling the reactor with proper positioning of the probe, inserting the consumable anode through the anode holder and adjusting the gap between the electrodes by viewing through the window. The anode feed rate was then set according to the power input from the generators. Vacuum was then applied to the reactor to remove the air, gas flow (H_2 or CH_4) was started, followed by cooling water flow. A small fraction of the feed gas was directed through the probe for purging and preventing the probe from plugging before a gas sample of the arc zone was withdrawn.

Power was then applied to the electrodes and the arc starter and magnetic field switched on. When the arc struck between the



<u>Explanation of Symbols</u>

AS	Arc Starter and Stabilizer
AD	Anode Drive Mechanism
B	Barricade
BF	Magnetic Field Setup
CP1,2,3	Control Panels
E	Exhaust Line
G	Gas Cylinders
GCU	Gas Chromatography Unit
PR	Water Pump to Reactor
PP	Water Pump to Probe
R	Reactor
RC	Remote Controls
S	Sampling Line
W	Window

FIG. 9. Layout of High Temperature Facilities

electrodes, the anode feeder was started, and the vacuum was left on a sampling bottle. Just prior to withdrawal of a sample, the purge flow was stopped, the probe line evacuated and the sampling bottle under vacuum was connected for about 2 seconds with the reaction zone via the quenching probe.

After a run, the reactor was purged with helium before disassembling and the sample taken to the vapor chromatography unit for analysis.

Various views of the equipment can be seen in Pates I to VIII.

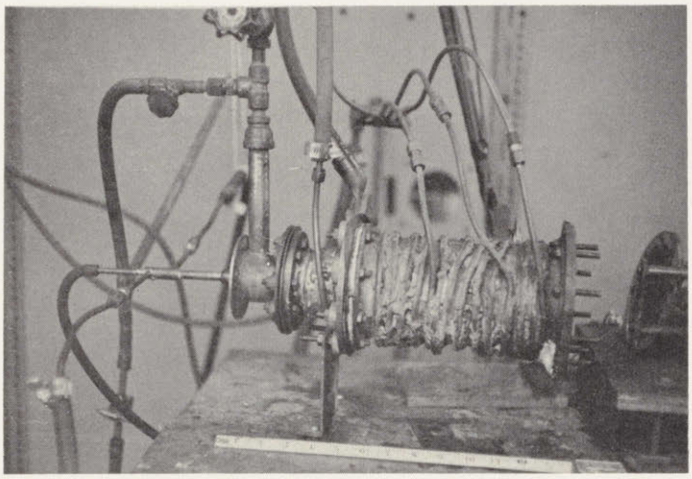


Plate I. View of the inserted probe, probe holder with pressure and exhaust lines, cathod holder and main reactor shell with cooling coils. At far right, part of the anode holder.

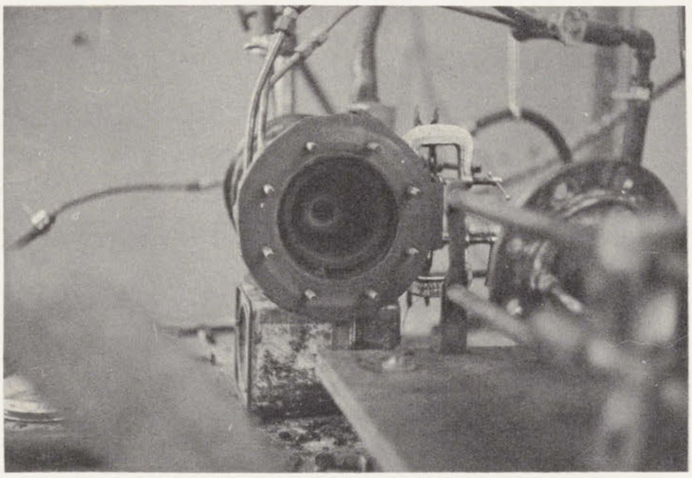


Plate II. Open end view of the reactor. Rubber insulation gasket, graphite radiation shield and cathode pipe can be seen. Note the grayish color of the cathode end, which showed after several runs.

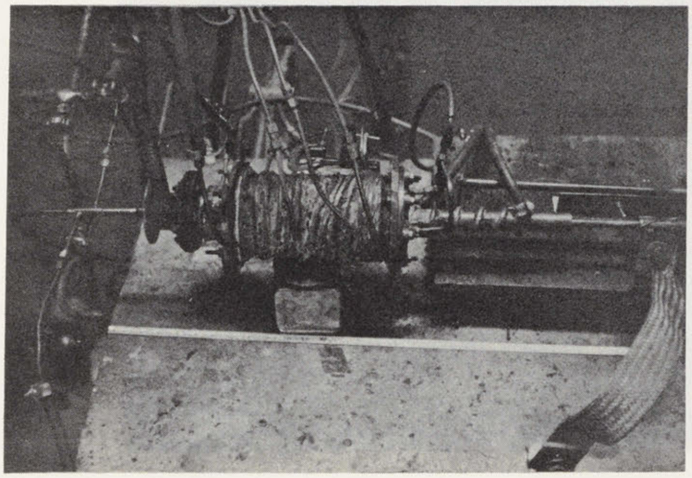


Plate III. Overall view of the assembled reactor. At far right, electrical connection to the plunger assembly of the anode holder.

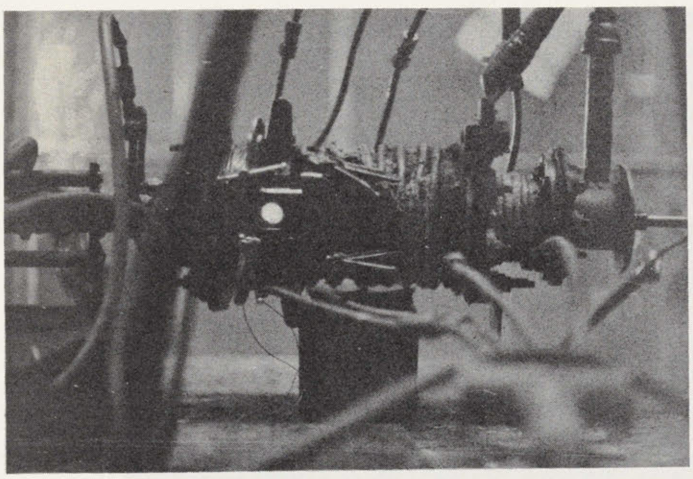


Plate IV. View of the window side of the reactor with the arc running

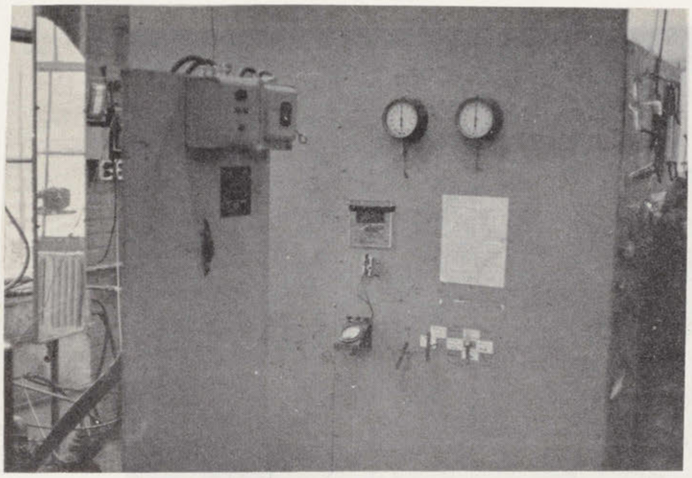


Plate V. View of the pump panel controls (left) and barricade. Pressure and vacuum gages, remote controls, ammeter for the magnetic field circuit and observation part are located on the barricade.

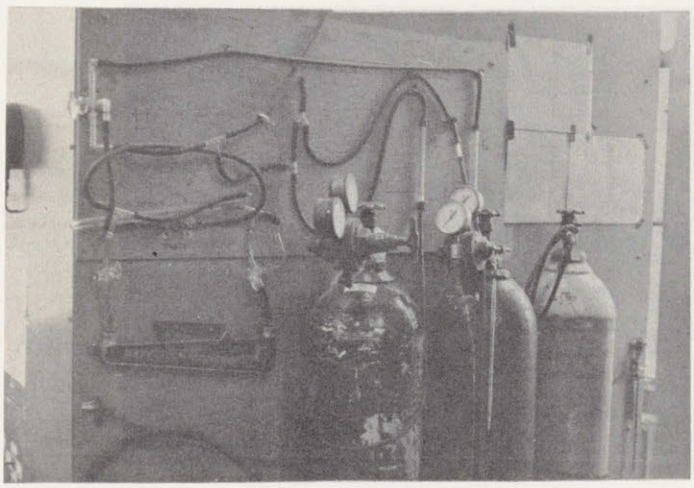
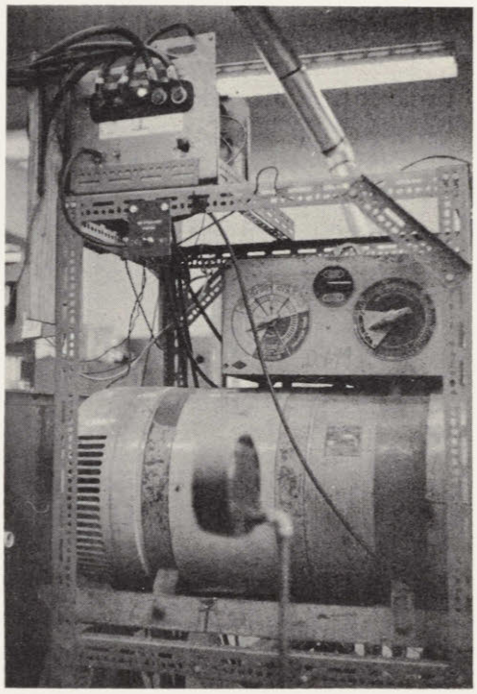


Plate VI. View of the gas supply and distribution system. The inclined draft gage controls the purge flow to the probe.

Plate VII. View of one generator with the Miller arc starter located at the upper left corner.



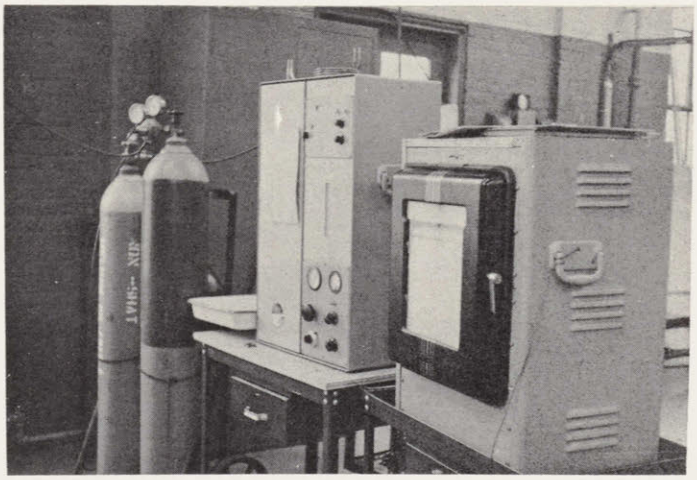


Plate VIII. Gas chromatography unit : carrier gas supply, Perkin Elmer fractometer and chart recorder.

IV. RESULTS & DISCUSSION OF RESULTS

(1) Theory

One objective of this thesis was to analyse thoroughly the carbon-hydrogen system at high temperatures and extend the work of Iwasyk[2, 16] who considered theoretically only one C/H_2 ratio. It is known[19] that the output of C_2H_2 from carbon-hydrogen reactions increases with the C/H_2 ratio, but there is no indication in the literature of the quantitative effects of increasing the C/H_2 ratio on C_2H_2 production. Also, only the simple cracking of methane has been analysed[1, 12, 22], and reactions of carbon vapors with CH_4 have not yet been considered.

Carbon-Hydrogen Reactions

Reliable thermodynamic data for C-H compounds at temperatures above 1,500°K are almost nonexistent in the literature[28]. To estimate thermodynamic data in the high temperature range where measurements have not been made, two techniques are commonly used. In one, low temperature data are extrapolated to a higher range. In the other, the data are based on estimates of interatomic distances and vibrational energies of the molecules. The first method may give erroneous values because of the uncertainty involved in extrapolating to a region where no data exist whereas the second is still only approximate because of the assumptions involved[3, 19, 26]. Spectroscopic data, such as those reported by Drowart[11] and Chupka[6], taken at high temperatures are needed in order to provide more reliable values of thermodynamic properties of species containing carbon and hydrogen.

Kroepelin and Winter[19] studied theoretically the carbon-hydrogen system between 2,000° and 6,000°K but failed to consider the existence of radicals of the general form C_xH which were found to be important at high temperatures. In particular, Plooster and Reed[26] and Iwasyk[2, 16] postulated the C_2H radical as precursor to C_2H_2 and the work of Bauer and Duff[3] points to an equally high concentration of C_3H and C_4H radicals at high temperature.

After careful examination of the available data at high temperatures, it was assumed that, under equilibrium conditions, a reacting mixture of solid carbon, C_s, and hydrogen at 3,000 to 4,000°K would probably consist predominantly of C_1, C_2, C_3, H, H_2, C_2H_2, C_2H, C_3H, C_4H, CH, CH_2, and C_4H_2. Of the polyatomic forms of carbon vapor, only species containing from one to three atoms of carbon are important at high temperatures[11]. Dissociation of hydrogen gas occurs between 2,000 and 6,000°K, while ionization begins around 8,000 to 9,000°K. The C_4H_2 molecule (diacetylene) was included because recombination of C_2H radicals[30] or reaction of C_2H with C_2H_2[21] can produce C_4H_2. The presence of the C_2H radical is further supported by the spectroscopic work of Chupka[6] and theoretical considerations by Marynowski[24]. A recent analysis[3] indicates that CH_2 and CH may become significant above 4,000°K.

Calculations of the equilibrium composition of the carbon-hydrogen system in both the heterogeneous and homogeneous regions have been performed on the IBM 7090 computer at the M.I.T. Computation Center, taking into account the twelve species listed above. The whole computer program appears in Appendix A.

For the heterogeneous region, the following reaction scheme was adopted:

$C_s \longrightarrow C_1$	(K_1)	(14)
$2\ C_s \longrightarrow C_2$	(K_2)	(15)
$3\ C_s \longrightarrow C_3$	(K_3)	(16)
$2C_s + H_2 \longrightarrow C_2H_2$	(K_4)	(17)
$H_2 \longrightarrow 2\ H$	(K_5)	(18)
$C_2H_2 \longrightarrow C_2H + H$	(K_6)	(19)
$3\ C_s + H \longrightarrow C_3H$	(K_7)	(20)
$4\ C_s + H \longrightarrow C_4H$	(K_8)	(21)
$2\ C_2H \longrightarrow C_4H_2$	(K_9)	(22)

For the homogeneous region, the following reactions were involved:

$H_2 \longrightarrow 2\ H$	(K_5)	(18)
$C_2H_2 \longrightarrow C_2H + H$	(K_6)	(19)
$2\ C_2H \longrightarrow C_4H_2$	(K_9)	(22)
$C_3 \longrightarrow C_2 + C_1$	(K_{10})	(23)
$C_2 \longrightarrow 2\ C_1$	(K_{11})	(24)
$C_2 + H_2 \longrightarrow C_2H_2$	(K_{12})	(25)
$C_3 + H \longrightarrow C_3H$	(K_{13})	(26)

$$C_2 + 2\ C_1 + H \longrightarrow C_4H \qquad (K_{14}) \tag{27}$$

$$C_1 + H \longrightarrow CH \qquad (K_{15}) \tag{28}$$

$$C_1 + 2\ H \longrightarrow CH_2 \qquad (K_{16}) \tag{29}$$

Values of the free energy functions, on the enthalpy of formation for various components in the ideal state and of the calculations leading to the equilibrium constants for these reactions as calculated by the method of Bauer and Duff[3] are given in Tables A-4, A-5, A-6, and A-7 of Appendix A. The basic constants for these calculations based on estimates of interatomic distances and vibrational energies of the molecules are also given in Table A-3 of the same Appendix, together with a reference list of all the sixteen chemical reactions examined.

In the heterogeneous region, the sum of the partial pressures of various components must equal the total pressure. In the homogeneous region, besides this condition, the carbon to hydrogen ratio must remain the same throughout the whole temperature range, thus involving a rearrangement of the various species over this range.

The solution of the first system of equations results in a quadratic equation with the partial pressure of H atoms to be determined, from which all other component concentration can be easily derived. The homogeneous system gives two quadratic equations that must check simultaneously, a situation most efficiently handled by a computer. A detailed explanation of the computer program leading to the determinations of the equilibrium composition at high temperatures is discussed in Appendix B, and results of the calculations are presented in Table B-1 for the heterogeneous region and in Table B-2 for the homogeneous region at various C/H_2 ratios and total pressures.

The results of such calculations are also presented in graphical form in Figs. 10 to 18 inclusively, for the heterogeneous region (Fig. 10) and for C/H_2 ratios of 0.5, 1.0, 2.5, 5.0, 7.5, and 15.0 (Fig. 11 to 16 inclusively) at one atmosphere pressure. The influence of pressure is shown in Fig. 17 and 18, which are plotted for a pressure of 0.1 and 10.0 atmospheres respectively at a C/H_2 ratio of 5.0. Note that $C/H_2 = 0.5$ would actually correspond to pure methane feed, but CH_4 is practically nonexistent above 2,000°K and is not taken into account in these calculations.

On these plots, the dashed line represents the sublimation temperature for the particular carbon to hydrogen ratio, i.e., the maximum temperature at which solid carbon exists and the temperature at which the homogeneous region begins. For any carbon to hydrogen ratios, those portions of the curve which lie in the heterogeneous region coincide. Although CH and CH_2 were not considered in the calculations of the heterogeneous region (see Table B-1), they were included in the above graphs by reference to the work of Bauer and Duff[3]. Since their concentrations are small, they do not influence the overall results in the heterogeneous region, CH and CH_2 were however taken into account in the homogeneous region.

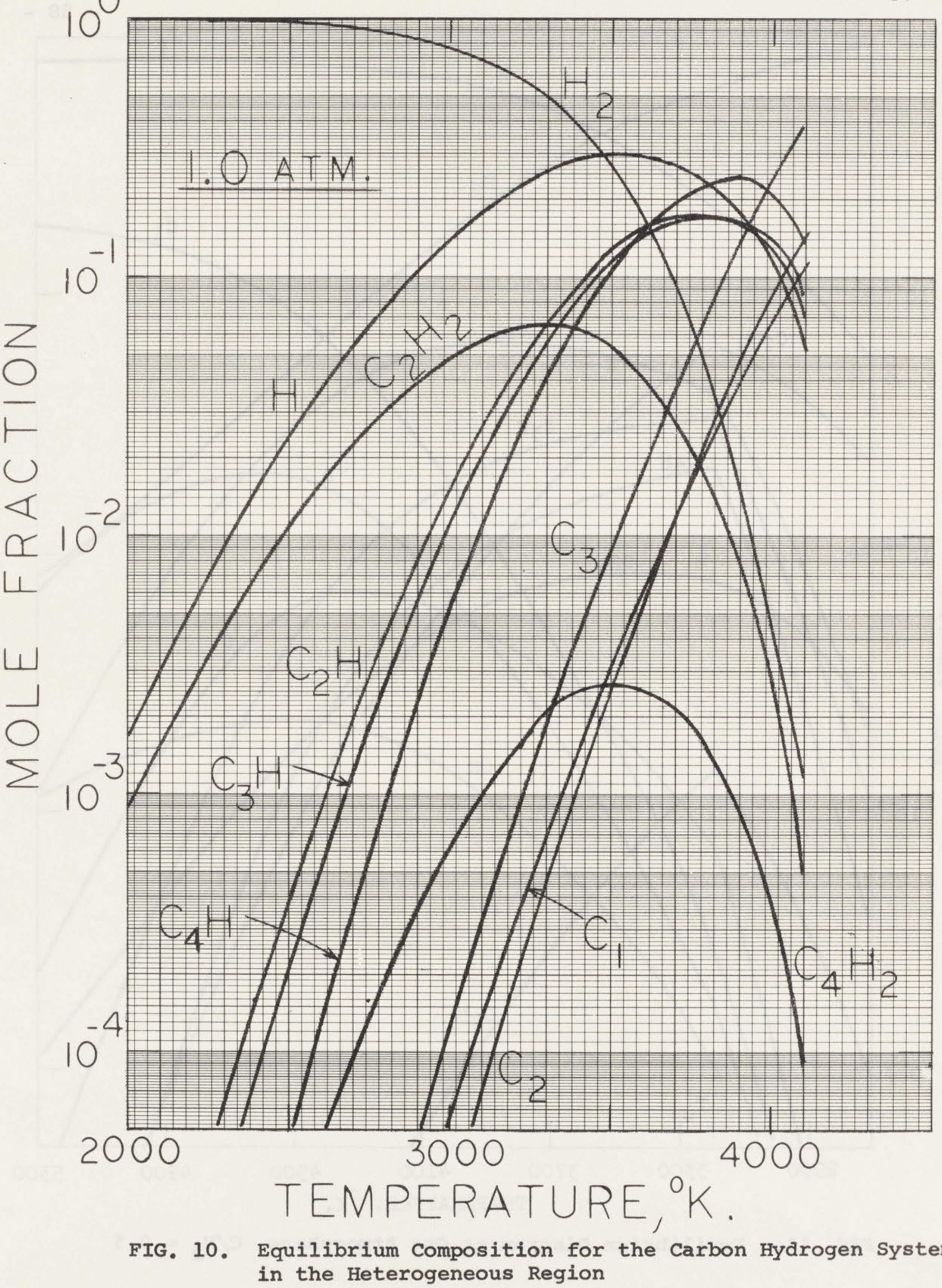


FIG. 10. Equilibrium Composition for the Carbon Hydrogen System in the Heterogeneous Region

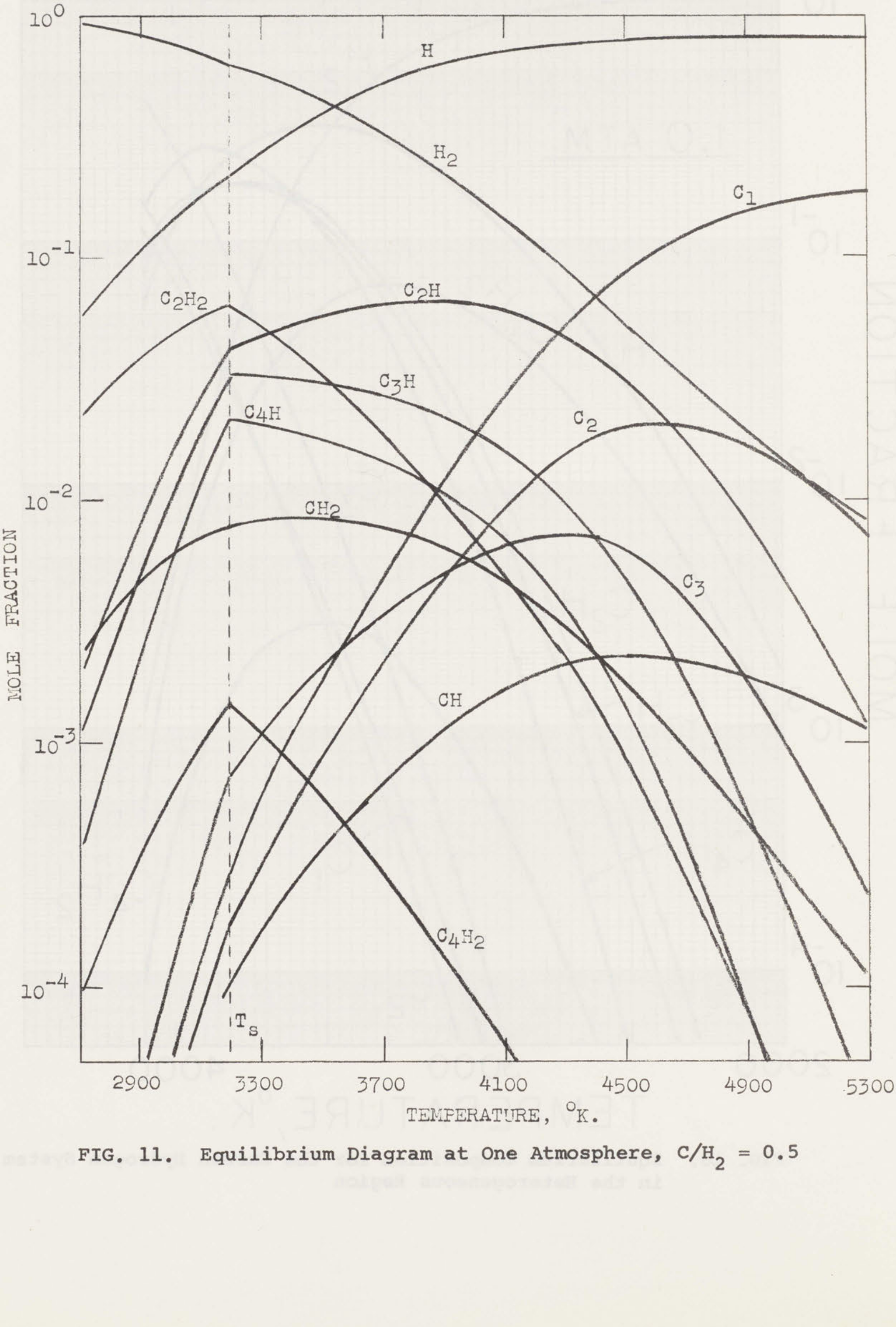


FIG. 11. Equilibrium Diagram at One Atmosphere, $C/H_2 = 0.5$

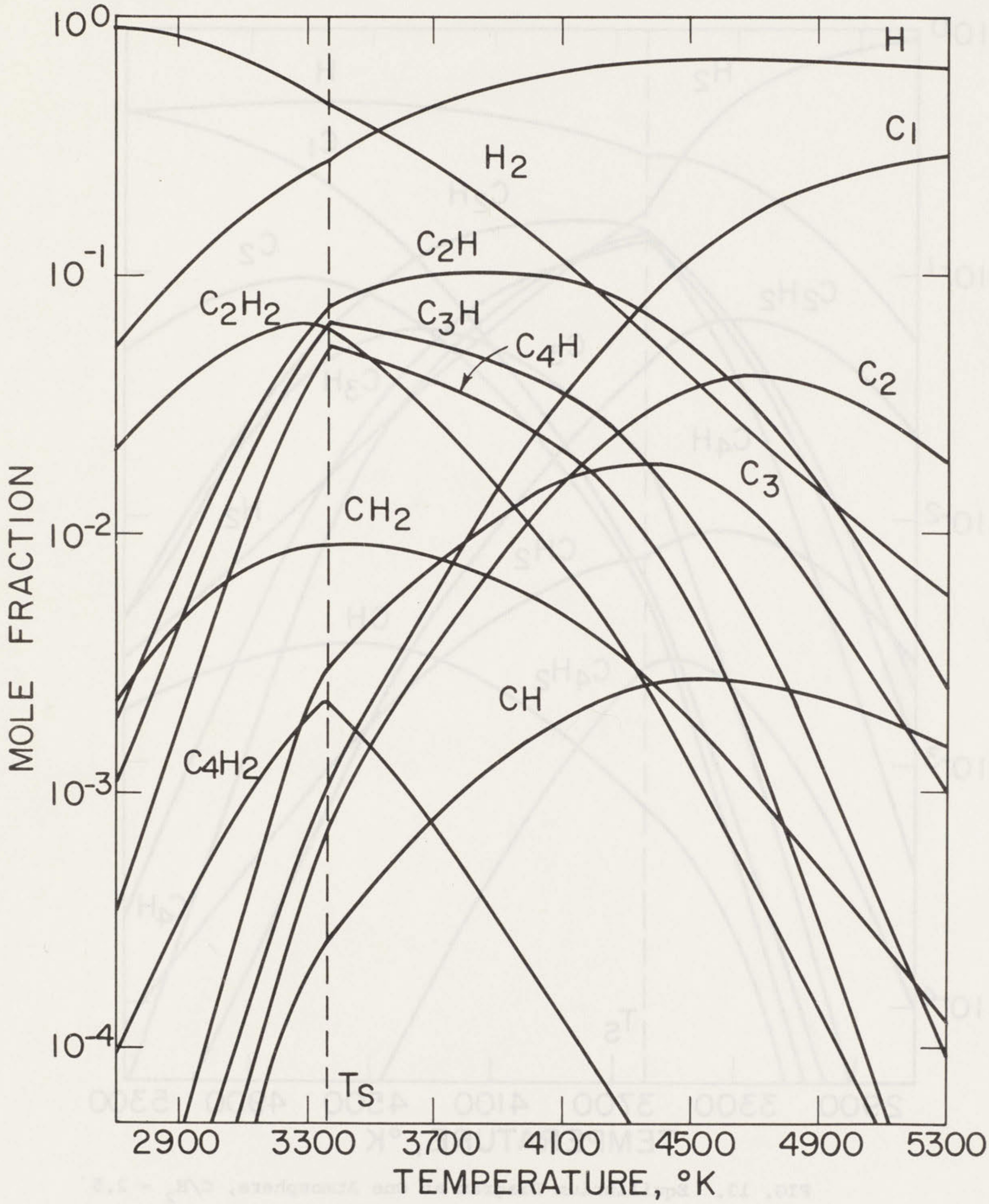


FIG. 12. Equilibrium Diagram at One Atmosphere, $C/H_2 = 1.0$

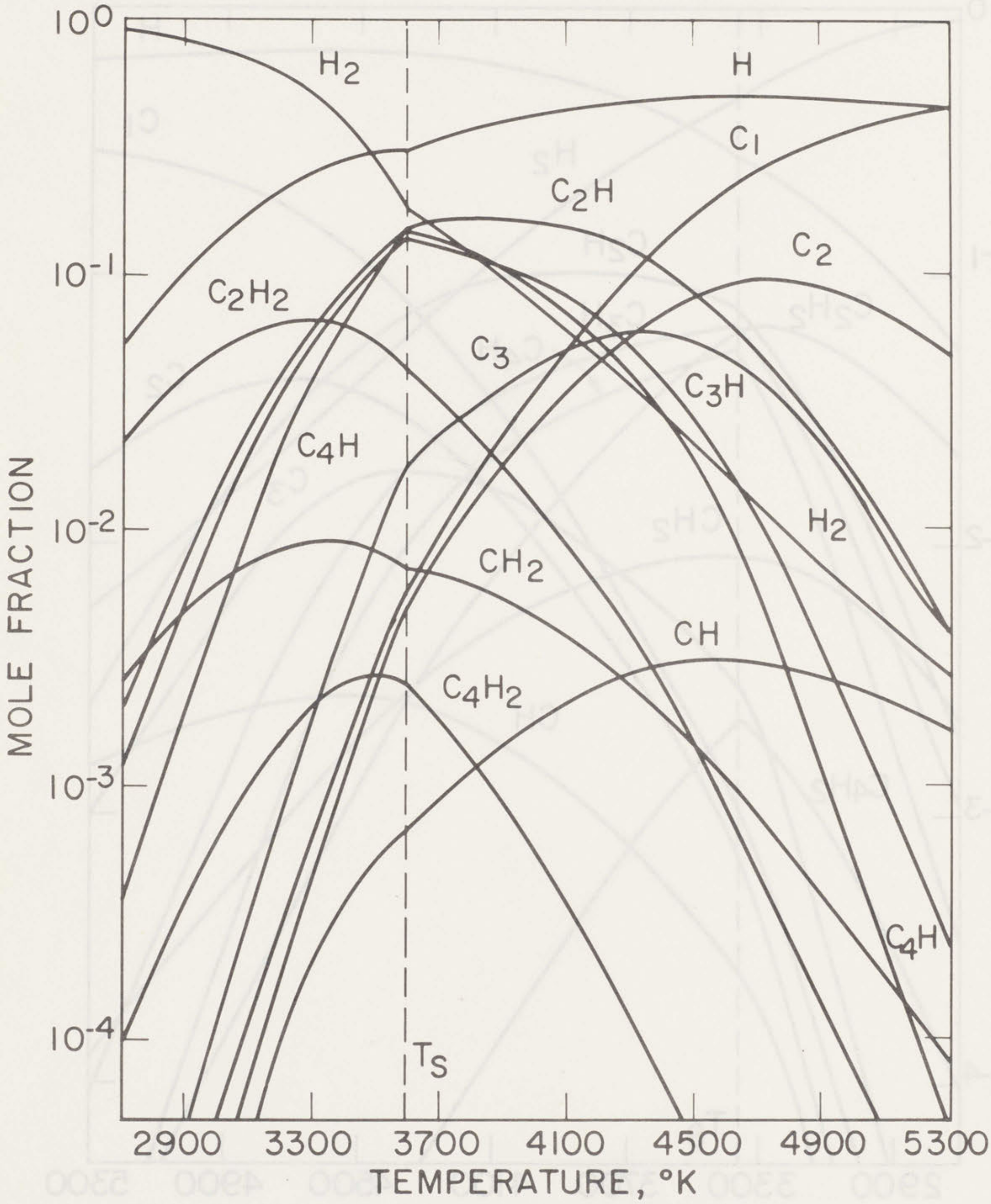


FIG. 13. Equilibrium Diagram at One Atmosphere, $C/H_2 = 2.5$

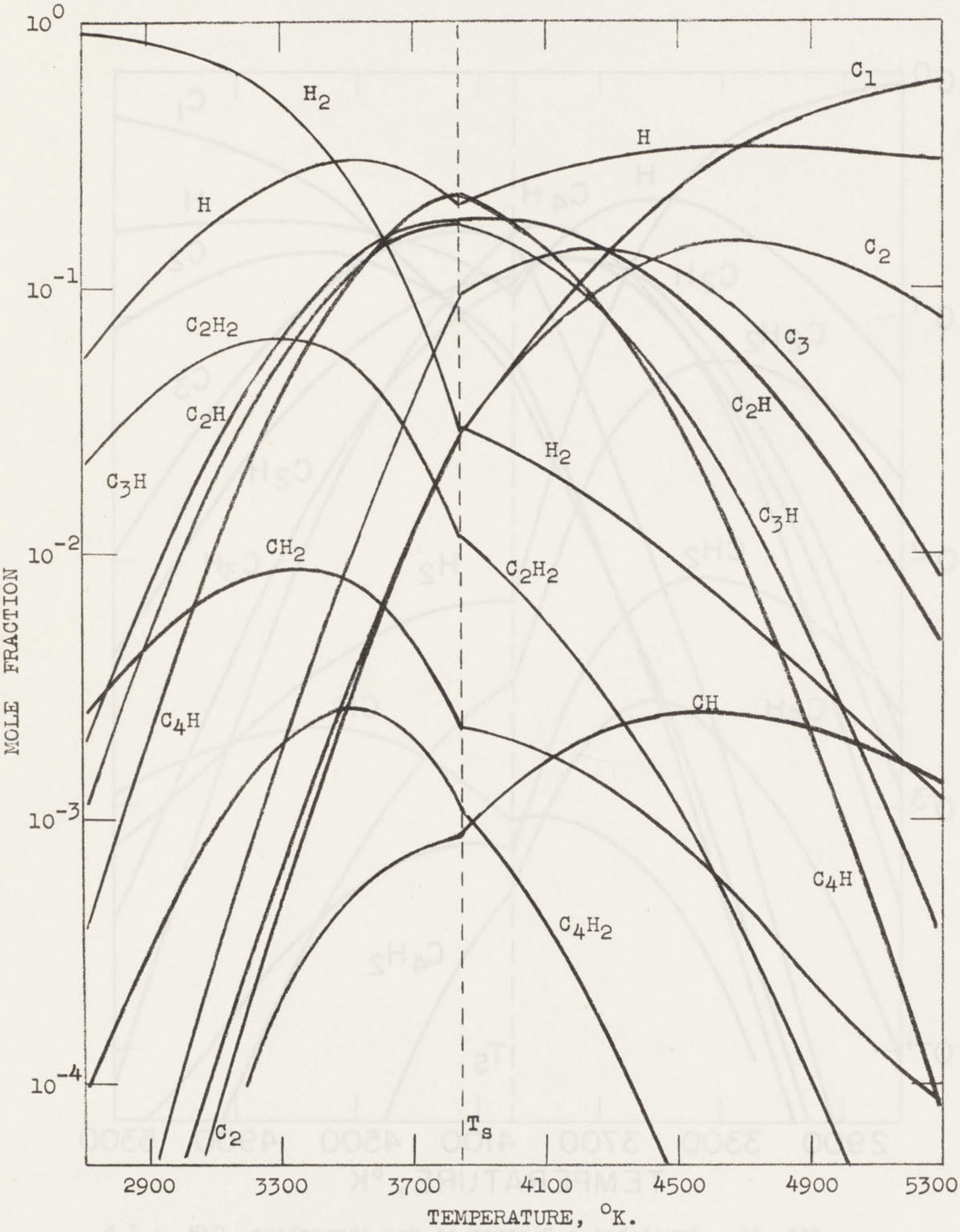


FIG. 14. Equilibrium Diagram at One Atmosphere, $C/H_2 = 5.0$

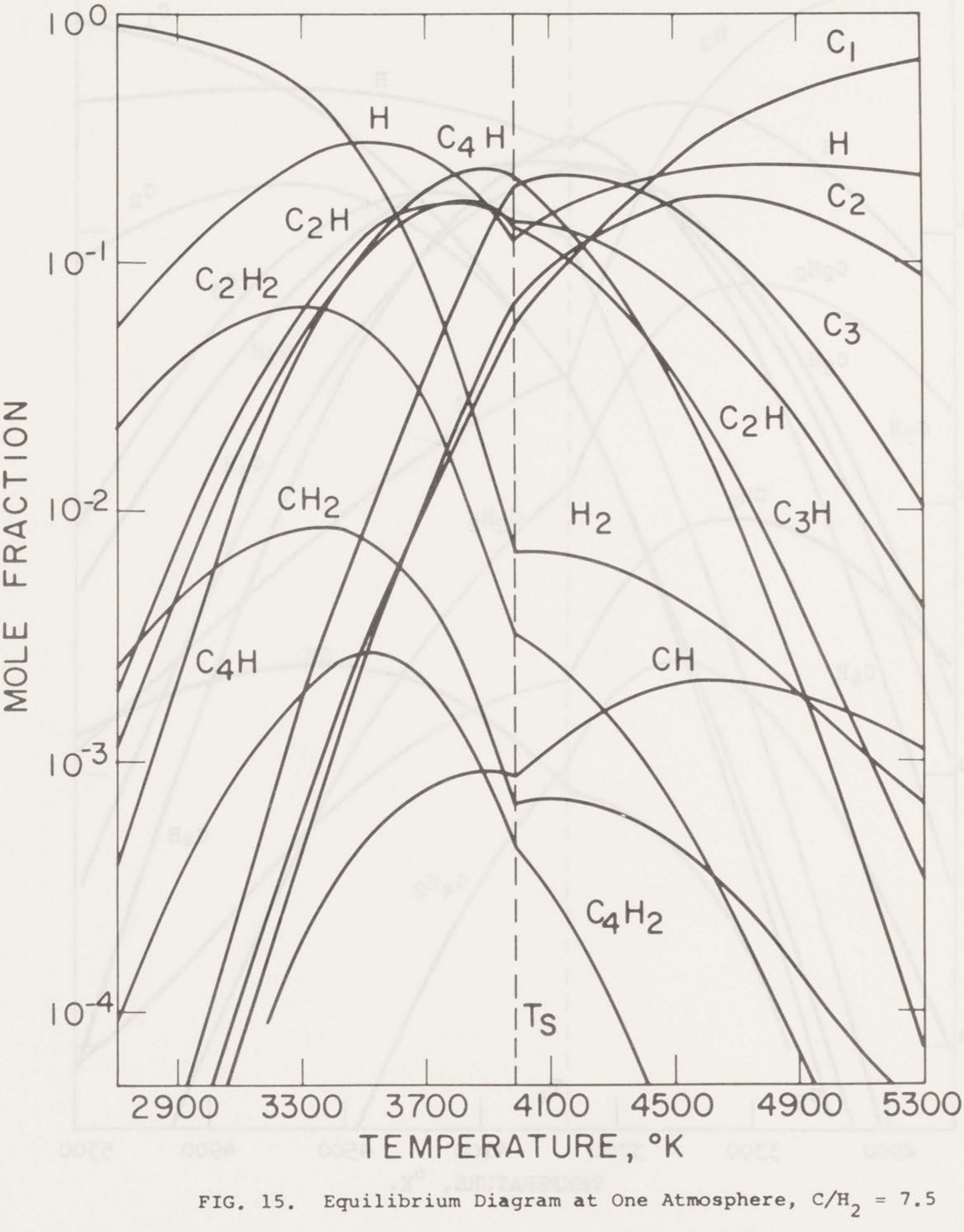


FIG. 15. Equilibrium Diagram at One Atmosphere, C/H_2 = 7.5

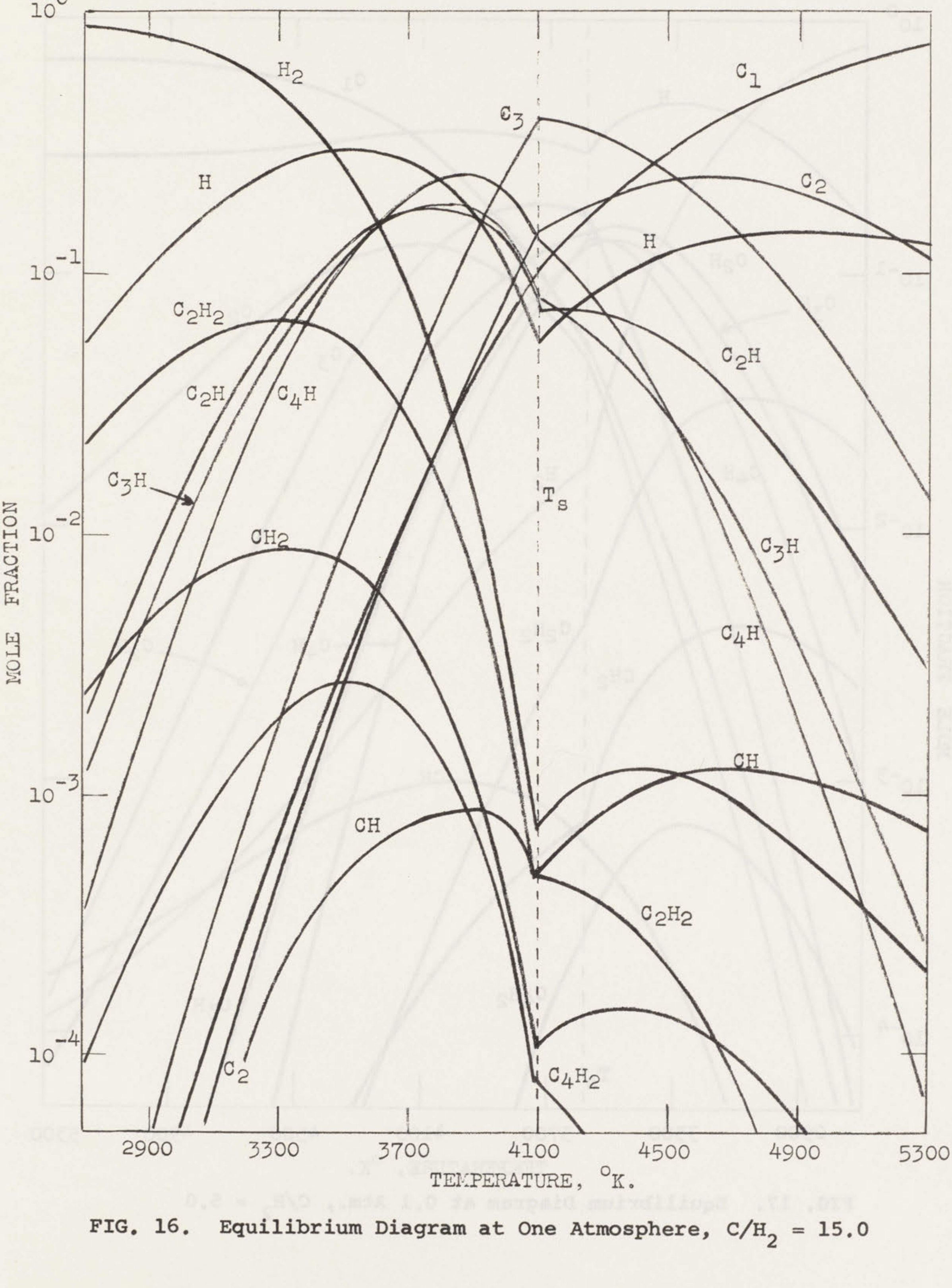


FIG. 16. Equilibrium Diagram at One Atmosphere, C/H_2 = 15.0

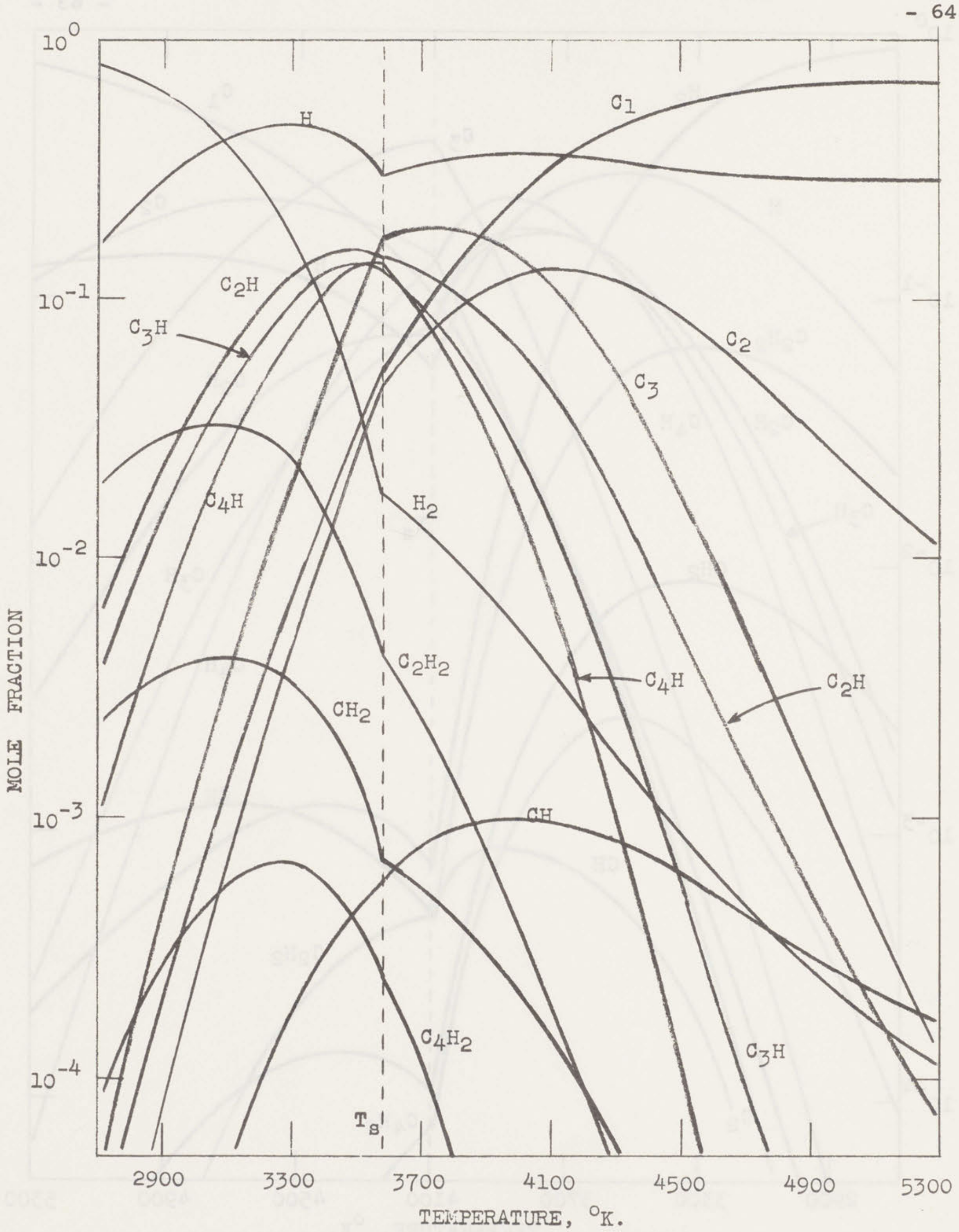


FIG. 17. Equilibrium Diagram at 0.1 Atm., $C/H_2 = 5.0$

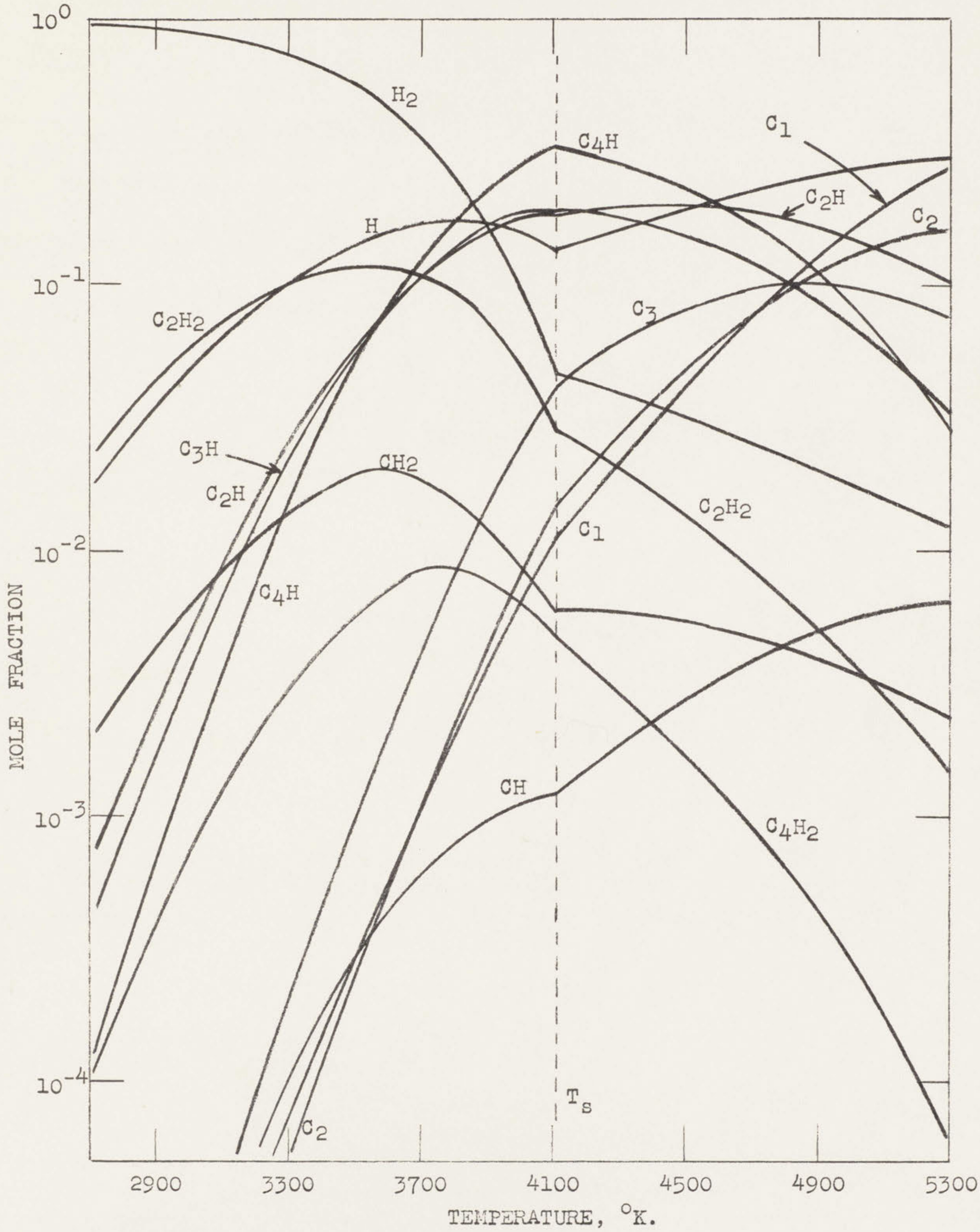


FIG. 18. Equilibrium Diagram at 10 Atm., C/H_2 = 5.0

The homogeneous region is characterized by a rearrangement of the different species obtained at the sublimation point and the relative distribution of the various components depends on the carbon to hydrogen ratio as can be seen from Figs. 11 to 18. The predominant components in this zone are carbon vapors and radicals C_2H, C_3H, and C_4H, the radicals reaching a maximum concentration near the sublimation point and having approximately the same order of magnitude. The carbon species, except C_1, decrease at temperatures above 4,700°K. Above 6,000°K, only H and C_1 remain in appreciable amount and their relative concentration approaches that calculated from the fixed carbon to hydrogen ratio. Hydrogen atoms have approximately the same concentration from 4,500°K.

The transition from the heterogeneous region to the homogeneous region is smooth at low C/H_2 ratio, but breaks sharply at higher ratios. This provides a means of defining the sublimation point for various conditions. Since both regions are calculated independently, drawing the curves for the heterogeneous region and for the homogeneous region from the low and high ends of their range respectively should bring the concentration of each component to the same value at the sublimation point, as was done in Figs. 11 to 18. Another way to determine this temperature is to approach it from the heterogeneous region, by calculating at each temperature the C/H_2 ratio from the gas phase composition. Plotting these values (Table B-1) resulted in Fig. 19, which shows that the heterogeneous region can be extended by either providing a larger proportion of carbon or by operating at higher pressures.

Acetylene concentration as calculated from the equilibrium diagrams goes through a maximum mole fraction of 0.07 at 3,300°K at one atmosphere in the heterogeneous region. A higher concentration is obtained with increasing pressure, but it decreases steadily in the homogeneous region. These equilibrium values of C_2H_2 concentration are considerably lower than those obtained experimentally by sampling the hot gas through a water-cooled probe, which was explained in terms of C_2H and H combination in the probe to yield additional C_2H_2 [(2)]. This illustrates the importance of considering all important high temperature species when attempting to predict the composition of the quenched gas from a high temperature reactor.

Since C_3H, C_4H, CH, and CH_2 were not all considered in previous workd [(2, 16, 19, 26)], the maximum C_2H_2 concentrations obtainable under optimum quenching conditions were computed from the results of the calculations discussed above. See Appendix B for a detailed explanation of the quench mechanism and calculations reported in Tables B-3 to B-6. The quench mechanism adopted was the following: all C_2H_2, H_2 and C_4H_2 present remain unchanged, C_2H recombines with H atoms to yield more C_2H_2, the remaining H not used by C_2H forms molecular hydrogen and C_3H, C_4H, CH, CH_2, C_1, C_2, C_3 go to solid carbon and H_2. It might be argued that CH can

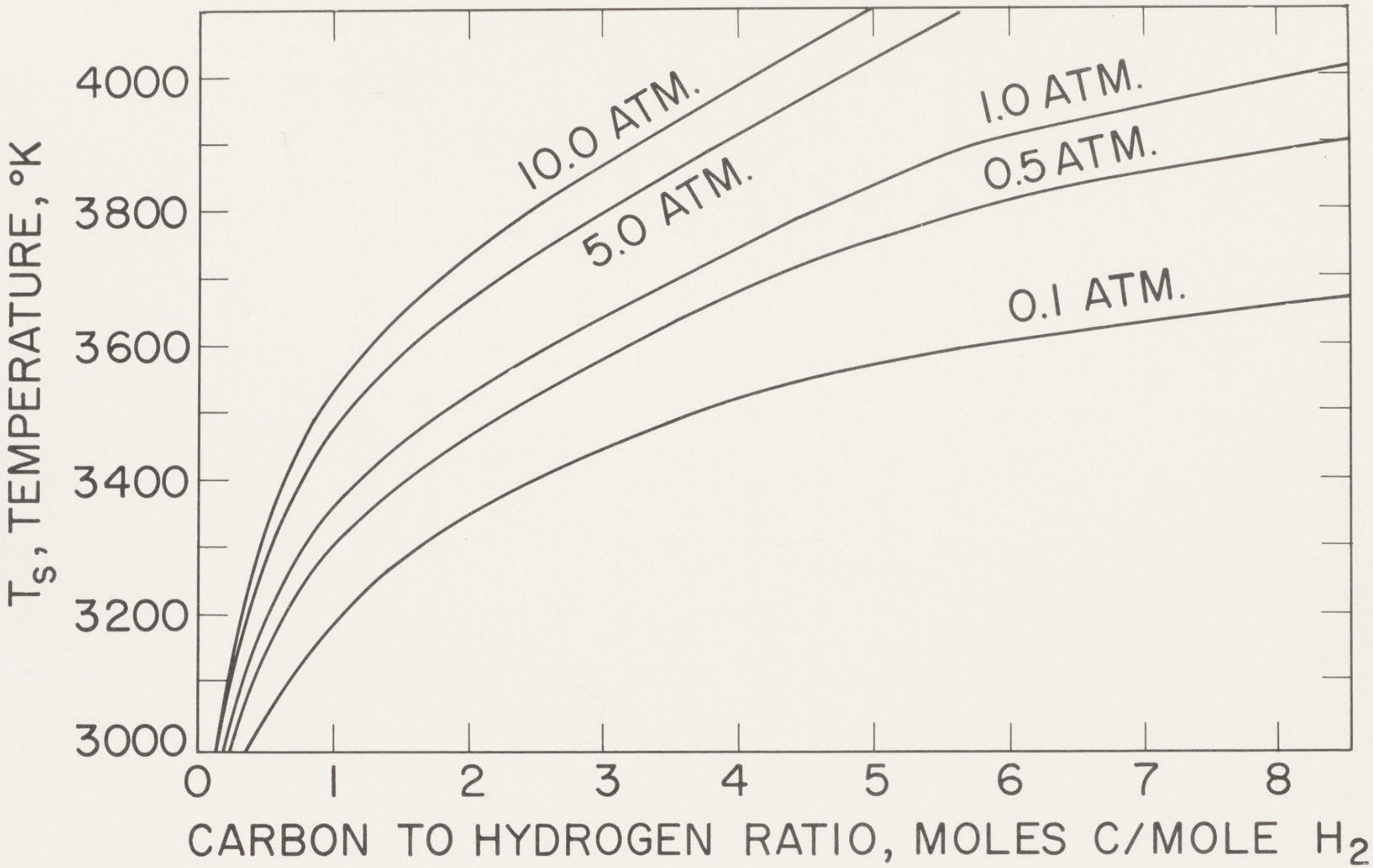


FIG. 19. Carbon Sublimation Temperature as a Function of the C/H_2 Ratio at Various Total Pressures

yield C_2H_2 directly from the dimerization of the radical, but its concentration is so low that the scheme adopted does not affect the overall results. Under these conditions, a perfectly quenched sample would contain only C_2H_2 and H_2 and also a minute amount of C_4H_2 (less than 0.5%). The results of those calculations are presented in Fig. 20 for a total pressure of one atmosphere and C/H_2 ratios from 0.5 to fifteen. The curve calculated for the heterogeneous region is common to all cases up to the specified C/H_2 ratio, as inferred from the equilibrium diagrams. The maximum acetylene concentration occurs in the homogeneous region for a carbon-hydrogen gaseous mixture quenched from about 4,000 to 4,500 °K. As the relative amount of carbon is increased, more acetylene can be obtained. The effect of increasing the C/H_2 ratio from 1 to 5 is more pronounced, however, than from 5 to 15. For instance, for a C/H_2 = 100 at 4,500°K, the quenched gas would contain only 50% C_2H_2, whereas a similar result can be obtained at 4,300°K for C/H_2 = 15. Above 5,000°K, C_2H_2 concentration is low for all mixtures of carbon and hydrogen, and operation between 3,500 and 4,500°K would provide maximum C_2H_2 concentrations.

The effect of increasing pressure on maximum C_2H_2 content (see Tables B-4, B-5, and B-6) is to shift the whole curves of Fig. 20 upward to the right, while decreasing pressures move the curves downward to the left. This is also shown in Fig. 21 where the calculated maximum C_2H_2 content is plotted for various total pressures and a C/H_2 ratio of 5.0 in the homogeneous region.

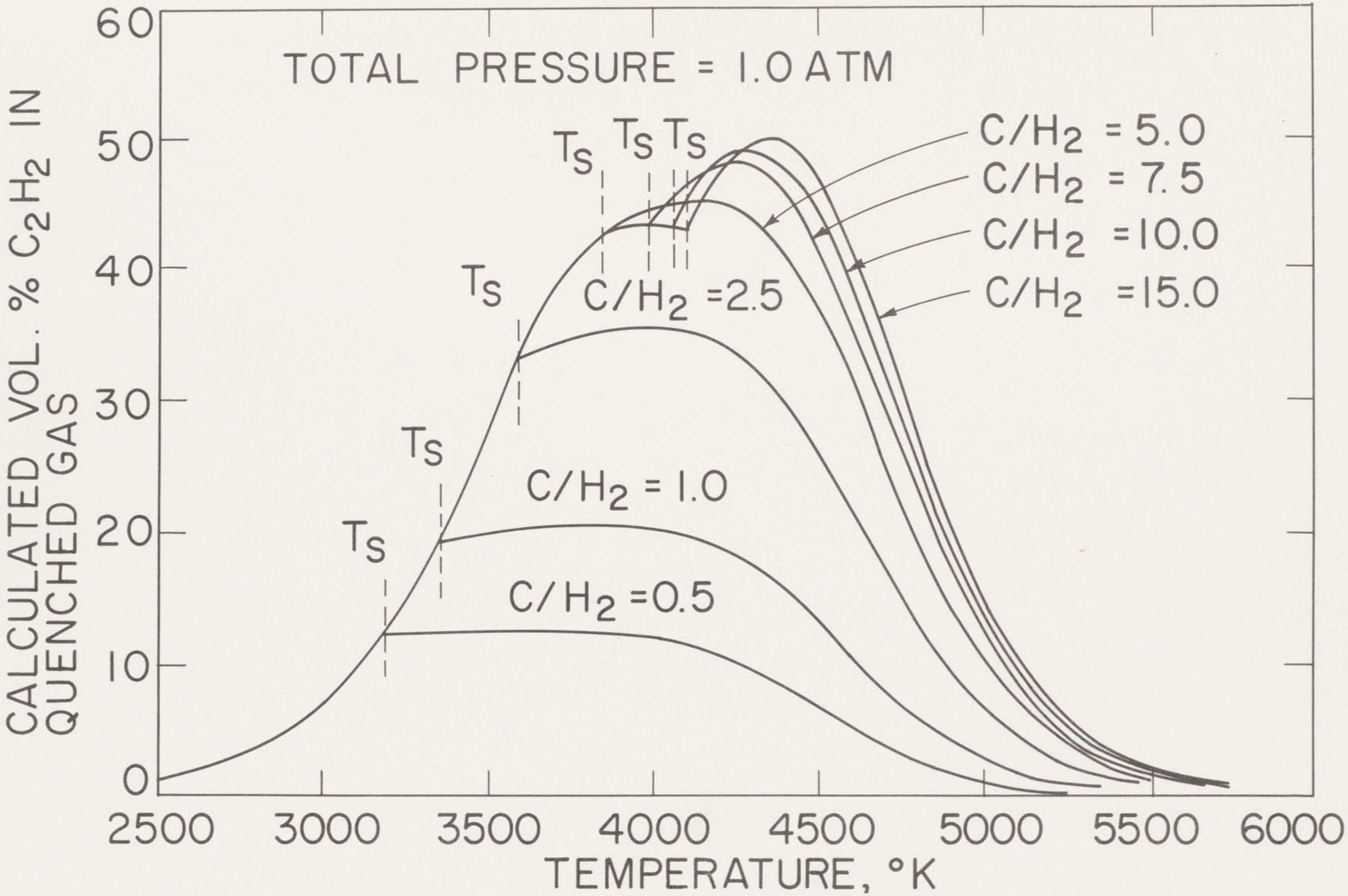


FIG. 20. Calculated Maximum C_2H_2 Content for Various C/H_2 Ratios at One Atmosphere

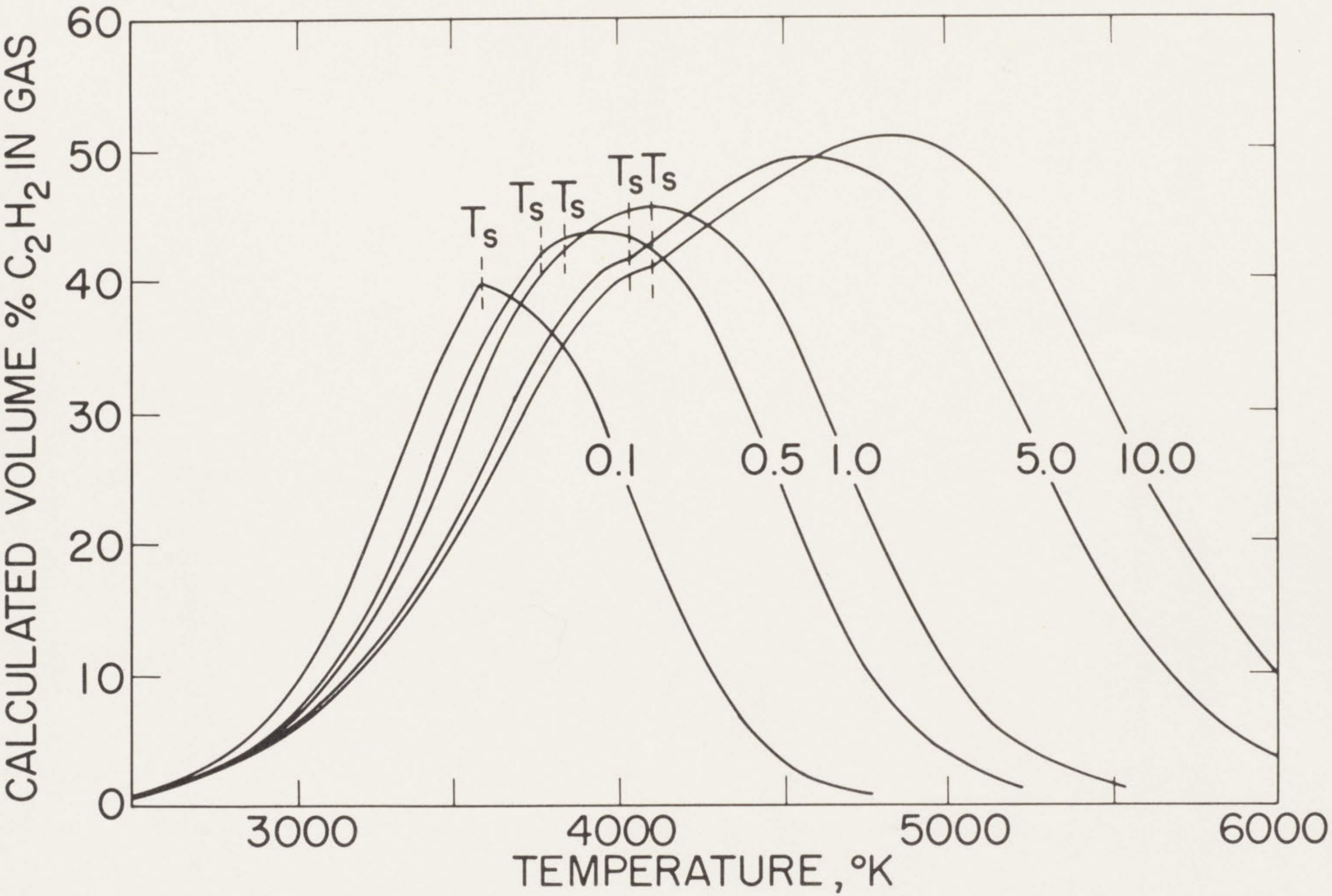


FIG. 21. Maximum C_2H_2 Content at Various Total Pressures (Atm.), C/H_2 = 5.0 in the Homogeneous Region

Iwasyk[2, 16] and Plooster and Reed[26] disclose that lower pressures should increase C_2H_2 formation, but this is true in the heterogeneous region only. The most favorable conditions for C_2H_2 production would be found for a gas mixture quenched from the homogeneous region at higher pressures, as can be seen from Fig. 21. However, operation at higher pressures is restricted by the danger of handling acetylene under pressure.

Carbon-Methane Reactions

Since the reaction of carbon vapor with hydrogen to form acetylene is exothermic, it is interesting to consider a reaction scheme whereby the endothermic heat of methane cracking would be furnished by this exothermic heat of reaction.

Consider the following reactions:

$$2\ C_1 + H_2 \longrightarrow C_2H_2 \quad \text{(at T)} \qquad (30)$$

$$2\ CH_4\ (298°K) \longrightarrow 2\ CH_4\ \text{(at T)} \qquad (31)$$

$$2\ CH_4 \longrightarrow C_2H_2 + 3\ H_2\ \text{(at T)} \qquad (32)$$

Reaction (30) may be used to furnish the sensible heat required to bring CH_4 to reaction temperature, reaction (31) and to carry out the cracking reaction at that temperature, reaction (32). Below 2,000°K, however, reaction (32) is equilibrium limited as seen by Fig. 22, (taken from Anderson and Case[1]), which represents the composition and yield from that reaction.

The energy required for making one mole of acetylene as a func-

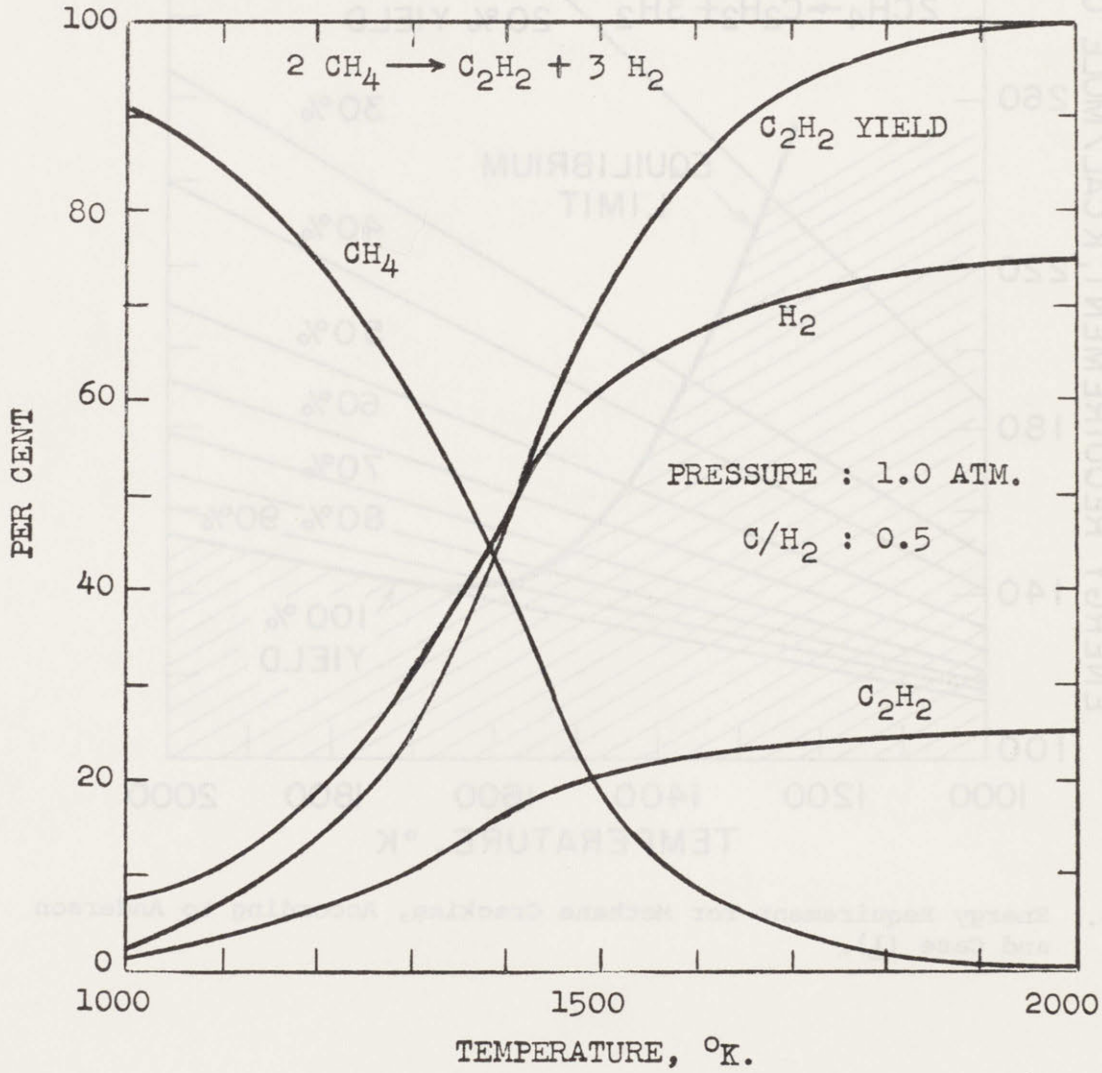


FIG. 22. Equilibrium Limitation on the Cracking Reaction of Methane $2\ CH_4 \longrightarrow C_2H_2 + 3\ H_2$ According to Anderson and Case (1).

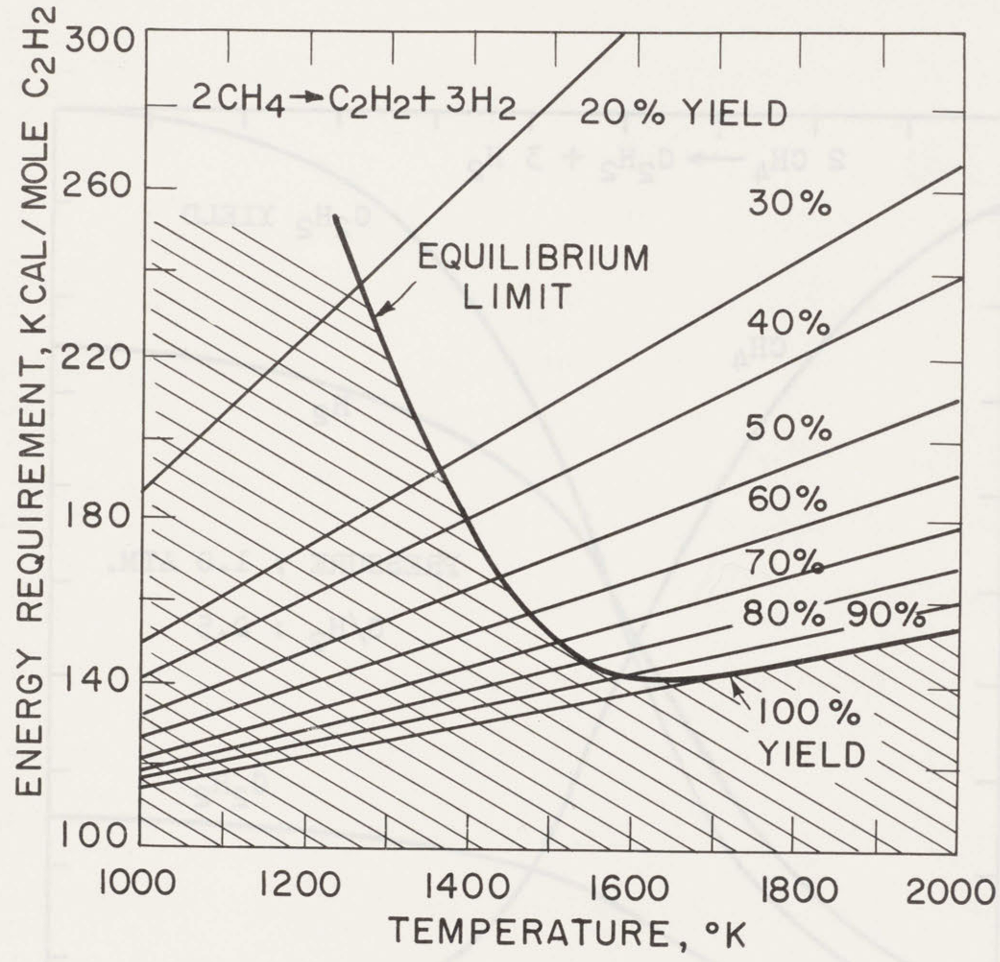


FIG. 23. Energy Requirement for Methane Cracking, According to Anderson and Case (1).

tion of temperature is shown in Fig. 23, taken from Anderson and Case[(1)]. This includes the heat requirement for reactions (31) and (32) in the range from 1,000°K to 2,000°K. The parameter used is the yield or percent of methane decomposed that is converted to acetylene. The region at the left of the equilibrium line, transposed from Fig. 22, is not thermodynamically possible and it is seen that above 2,000°K all methane can be decomposed to yield C_2H_2 and H_2.

Reaction (30) can also produce acetylene and the overall reaction scheme can give more C_2H_2 than the 25% possible by reaction (32) only.

The heats of reaction of the different reactions have been calculated (see Appendix D) from the heats of formation for the temperature range 1,500°K to 4,000°K, using the data of Rossini[(28)] when available and extrapolating to high temperatures by the method of Bauer and Duff[(3)] when necessary. Table D-1 shows the $\Delta H°_{Tf}$ of C_2H_2, C_1, H_2, H, and CH_4 as obtained by the various procedures, and also the sensible heat ($H^\circ_T - H^\circ_O$) for methane.

The overall reaction may be written as:

$$C_1 + CH_4 \longrightarrow C_2H_2 + H_2 \qquad (33)$$

The heat of reaction for this reaction, i.e., for the sum of reactions (30), (31), and (32) has been calculated, taking into account the equilibrium limitation on methane cracking. The results are plotted in Fig. 24. From 2,000°K to 4,000°K, the overall heat of reaction decreases steadily with increasing

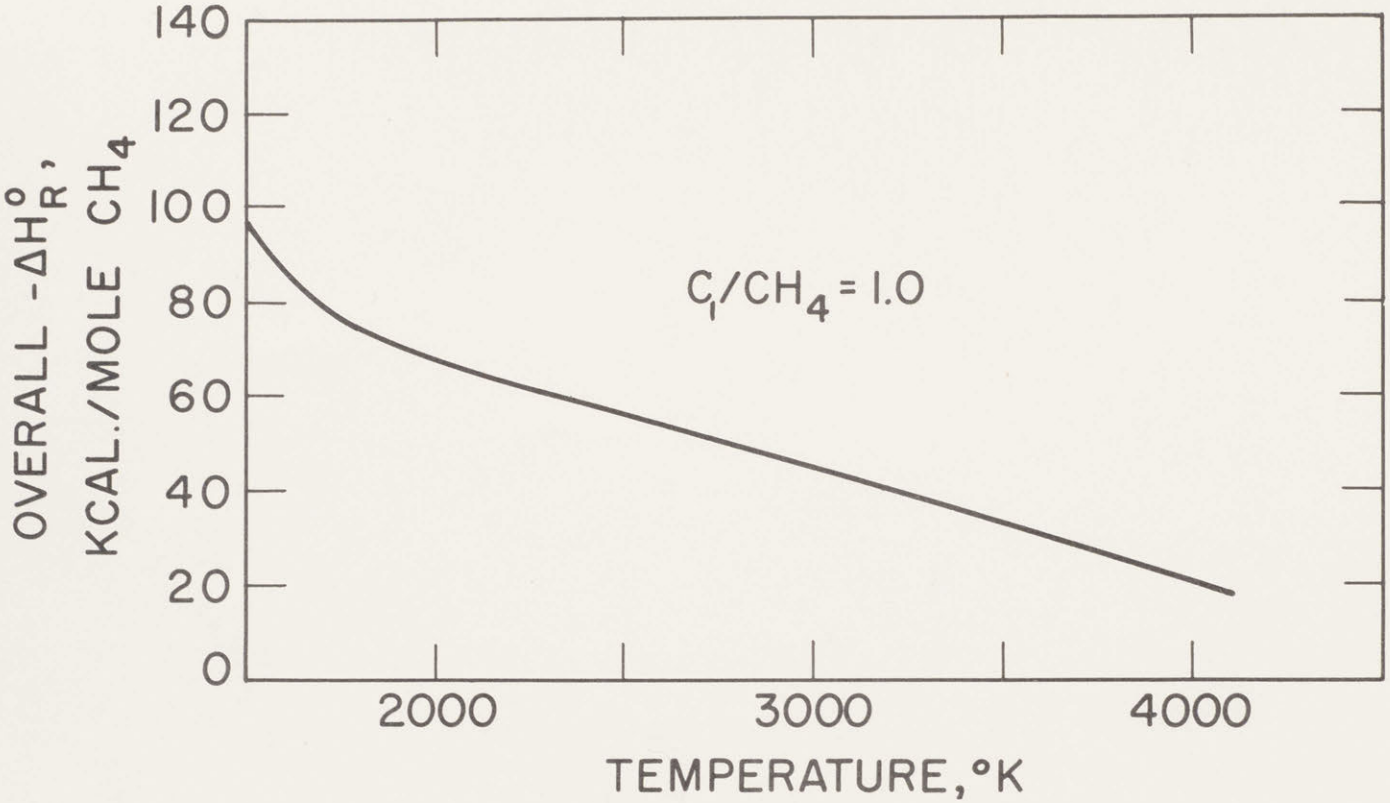


FIG. 24. Net Heat of Reaction

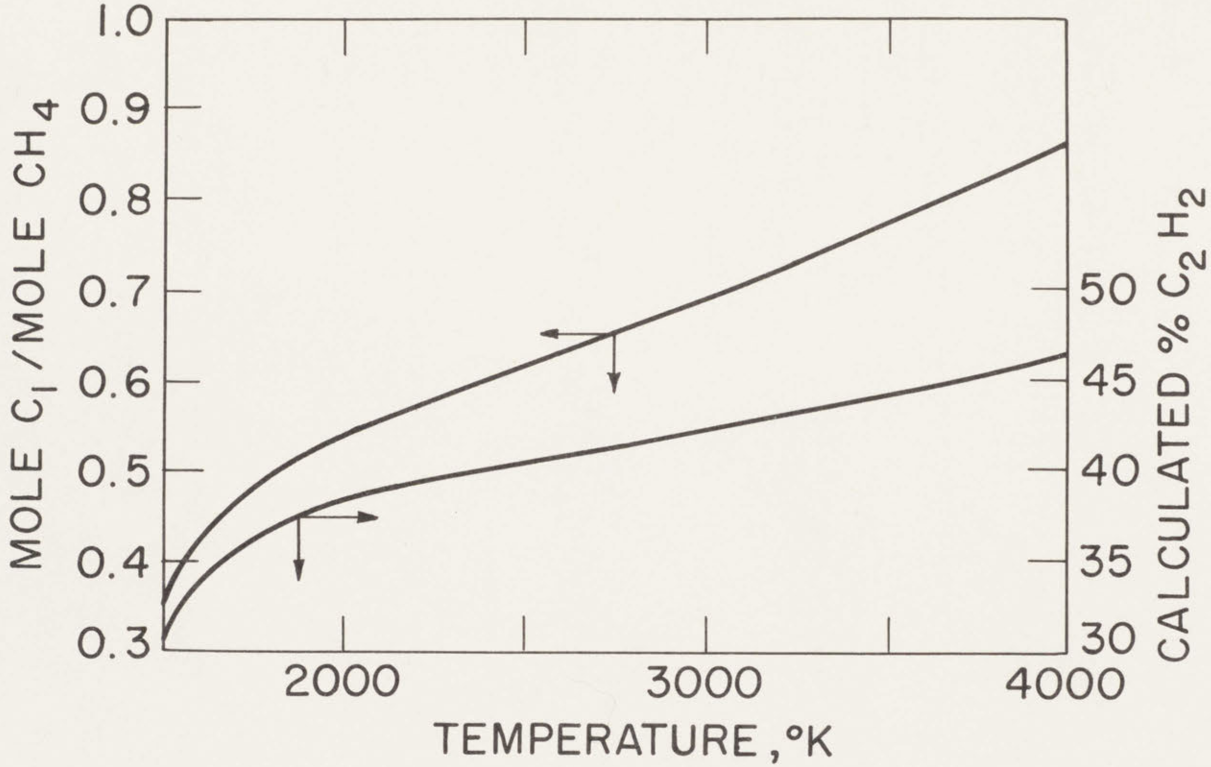


FIG. 25. Carbon Requirement for Null Reaction Heat

temperature, but rises sharply near 1,500°K where equilibrium limits the reaction. This graph also shows that an excess of exothermic heat is still present at 4,000°K and can be used to react more methane.

Another way of analysing the results would be to determine the number of moles of carbon vapor necessary to carry out reactions (31) and (32) by using all the exothermic heat available from reaction (30). This procedure is given in Appendix D and the results are presented in Table D-2. As deduced from Fig. 24 for the entire procedure range, it will take fewer moles of carbon vapor reacted than moles of methane to be processed.

Fig. 25 shows this effect for a net ΔH°_R equal to zero, the bend in the curve below 2,000°K being due again to the equilibrium limitation imposed on reaction (32). Also represented on this plot is the theoretical concentration of C_2H_2 as calculated for the ratio of C_1 to CH_4 that gives a null overall heat of reaction. For the temperature range of interest in the operation of a carbon arc reactor, a C_2H_2 concentration of 40% to 47% could be theoretically obtained.

Although other processes such as the endothermic dissociation of hydrogen

$$H_2 \longrightarrow 2H$$

or the highly exothermic reaction of atomic hydrogen with carbon vapor

$$2\ C_1 + 2\ H \longrightarrow C_2H_2$$

which also produces more acetylene, or the formation of higher carbon species, which can also react with hydrogen to form further acetylene, or degradation of methane to solid carbon and hydrogen were not included in this analysis, the results nonetheless point out that it is possible to obtain appreciable concentrations of C_2H_2 by reacting carbon vapors with methane, much more than the theoretical 25% possible by reaction (32) alone and the 12% claimed by the patent issued to Weir[(35)]. For example, a 50-75% C_2H_2 gas may very well be possible from the cracking of methane in a high intensity arc reactor using consumable graphite anodes.

As a point of economic interest, a quantity defined as the specific energy[(10)] might be examined. It is a measure of the energy used to produce a given amount of C_2H_2:

$$A = \text{specific energy} = \frac{k\ P}{\beta G a'} \tag{34}$$

where P is the power in kw, a' the outlet C_2H_2 concentration, G the reactant gas flow rate in liters/min. at 70°F and β is the coefficient of volume expansion. The coefficient of volume expansion can be derived from stoichiometric considerations and can be calculated directly from the composition of the reacted gas. See Appendix E for the derivations. The constant k in Eq. 34 is a conversion factor equal to 7.02 for A in kw-hr/lb. C_2H_2.

For reactions (30) and (32), $\beta_{max.} = 1$ and $\beta_{max.} = 2$ respectively. Thus the methane-carbon system has the potential of a considerably lower energy because of the higher maximum value of β.

A last quantity might be considered in order to relate the fraction of carbon of the feed that is found in the output gas as C_2H_2 after reaction at high temperature. This quantity, termed Ω, is defined by

$$\Omega = \frac{C/H_2 \text{ in the output gas}}{C/H_2 \text{ in the feed}} \qquad (35)$$

It is a measure of the efficiency of carbon utilization for acetylene production in either the carbon-hydrogen system or the carbon-methane system. Details of derivation and determination of Ω are presented in Appendix E.

(2) Experimental Results

Two categories of experiments were performed in the high temperature reactor: one used hydrogen as feed gas and the other methane. A summary of the measured and derived quantities is presented in Appendix C. Table C-1 shows the data obtained for the hydrogen runs, while the methane runs are reported in Table C-2. In these runs, the power P has been taken as the average between the beginning and the end of any one experiment.

Carbon-Hydrogen System

Operational characteristics of the high intensity arc reactor

Two sizes of anodes were used for the hydrogen runs: 1/4 in.

and 3/8 in. The inner hole of the cathode cap was drilled to give a 1/8 in. spacing between the cathode and anode as seen in the details of the reactor (Fig. 7). Accordingly, the cathode cap hole measured 1/2 in. in diameter for the 1/4 in. anodes and 5/8 in. for the 3/8 in. anodes. The length of the cap was kept at 1/2 in. in all cases. The arc characteristics were determined from the data of various runs and are shown in Fig. 26. The rising voltage-rising current points, characteristic of a high intensity arc, exhibit rather wide scattering, and it is seen that the slope depends on the size of the gap between the electrodes or on the anode size only. Even if the spacing between the electrodes is the same in both cases, the arc length will not be the same, when taking the middle point as a reference point. A longer arc length seems to reduce somewhat the high intensity effect by lowering the burning voltage. There was no detectable influence of the gas flow rate on the arc characteristics.

It was observed during actual runs that the voltage and current varied in opposite directions so that the VI product was almost constant, i.e., the power fed to the electrodes was constant despite fluctuations of voltage and current. This is shown in Figs. 27 and 28 where the carbon vaporization rate is plotted as a function of power. A direct relationship applies between these two quantities, but the slope is different for the two sizes of anodes used for the hydrogen runs.

Considering Fig. 27, the carbon vaporization rate (CVR) can be

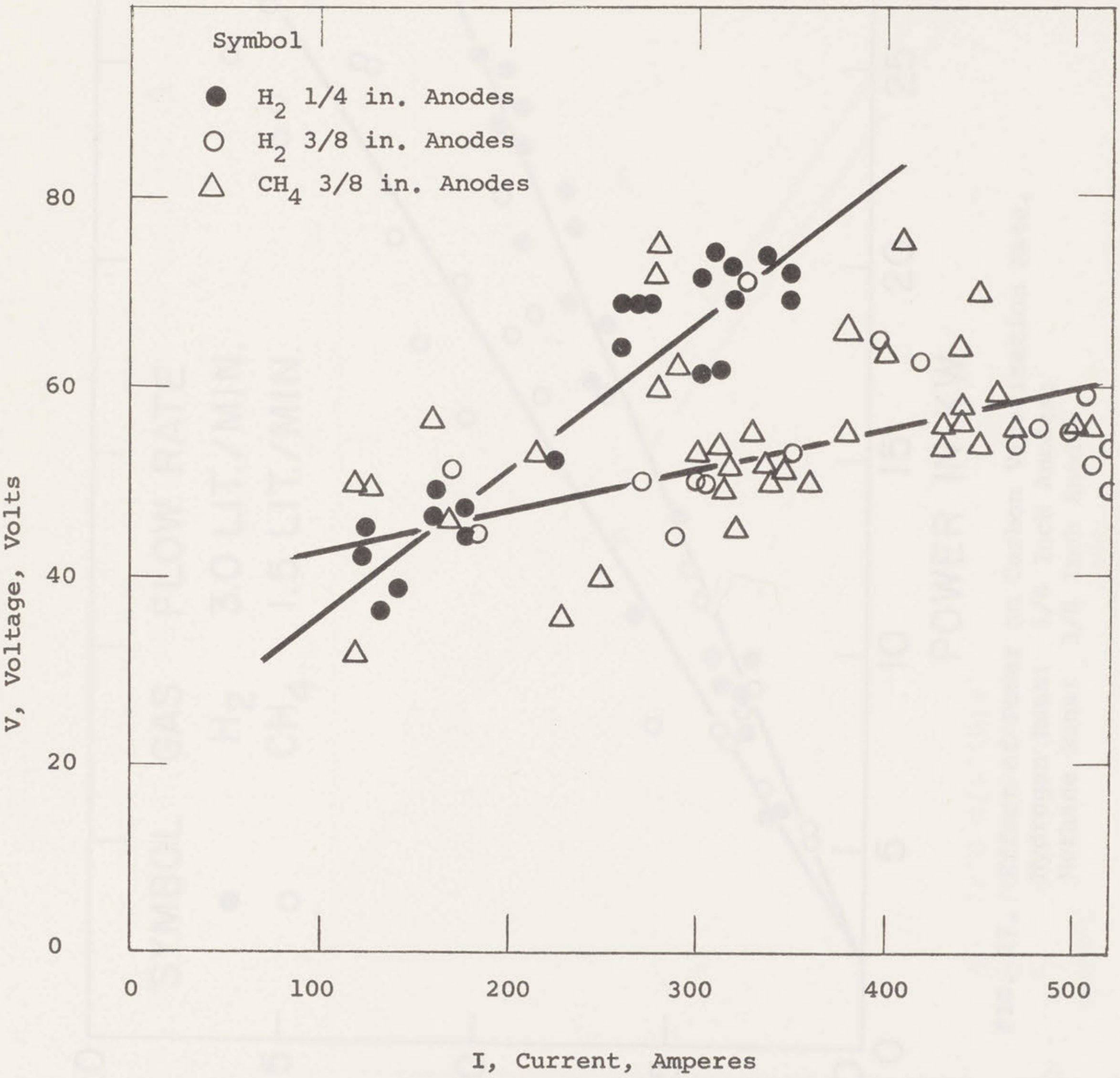


FIG. 26. Arc Voltage-Current Characteristics of the High Intensity Arc

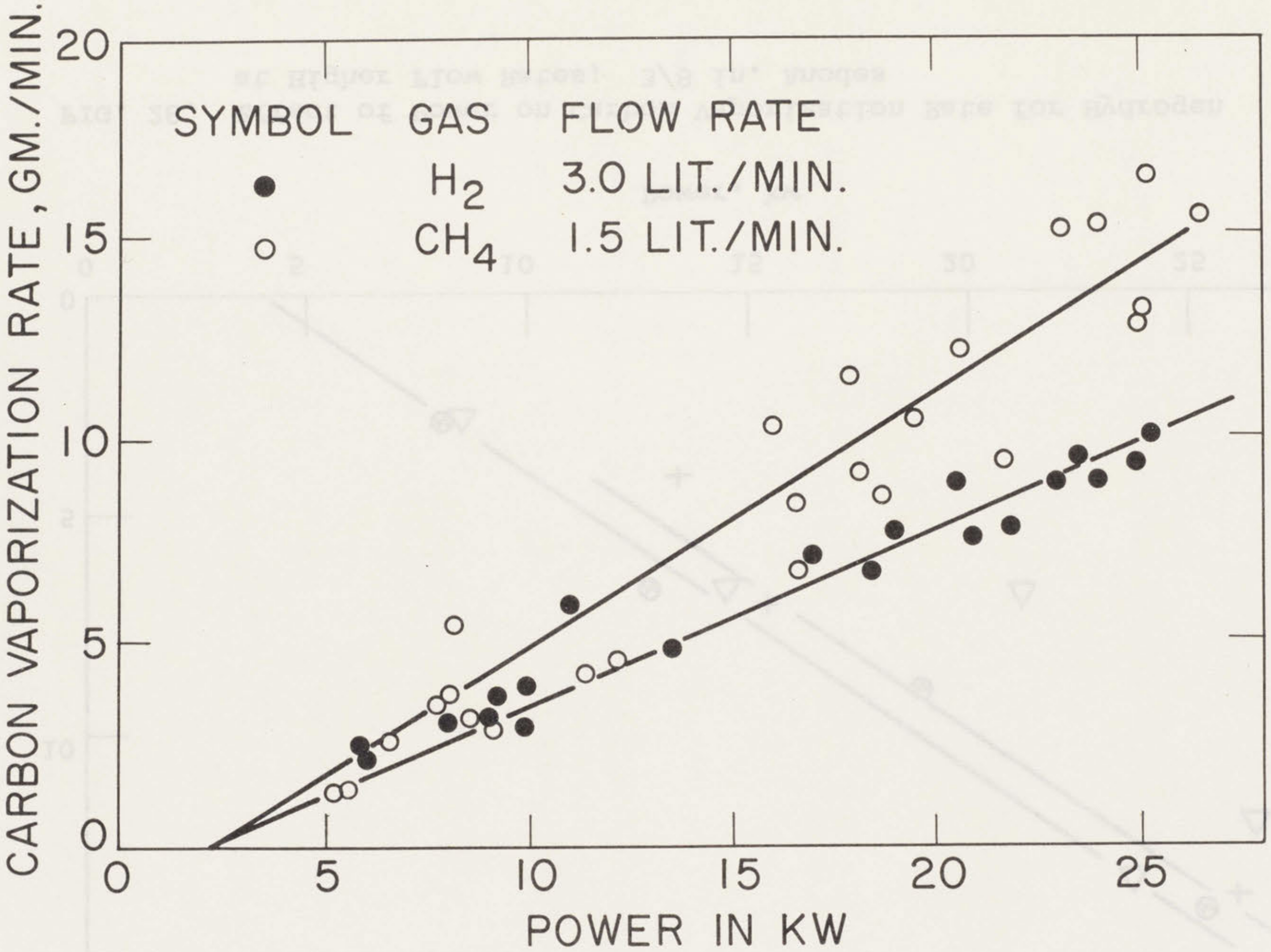


FIG. 27. Effect of Power on Carbon Vaporization Rate.
Hydrogen Runs: 1/4 Inch Anodes;
Methane Runs: 3/8 Inch Anodes.

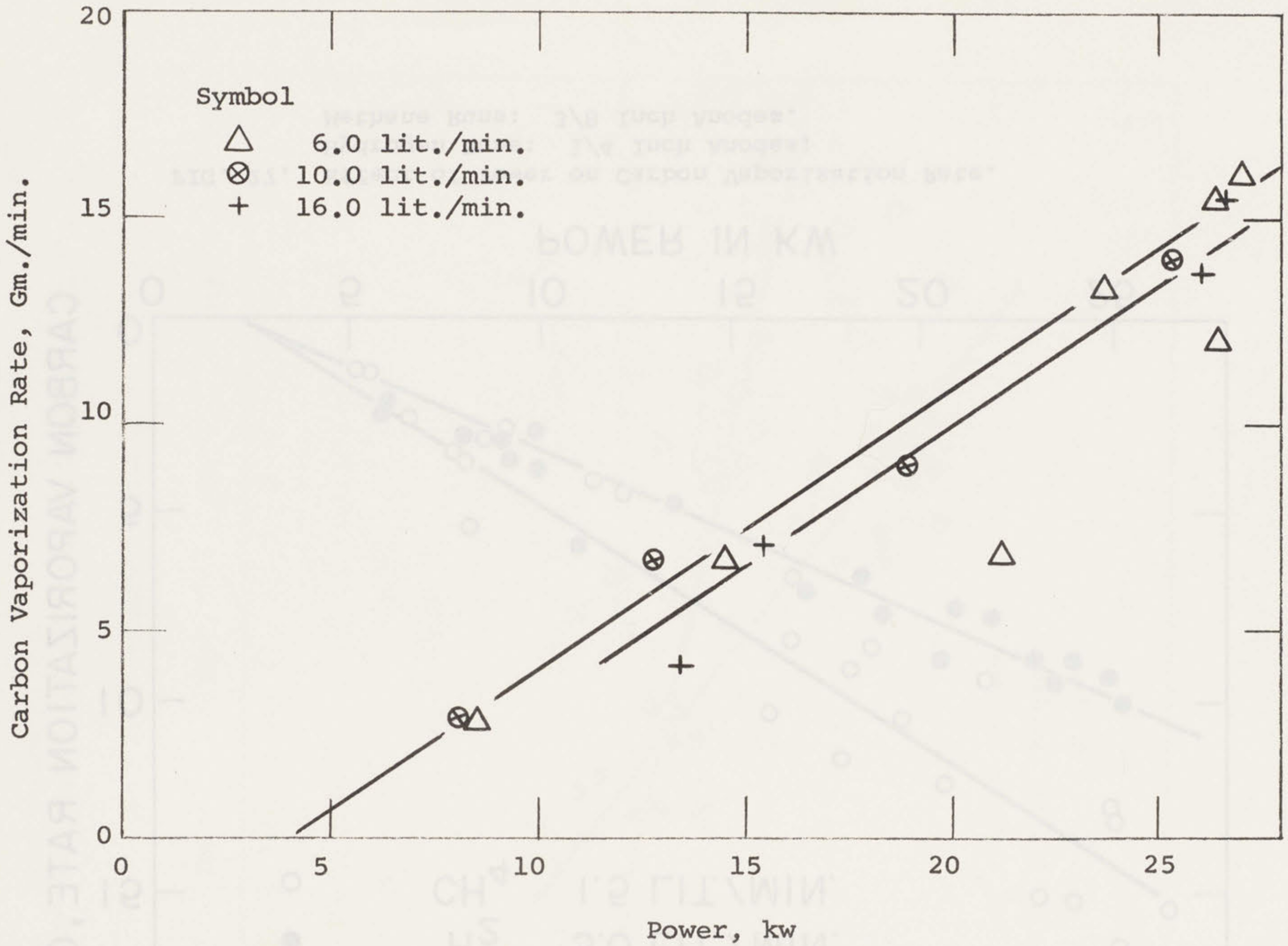


FIG. 28. Effect of Power on Carbon Vaporization Rate for Hydrogen at Higher Flow Rates; 3/8 in. Anodes

represented by

$$(CVR)_{\substack{1/4\ in.\\ anode}} = 0.435\ (P-2.5) \qquad (36)$$

while from Fig. 28, at higher flow rates,

$$(CVR)_{\substack{3/8\ in.\\ anode}} = 0.675\ (P-4) \qquad (37)$$

Taking the ratio of the slopes for 3/8 in. and 1/4 in. anodes, we get

$$\frac{(CVR)_{3/8}}{(CVR)_{1/4}} = 1.55 \qquad (38)$$

If one assumes now, as discussed in the Introduction, that the current density is constant at the electrodes, the carbon vaporization rate should depend only on the area of the arc. The cathode cap cylindrical chamber is 5/8 in. and 1/2 in. for the 3/8 in. and 1/4 in. anodes respectively, giving an area ratio

$$\left(\frac{5/8}{1/2}\right)^2 = 1.5625$$

which is approximately equal to the ratio of the slopes by Eq. 38. One other fact that seems to ascertain that the CVR is dependent upon the arc area is the power needed to begin vaporization of the carbon anodes. The higher power (see Figs. 27 and 28) needed to vaporize bigger anodes could be explained by the radiation losses which are larger, the larger the area of the plasma, if we assumed that the latter retain approximately the same volume, since it is confined by the electric and magnetic fields and the cold surrounding gas. The ratio of area to volume would then be greater, the larger the anodes. It would also be larger if we increase the flow rate, which has the effect of arching the arc and producing a larger area, as exhibited in Fig. 28 where the CVR is smaller at higher flow rates. This could be a plausible reason why the CVR-P lines are shifted to the right with increasing flow rates.

It was also found experimentally that about half of the vaporized carbon condensed inside the cathode cap and formed hard deposits, grayish in color; this reduced the cathode opening after a run to about half the initial diameter. Most of the remaining carbon was found on the cold reactor walls. The probe was coated for a length of 3 to 4 inches from the tip and a small amount of carbon was deposited inside the probe, sometimes plugging the hypodermic needle tubing and preventing a sample from being withdrawn. In some cases, carbon deposits were found in the sampling bottle after sampling.

Effect of Power on the C_2H_2 Content of the Quenched Gas

The concentrations of acetylene obtained in the quenched samples are shown in Figs. 29 and 30 as a function of the power fed to the arc. In Fig. 29 for 1/4 in. anodes, data for the smaller, 19 gage (0.043 in. i.d.), probe were difficult to duplicate. The hypodermic tubing used plugged in each run and thus good samples (25 ml or more) were rather the exception. The 14 gage probe (0.063 in. i.d.) results are more reliable since plugging

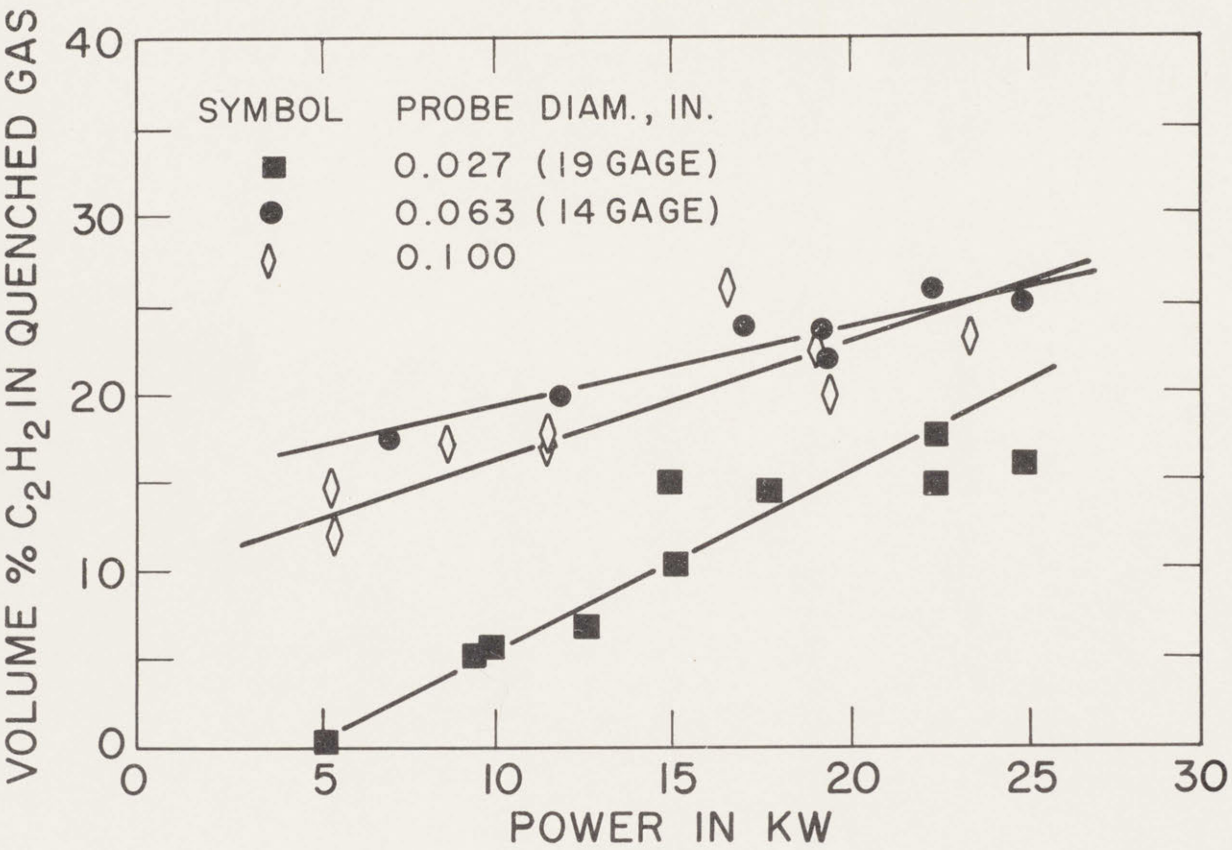


FIG. 29. C_2H_2 Concentration Versus Power Input,
H_2 Flow Rate: (●, ■): 3.0, (◊): 1.5 lit./min.
1/4 in. Anodes

did not occur and any size sample could be collected. This probe also gave higher C_2H_2 concentration as compared with the other two probes and it may well be close to an optimum quenching diameter, as discussed by Plooster and Reed[(26)]. The probe position for the 14 gage probe was 1/2 in. from the anode tip in each run. For the smaller probes, this distance was varied from one inch to 1/2 inch. In Fig. 30 are shown the data for the larger anodes and probes at different positions and for higher flow rates of H_2 feed. This plot shown that the same concentration of C_2H_2 can be obtained by changing simultaneously both variables power and flow rates of feed gas. The C_2H_2 output is directly proportional to the power and inversely proportional to the rate of flow of gas, or expressed otherwise, to P/G. Due to power limitation from the generators, no clear cut trend with respect to acetylene concentration can be ascertained for extrapolation to power levels higher than 29 kw. The highest C_2H_2 concentration obtained was 26.2% at 27 kw.

Of perhaps more significance is the C_2H_2 concentration as a function of the C/H_2 ratio, shown in Fig. 21 for the results of Fig. 31. It is believed that the acetylene output is more directly related to the C/H_2 ratio than to the power, since the quantity P/G discussed above is directly proportional to the C/H_2 ratio. The correlations for the three probes seem to present a direct relationship between the two quantities, although the 19 gage probe results are a little erratic. Operation with the 0.100 in. probe at a H_2 flow rate of 1.5 lit./min. (thus giving a twofold increase in the

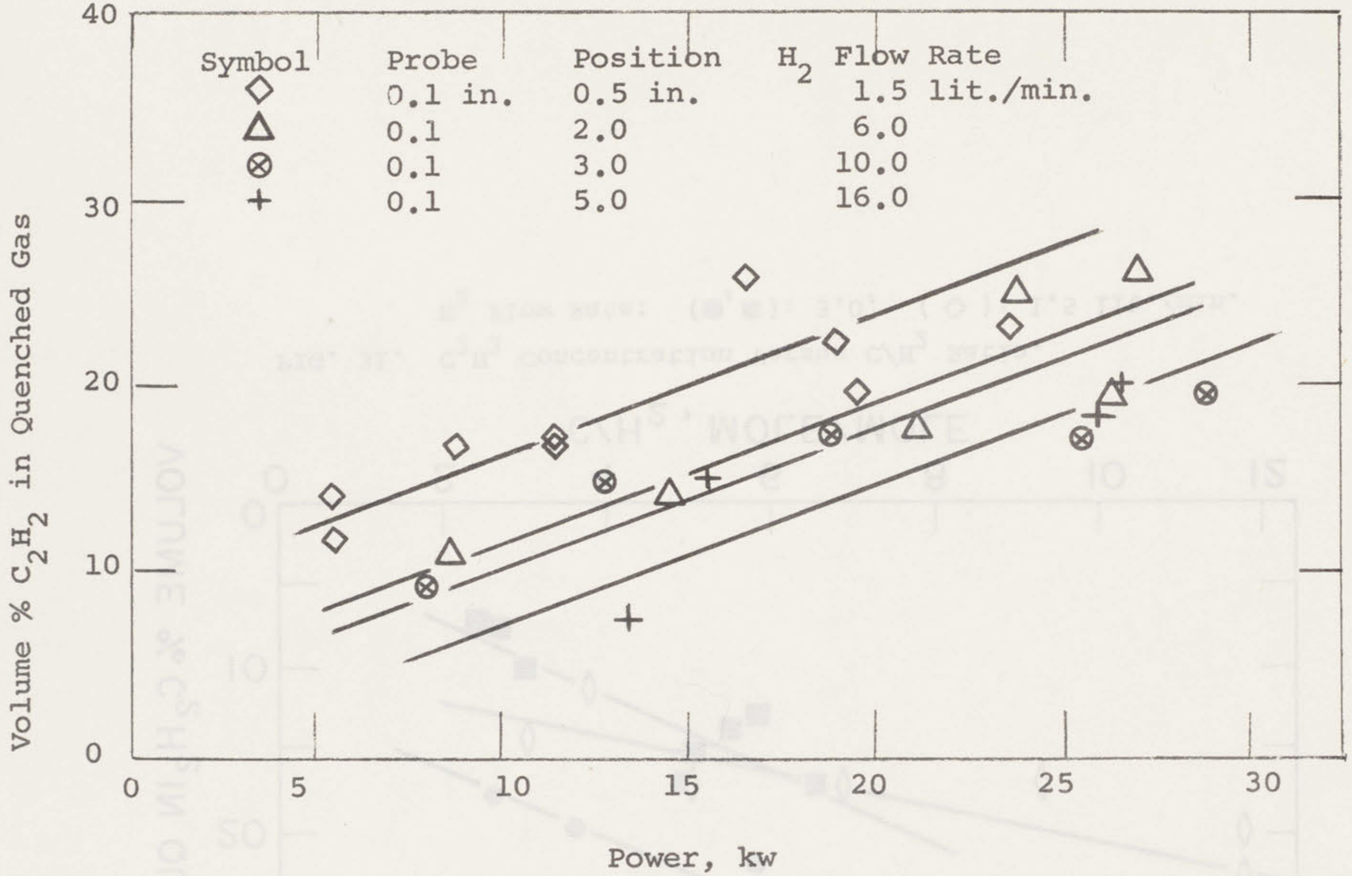


FIG. 30. Measured C_2H_2 Concentration versus Power Input for Hydrogen at Higher Flow Rates.

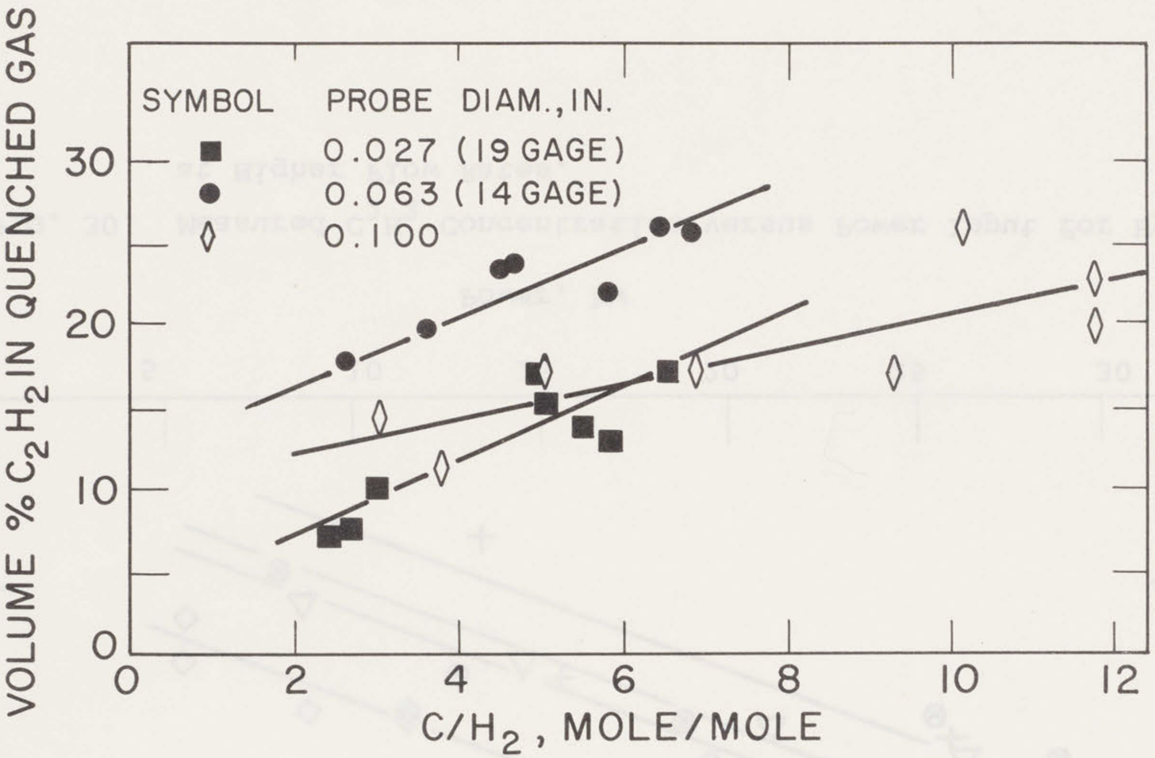


FIG. 31. C_2H_2 Concentration Versus C/H_2 Ratio.
H_2 Flow Rate: (●, ■): 3.0, (◇): 1.5 lit./min.

C/H_2 ratio for the same power input as compared with a flow rate of 3.0 lit./min.) indicates C_2H_2 concentrations equal to the ones obtained previously at 3.0 lit./min, for a slightly higher C/H_2 ratio.

At this state in the course of the present study, the computer results were analysed more carefully in an effort to determine a way of comparing theory with experiments. Referring back to Fig. 20, a cross-plot was made with the C/H_2 ratio as an independent variable and temperature as a parameter. Along an isotherm the C_2H_2 concentration does not rise appreciably with increasing carbon to hydrogen ratios, as inferred from the above graph. However, the temperature is the important factor to consider as the maximum C_2H_2 concentration occurs in a rather narrow temperature band spread.

Should the gas sampling be performed isothermally, then the C_2H_2 output could be correlated with the C/H_2 ratio for a chosen value of temperature. This was done in Fig. 32 where the solid lines represent the theoretical lines as calculated, and the points are the actual data. On this graph, only the two lower lines were plotted first, corresponding to the results of Fig. 21 for the 14 gage and 0.100 in. probes; the 19 gage probe results were omitted because of experimental difficulties encountered with this probe. It was found that the data could be matched very closely with one isotherm, even though there is scattering of the data.

These findings prompted the verification of this assumption of isothermal sampling. As seen in Fig. 32, the output gas was sampled at excessively high temperatures. The sampling temperature had to be lowered and the C/H_2 ratio had to be decreased in order to get results with more acetylene, according to the theoretical calculations. This could be accomplished in two ways: first, increasing the gas flow rate would provide a cooler flame, and second, sampling further back from the arc would also result in a lower temperature at the probe inlet.

Both techniques were tried, and again the actual data could be matched accurately with one isotherm. This is shown in Fig. 32 where the isotherm at 4,680°K represents the data taken at an H_2 flow rate of 6.0 lit./min. and sampled 2 in. from the anode tip, the 4,600°K line, the data for 10 lit./min. of H_2 and probe distance 3 in. and the 4,500°K isotherm for 16.0 lit./min. and sampling position at 5 in. back from the cathode face. This plot also shows that a very low temperature gradient exists inside the cathode pipe chamber, the main factor reducing temperature being the higher flow rates of gas fed to the arc.

It was discussed by Plooster and Reed[26] and Iwasyk[2, 16] that the probe design for optimum quenching conditions would lie somewhere between the two extremes of large tubing with high gas flow rates which can sample higher temperature gas and small tubing which reduces the gas flow through the probe and leads to a poorer quench, since any element of gas would spend more time in the region of decreasing temperature in the gas near the cold probe tip. Looking at the results of Fig. 32, it is seen that the

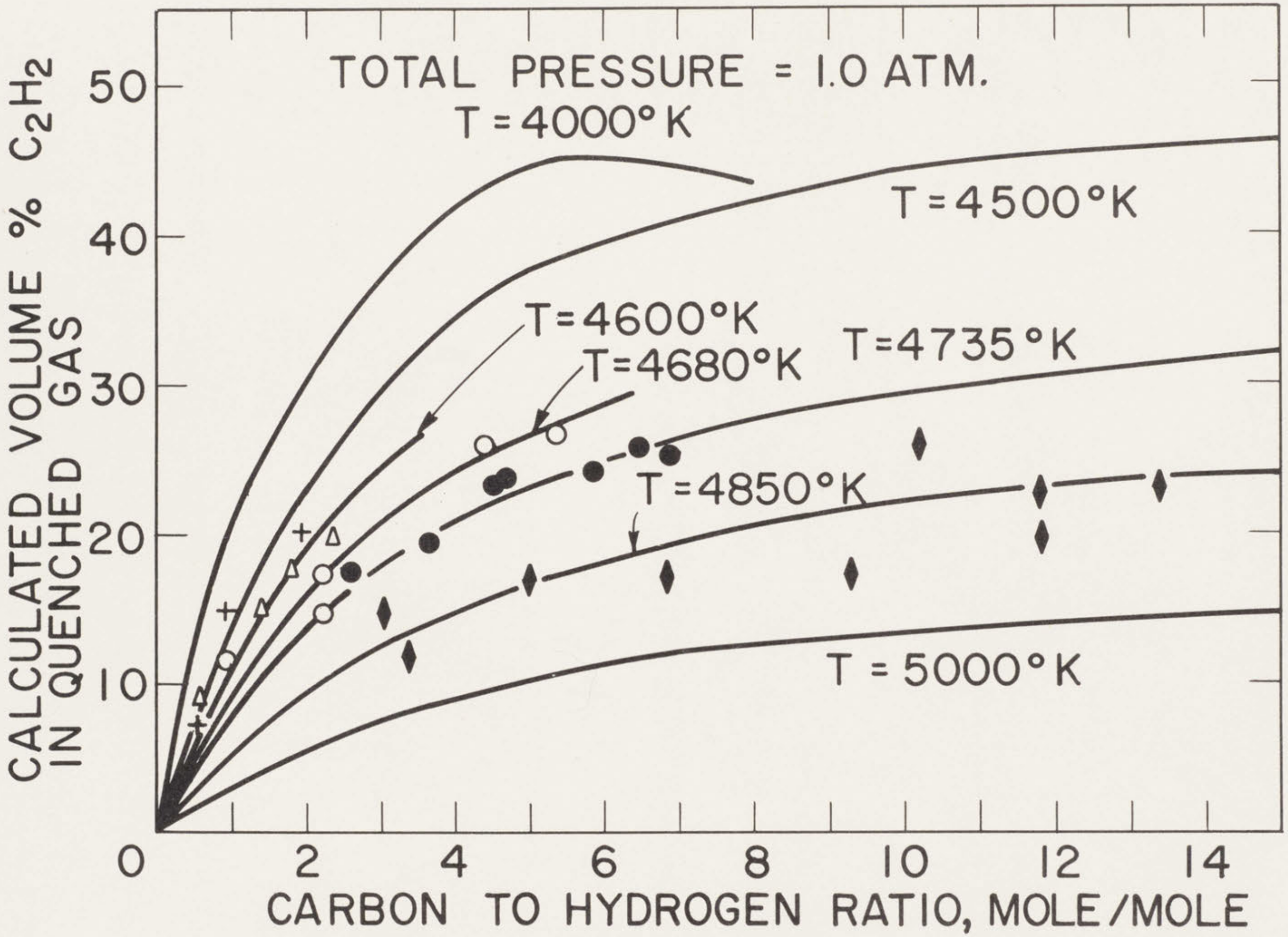


FIG. 32. Maximum C_2H_2 Content as a Function of C/H_2 Ratio for Various Quenching Temperatures at 1.0 Atm.
(♦): 1.5 lit./min., 0.1 in. Probe: 1/2 in.;
(●): 3.0 lit./min., 14 g. Probe: 1/2 in.;
(○): 6.0 lit./min., 0.1 in. Probe: 2 in.;
(△): 10.0 lit./min., 0.1 in. Probe: 3 in.;
(+): 16.0 lit./min., 0.1 in. Probe: 5 in.

optimum quenching conditions depend only on the sampling temperature and agree more or less with Plooster and Reed's assumption. A lowering of temperature could be obtained in two ways: either a higher feed rate of gas or a smaller probe diameter. However, going to a too small diameter reduces the temperature so much as to limit the C_2H_2 content to a low concentration, as deduced from Figs. 20 and 32 for temperatures below 3,500°K.

The probes used in this thesis are very efficient devices for cooling very rapidly the hot gases from the reaction zone to room temperature. Skrivan and Freeman[(29)] have disclosed that quench rates were of the order of 50 x 10^6 °C/sec., whereas calculations performed by Iwasyk[(16)] showed approximately the same order of magnitude. It is also seen that quenching occurs within the first inch of the sampling probe and that the remainder of the probe length serves mostly to cool most of the gas which is exhausted to the atmosphere.

Economic Considerations

Of economic significance, it is interesting to compute the energy necessary to produce a given C_2H_2 concentration from reactions of solid carbon and hydrogen in the high intensity arc reactor used in the present study. This is presented in Fig. 33 where the C_2H_2 content is plotted as a function of the specific energy, as defined by Eq. 34.

From this graph, it is deduced that reactions of carbon with

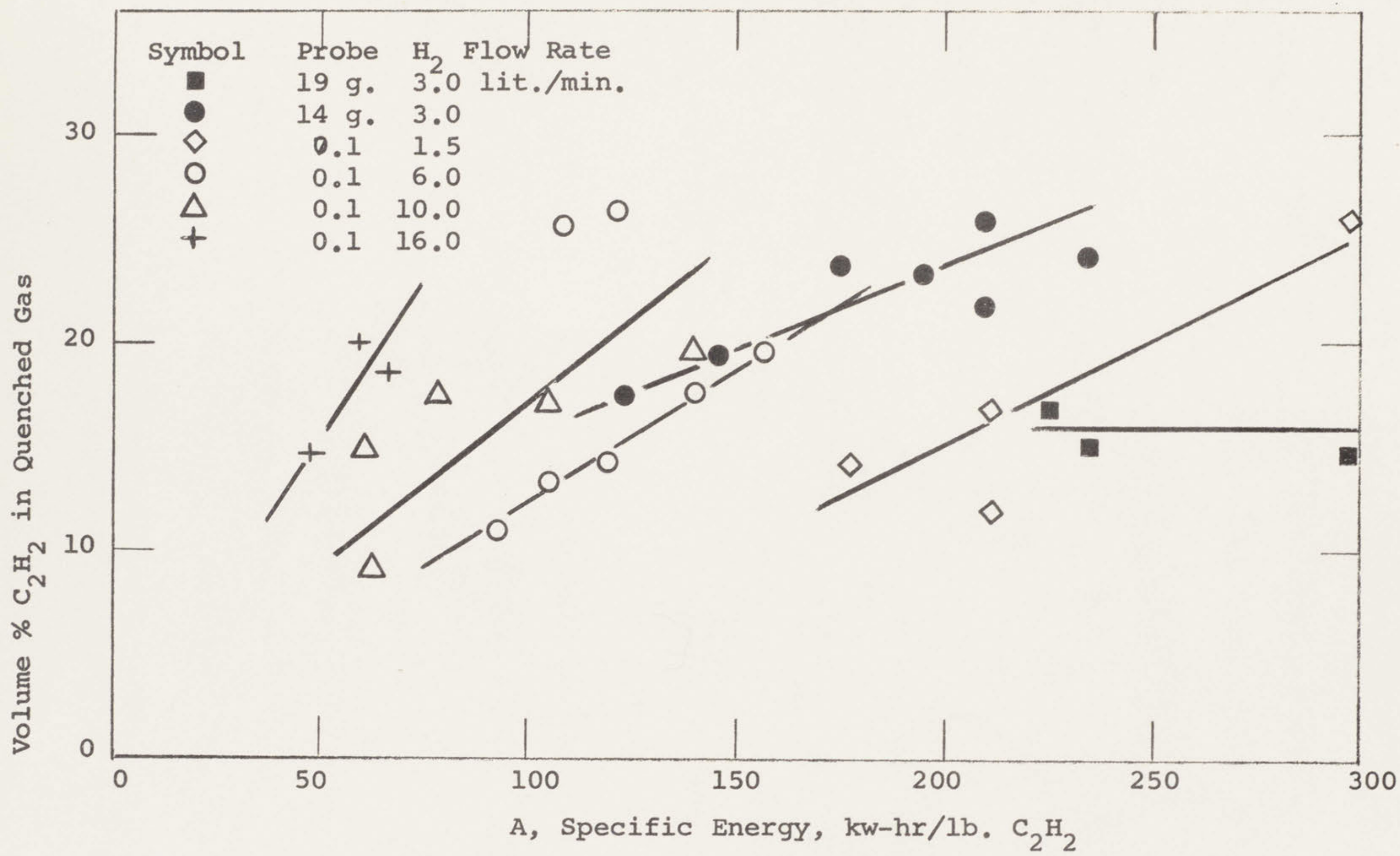


FIG. 33. Measured C_2H_2 Concentration versus Specific Energy for the Carbon Hydrogen System.

hydrogen using a high intensity arc as the source of high temperatures would not be competitive with the usual processes for making acetylene, since the latter operate between 5 and 10 kw-hr/lb. C_2H_2 whereas the lowest value obtained in this study was about 50 kw-hr/lb. C_2H_2. For a higher content of C_2H_2 in the gas, the specific energy also increases: to be competitive, the high intensity arc process would have to operate at low C_2H_2 concentrations and operate at very high flow rates of H_2 feed gas; but then the cost of separating the products is higher for this case.

It should be noted, however, that the maximum C_2H_2 concentration obtained with the carbon-hydrogen system was 26% and this is higher than any previously reported value in the literature for reactions between the elements. It should be recalled also that the two major variables controlling the C_2H_2 output are the C/H_2 ratio (where C/H_2 = 5 to 6 seems to be optimum) and the sampling temperature of the quenched gas (which has a somewhat narrow spread between 3,700 and 4,500°K) as seen in Figs. 20 and 32.

Carbon-Methane System

Operational Characteristics of the High Intensity Arc Reactor

The experiments with methane feed gas were planned along the same pattern as with H_2 feed gas. In order to produce more carbon vapors, only 3/8 in. graphite anodes were used.

The arc characteristics, shown in Fig. 26, are identical with those obtained with hydrogen for the 3/8 in. anodes. Thus the burning voltage and current for the high intensity arc used in this thesis is a function of the anode size only or, as discussed for the hydrogen results, a function of the arc length only. Although the scattering of the data is very pronounced, the trend is clearly discernable and does not depend at all on the feed rate of methane.

In Fig. 27 are compared the vaporization rates of carbon obtained with the same input of hydrogen from either methane or hydrogen, since the hydrogen flow rate is twice that of methane. It must be pointed out, however, that in that plot the anode sizes were different. The carbon vaporization rate as a function of power input for methane feed is shown in Fig. 34, where the effect of higher flow rates is to reduce somewhat the vaporization rate. The data points are still more scattered in this case than with hydrogen, but if Fig. 34 is compared with Fig. 28 the same straight line is obtained for flow rates above 5 lit./min. Thus, no dependence on the feed gas is observed in the operation of the high intensity arc reactor. The anode size, hence the arc spacing, controls the characteristics of the gaseous discharge for the geometry used in this work.

For the methane-carbon system, visual observation revealed that much more solid carbon was deposited on the inside walls of the cathode and on the walls of the reactor than was the case for hydrogen. It was found necessary to scrape a coat of carbon as thick as 1/8 in. off the inside cathode walls after each run. A rapid diffusion of carbon to the walls was also observed through the

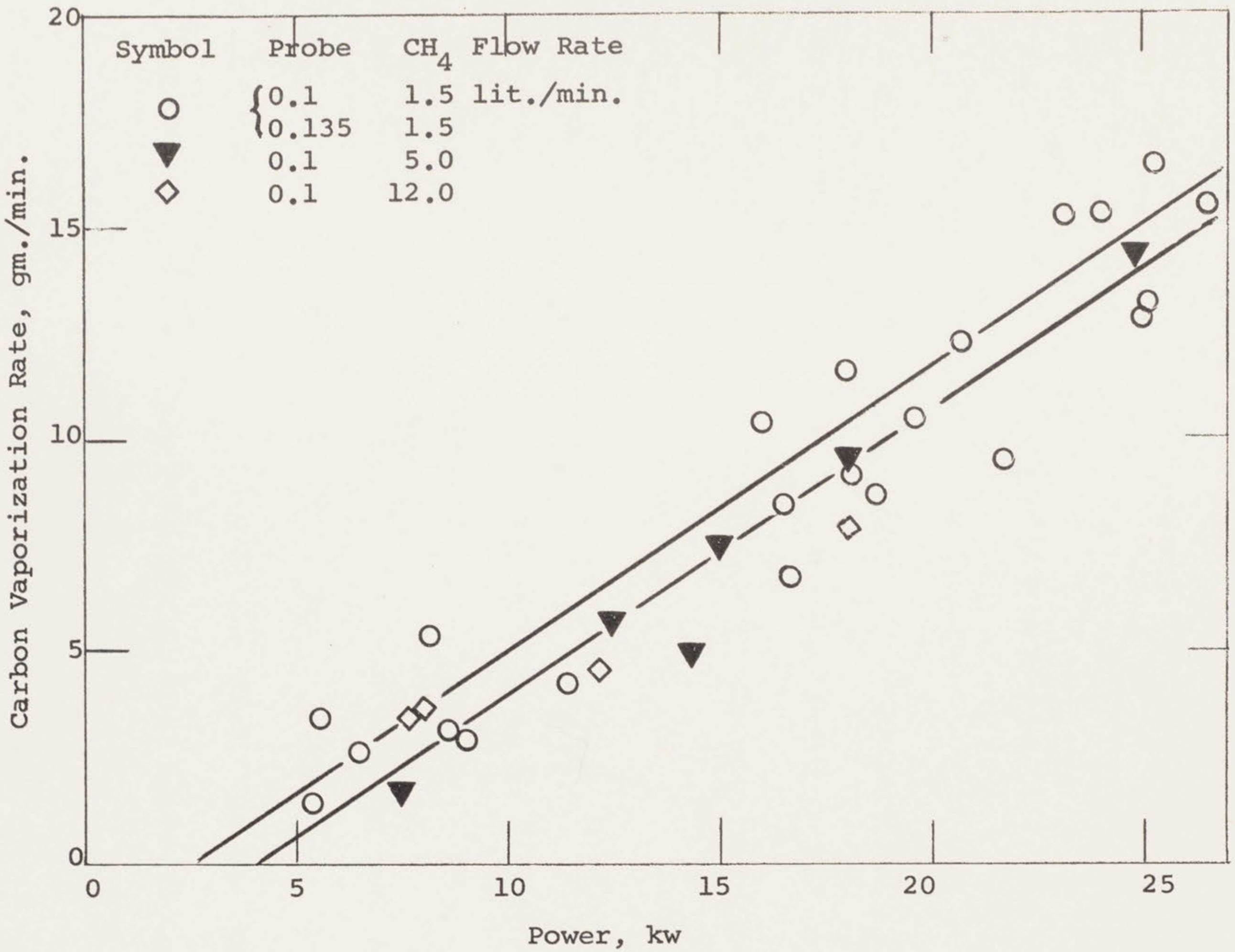


FIG. 34. Effect of Power Input on Carbon Vaporization Rate for Methane at Higher Flow Rates.

window and sometimes the view was obstructed by carbon particles condensed on the Vycor plate glass.

Effect of Power on the C_2H_2 Content of the Quenched Gas

In Fig. 35, it is seen that the acetylene content increases linearly with power input, as was the case with hydrogen. However, the slope of the line is considerably higher with methane feed gas for low flow rates. At 26 kw power input, the C_2H_2 content was 52%, compared with 26% for hydrogen feed, for a net feed rate of hydrogen to the reactor equal in both cases (1.5 lit./min. CH_4 and 3.0 lit./min. H_2). At higher methane flow rates, the slope of the lines in Fig. 35 is approximately the same as that for hydrogen, but a little steeper.

In contrast with the hydrogen runs, probe diameter appears to have no effect in the methane runs at low flow rates. However, considerable carbon deposition occurred on the inside of the probe along a distance up to 2 in. This limited the minimum operable probe diameter to about 0.1 in. Further, the carbon deposition was more severe for the larger probe than for the smaller one, so that the free opening diameters in the two cases were not so different which perhaps explain the lack of dependence of the acetylene concentration on probe diameter, or, as discussed previously, on sampling temperature. The effect of probe plugging was not evidenced at higher flow rates, partly because the sampling was performed at 5.0 in. back from the anode tip, as compared with 1/2 in. distance at

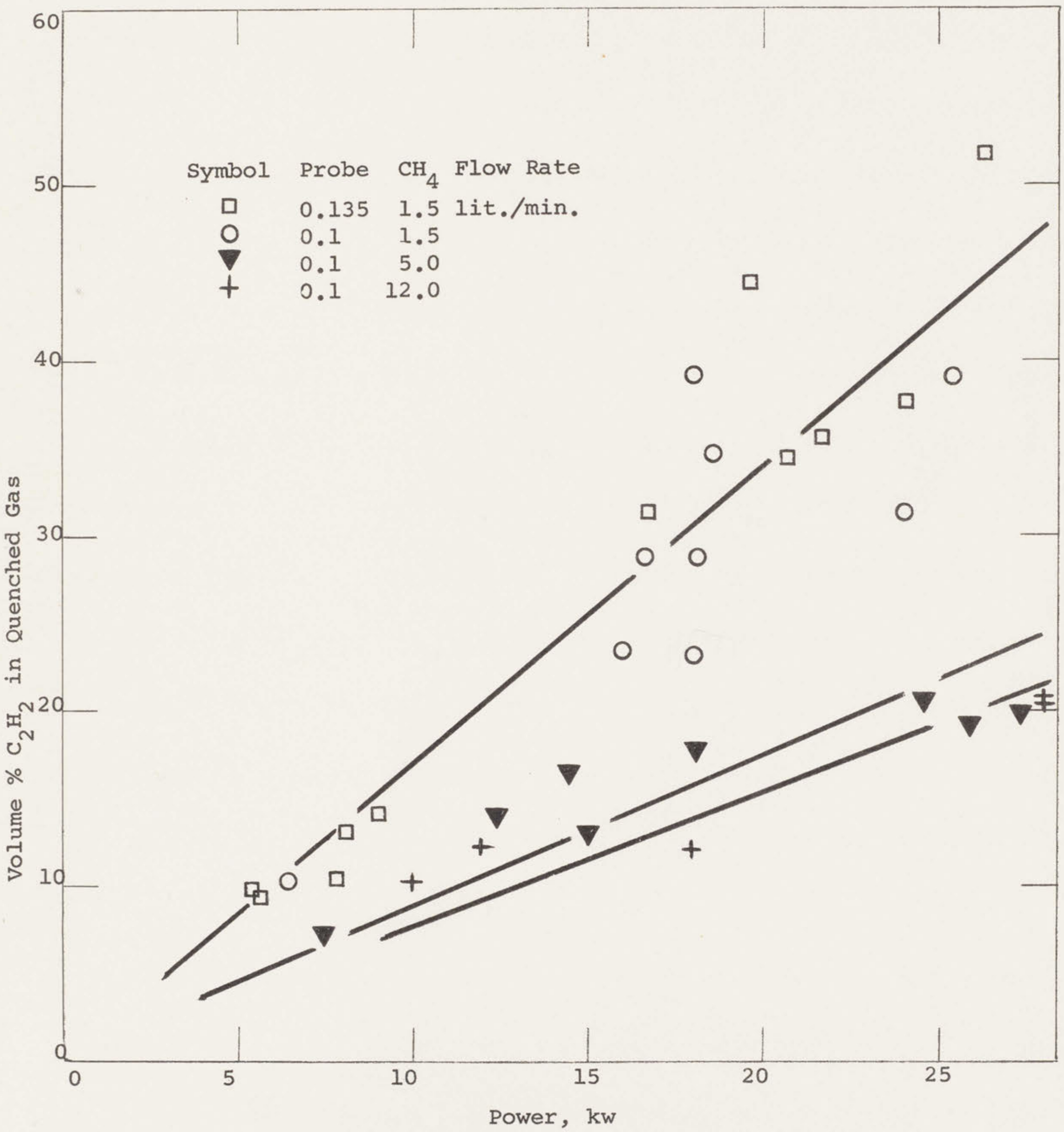


FIG. 35. Measured C_2H_2 Concentration versus Power Input for Methane

1.5 lit./min.

A similar result is shown in Fig. 36 when acetylene concentration is plotted against the C/H_2 ratio. Again, for the runs made at 1.5 lit./min., there is no apparent effect of probe diameter. As mentioned above, a considerable amount of carbon vaporized in the arc is lost through rapid diffusion to the walls, thus reducing the available C/H_2 ratio of the feed that effectively goes to the hot arc zone. This could account for the lower C_2H_2 concentration that were found in quenched samples, as compared with those predicted in Fig. 25. According to Fig. 25 and Table D-2, as much as 40-46% C_2H_2 could be expected with C/H_2 ratios between 0.8 and 0.9, if all of the available heat from reaction (30) is used for heating and cracking methane by reactions (31) and (32). The results of Fig. 36 show a situation that is far from approaching the theoretical results. But the theoretical calculations included also a null overall heat of reaction, whereas in actual operation heat losses are likely to account for a part of the heat given off by reaction (30) (see Appendix D).

Also shown in Fig. 36 is the effect of a cooler sampling temperature with increasing gas flow rate and sampling distance from the arc zone, thus exhibiting the same trend as that for the hydrogen runs in Fig. 32. Sampling at distance greater than 5 in. from the cathode face was not performed because of methane and ethylene increasing concentrations in the quenched gas, as seen in Appendix C. However, the C/H_2 ratio is twice as large and the % C_2H_2 half as

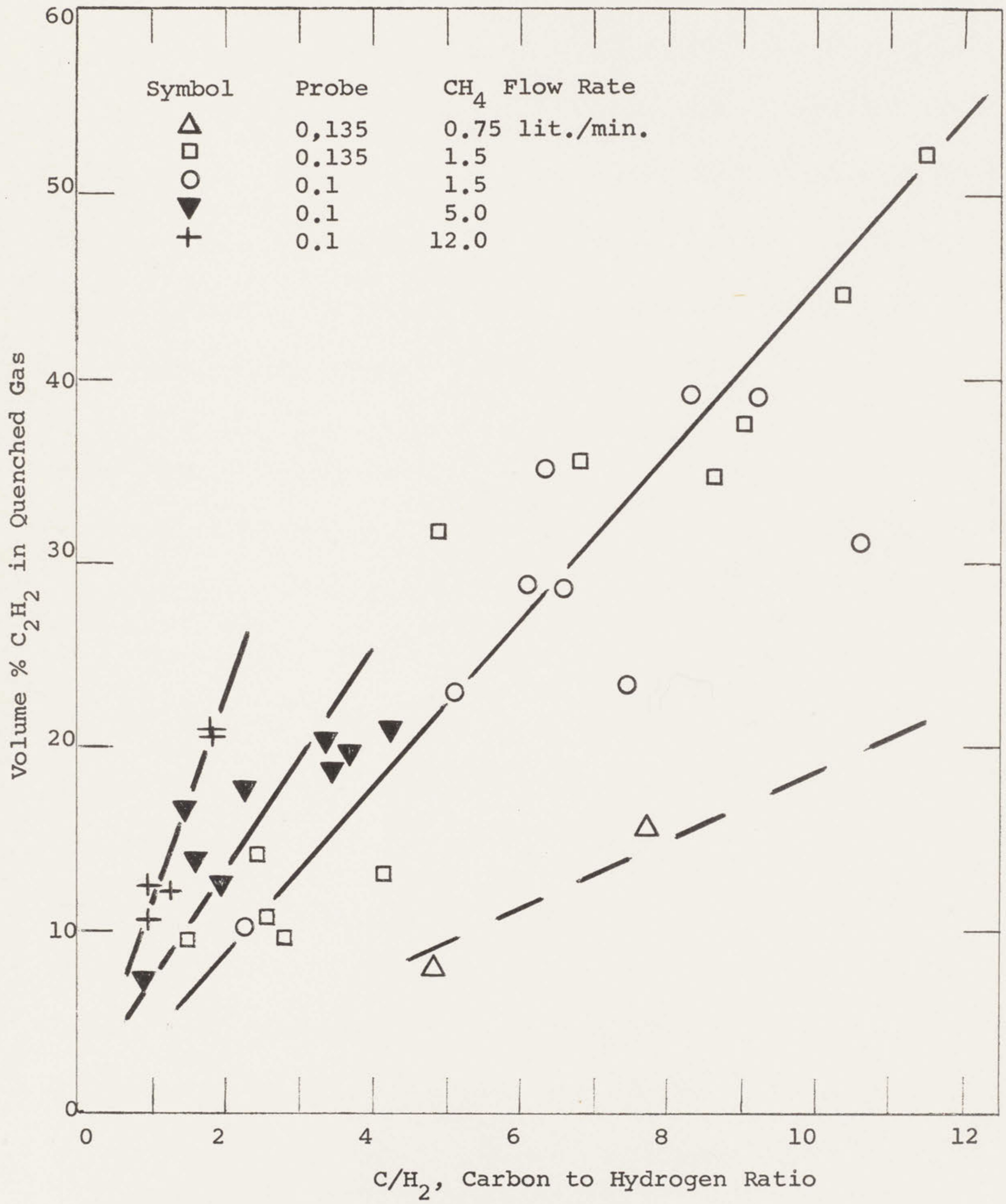


FIG. 36. Measured C_2H_2 Concentration versus C/H_2 Ratio for Methane

much for the 12.0 lit./min. methane runs as might be expected from the theoretical calculations. Higher flow rates of methane feed gas could not be accomplished, due to a slight pressure buildup in the reactor, which limited the experiments at the flow rates reported here. To attain the operating conditions suggested by the theoretical results, it was estimated that perhaps a 75 kw power input and gas flow rate of approximately 50 lit./min. would be necessary, but the actual experimental design was not adequate for these conditions.

Economic Considerations

The energy required for producing one pound of acetylene for a given C_2H_2 concentration is presented in Fig. 37 for the conditions studied in this thesis. Contrary to the hydrogen case, the specific energy becomes smaller with increasing C_2H_2 concentration in the output gas. Going to higher flow rates has the effect of decreasing also the specific energy. The lowest value was 30 kw-hr/lb. C_2H_2 obtained for a gas flow rate of 12 lit./min. giving 12% C_2H_2 in the gas. By extrapolating the lines to a value of 5 kw-hr/lb. C_2H_2 which would be competitive with the usual processes for making acetylene, it was found that the output gas had to contain as much as 85% C_2H_2. The region where such large concentrations would be expected could not be reached, because of design limitations of the reactor as discussed previously.

It should be noted here again that the 52% C_2H_2 obtained with the carbon-methane system is the highest content of acetylene

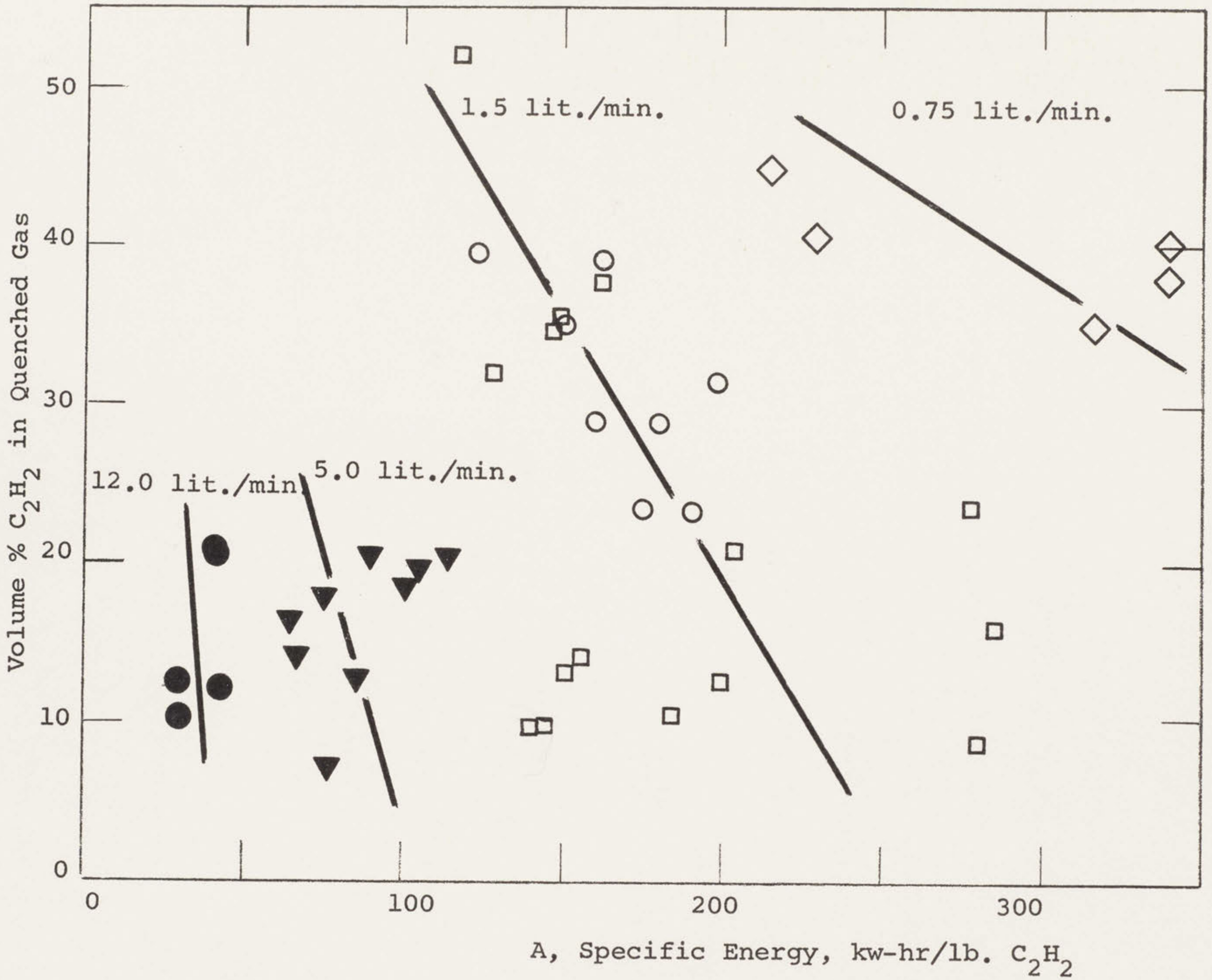


FIG. 37. Measured C_2H_2 Concentration versus Specific Energy for the Carbon-Methane System.

reported so far for the cracking reaction of methane, which cannot yield more than 25% C_2H_2 (1), or for reaction of carbon with methane which did not produce more than 12% C_2H_2 in the product gas (35), whereas usual processes using methane or natural gas do not yield more than 17% C_2H_2 (12, 4).

Comparison of the Methane and Hydrogen Systems

As a last point of interest, consider how efficiently the vaporized carbon was utilized in the high intensity arc process using both hydrogen and methane as feed gases.

In Fig. 38 is plotted the average efficiency of carbon utilization for acetylene production as a function of gas flow rate. Ω average, as defined by Eq. 26, is computed here according to the procedure described in Appendix E with results reported in Table E-1. As shown in this graph, more vaporized carbon is used when the flow rate of gas is increased and methane gas exhibits a greater utilization of carbon than hydrogen.

However, both systems are highly inefficient because about 75% to 90% of the carbon is lost through recondensation on the reactor or cathode walls for the best operating conditions. This is also evidenced by the actual observation of the diffusion of vaporized carbon to the cold reactor walls and the necessity of cleaning the reactor after every run.

The rather low value of Ω average can explain the low output of C_2H_2 in the quenched gas, since most, if not all, of the carbon in the gas was found as acetylene. Fig. 38 also points out that a

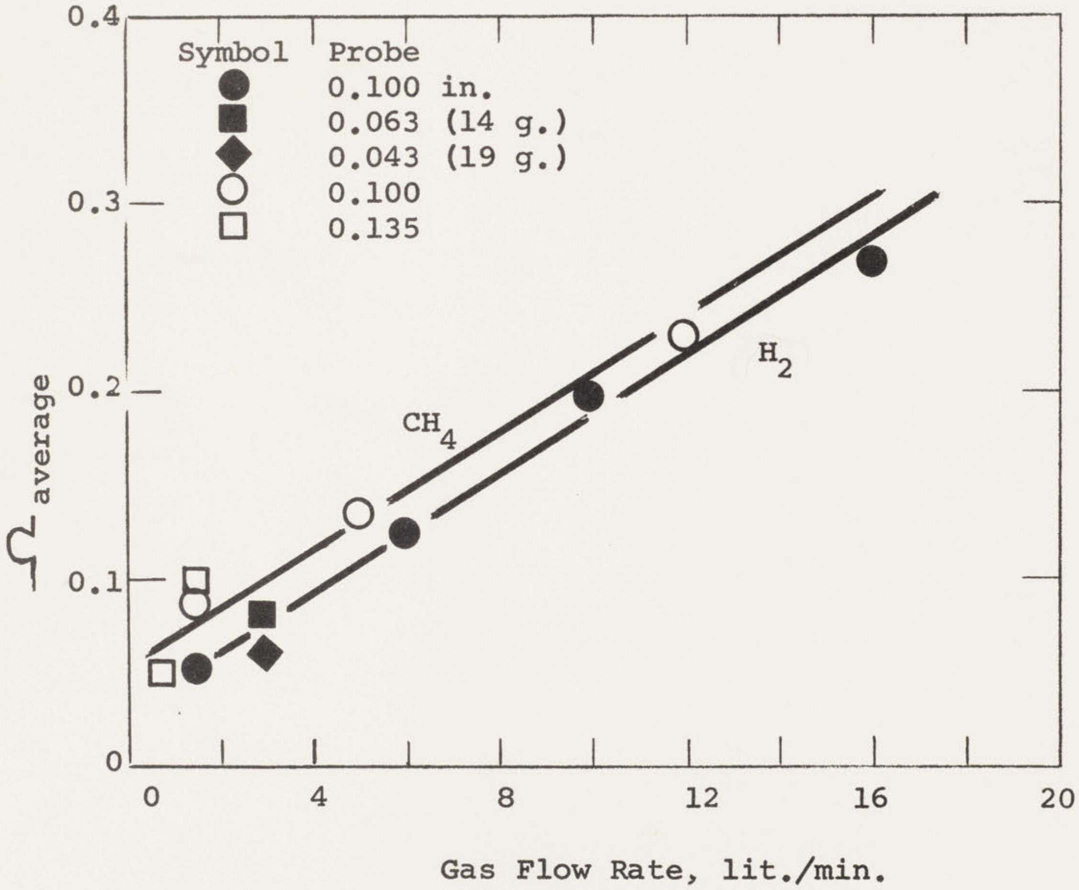


FIG. 38. Efficiency of Carbon Utilization as a Function of Gas Flow Rate for Hydrogen and Methane.

greater acetylene content can be obtained with the carbon-methane system, perhaps because of the carbon contribution by the methane molecule. The results also show that larger acetylene concentrations can be expected at higher flow rates if enough carbon vapor is provided to the arc zone for reaction with the gas.

V. CONCLUSIONS AND RECOMMENDATIONS

(1) Experiments performed in a high intensity arc reactor showed that a maximum of 26% C_2H_2 was obtained in the quenched gas for reactions of solid carbon with hydrogen and that a maximum of 52% C_2H_2 was attained with the carbon-methane system. These values are higher than any reported values in the literature for the cases considered, but still below the C_2H_2 content theoretically possible.

(2) The postulation of the existence of the C_2H radical by Plooster and Reed[26] and Iwasyk[2, 16], as precursor to C_2H_2 formation, has been supported experimentally by the number of times a C_2H_2 concentration larger than 10-14% (calculated without taking into account the C_2H radical[16, 19]) has been obtained at one atmosphere pressure.

(3) The analysis of the carbon-hydrogen system reveals that radicals C_2H, C_3H, and C_4H probably exist in considerable concentration at high temperature and that it is important to consider these species when attempting to predict the composition of the quenched gas from a high temperature reactor.

(4) It was also shown that the arc reactor was an inefficient device for utilizing the carbon vapor in order to make acetylene. The efficiency of carbon utilization increases, however, with larger gas flow rates. If further experiments are planned for either or both systems, it is recommended that a large capacity reactor be used in order to convert more efficiently carbon vapors into C_2H_2

at high flow rates of feed gas and high power.

(5) Operation of the high intensity arc reactor at pressures above one atmosphere should provide a higher C_2H_2 concentration, but is not recommended because of the dangers inherent in handling C_2H_2 under high pressures. Low pressure operation could be performed, however, in order to ascertain the basic theory of the carbon-hydrogen system.

Appendix A

(1) Calculations of carbon-hydrogen system, according to Iwasyk's scheme[2, 16] of seven components. Two values of ΔH°_{of} for C_2H were used: 115 kcal./mole (Table A-1) and 110 kcal./mole (Table A-2).

Table A-1

Equilibrium Composition of the Carbon-Hydrogen System at One Atmosphere $C/H_2 = 1.0$; Maximum C_2H_2 Concentration in Quenched Gas. $\Delta H^\circ_{of} = 115$ kcal./mole C_2H

T, °K	C_1	C_2	C_3	H	H_2	C_2H	C_2H_2	Max. C_2H_2 in Quenched Gas
				Heterogeneous Region				
2500	-	-	-	0.0246	0.965	0.0002	0.0098	0.0102
2750	-	-	-	0.0652	0.911	0.0013	0.0228	0.0250
3000	-	-	-	0.1415	0.807	0.0060	0.0449	0.0551
3250	-	-	0.0018	0.2630	0.647	0.0186	0.0693	0.1027
3500	0.0027	0.0046	0.0138	0.3945	0.448	0.0519	0.0853	0.1810
3750	0.0141	0.0263	0.0741	0.4840	0.234	0.0944	0.0723	0.280
				Homogeneous Region				
3800	0.0165	0.0299	0.0715	0.515	0.220	0.0865	0.0587	0.250
3900	0.0252	0.0392	0.0715	0.577	0.179	0.0708	0.0368	0.199
4100	0.0480	0.0580	0.0652	0.644	0.119	0.0502	0.0155	0.136
4300	0.0802	0.0738	0.515	0.699	0.073	0.0288	0.0054	0.078
4500	0.1250	0.0781	0.0323	0.709	0.043	0.0143	0.0018	0.040

Table A-2

Equilibrium Composition of the Carbon-Hydrogen System at one Atmosphere, $C/H_2 = 1.0$; Maximum C_2H_2 Concentration in Quenched Gas. $\Delta H^{\circ}_{of} = 110$ kcal./mole C_2H

T, °K	C_1	C_2	C_3	H	H_2	C_2H	C_2H_2	Max. C_2H_2 in Quenched Gas
				Heterogeneous Region				
2500	-	-	-	0.0246	0.965	0.0002	0.0098	0.0102
2750	-	-	-	0.0651	0.908	0.0003	0.0228	0.0265
3000	-	-	-	0.1410	0.802	0.0139	0.0446	0.0634
3250	0.0004	0.0005	0.0018	0.259	0.627	0.0472	0.0671	0.1560
3500	0.0027	0.0046	0.0138	0.375	0.404	0.1237	0.0770	0.2750
3600	0.0052	0.0052	0.0257	0.413	0.310	0.1643	0.0710	0.3510
				Homogeneous Region				
3700	0.0094	0.0154	0.0388	0.454	0.247	0.1791	0.0563	0.380
3900	0.0216	0.0288	0.0447	0.566	0.172	0.1410	0.0260	0.302
4100	0.0417	0.0437	0.0428	0.634	0.116	0.1102	0.0113	0.243
4300	0.071	0.0580	0.0377	0.686	0.071	0.0695	0.0041	0.163
4500	0.117	0.0684	0.0265	0.704	0.042	0.0392	0.0013	0.098

(2) Computer Program

A program to be processed by the IBM 7090 computer of the M.I.T. Computation Center was written in order to get (a) the equilibrium constants needed for calculating the equilibrium composition diagrams, (b) the mole fractions of the components in the heterogeneous region and (c) in the homogeneous region. The temperature range 2,000 to 6,000°K was covered. Since the heterogeneous and homogeneous regions are discussed in details in Appendix B, only the part related to the determination of the equilibrium constants will be examined here.

The free energy function as given by Bauer and Duff[(3)] can be calculated as a function of temperature by using a series of constants based on estimates of interatomic distances and vibrational energies of the molecules. These constants are given in Table A-3 together with the heat of formation at 0°K in the ideal state for thirteen components.

The equation used is as follows:

$$- (F^\circ_T - H^\circ_O)/RT = a\ (\ln T - 1) + bT + \frac{cT^2}{2} + \frac{dT^3}{3} + \frac{eT^4}{4} + k \qquad (1)$$

In the program, a subroutine named FREENE was written to give this function by reading directly the data of Table A-3 fed to the computer. The results from the computer are reported in Table A-4, for the temperature range 2,000 - 6,000°K.

In the same subroutine, another quantity labeled LOG 10 K (comp.) was also calculated, which gave for every component the results of the following computation:

$$\text{LOG 10 K (comp)} = \left(-\frac{(F^\circ_T - H^\circ_0)}{RT} - \frac{\Delta H^\circ_{of}}{RT}\right) \times 0.434295 \qquad (2)$$

where the figures 0.434295 represent the logarithm in base 10 of e = 2.71828, the base of natural logarithms. This quantity will be used later in the other subroutine to obtain the equilibrium constants of the sixteen equations that are also given in Table A-3.

According to Rossini[28], the logarithms of the equilibrium constants for such reactions as Reactions 1 to 16 of Table A-3 can be obtained by

$$\log K_{reaction} = \log K_{products} - \log K_{reactants} \qquad (3)$$

whereas the whole expression reverts to

$$-2.303 \log_{10} K_{reaction} = \sum\left[\left(\frac{\Delta H^\circ_{of}}{RT}\right)_{products} - \left(\frac{\Delta H^\circ_{0f}}{RT}\right)_{reactants}\right]$$

$$+ \sum\left[\Delta\left(\frac{F^\circ_T - H^\circ_0}{RT}\right)_{products} - \Delta\left(\frac{F^\circ_T - H^\circ_0}{RT}\right)_{reactants}\right] \qquad (4)$$

Instead of computing Eq. 4 separately for each reaction, it was found simpler to calculate separate functions for each component, as represented by Eq. 2, and use them as expressed in Eq. 3. For instance, the logarithm in base 10 of reaction 6 of Table A-3 would be computed as follows:

$$\log_{10} K_6 = \log K_{(H)} + \log K_{(C_2H)} - \log K_{(C_2H_2)} \qquad (5)$$

Results computed by the subroutine FREENE for Eq. 2 above are presented in Table A-5; this is an intermediary step.

The next subroutine, labeled EQCTS, takes the results of the first one in order to obtain the logarithms of the equilibrium constants for the sixteen reactions considered. It performs the calculations expressed by Eq. 3 (similar to Eq. 5) to give LOG $K_{(reaction)}$ and also converts the logarithms to the equilibrium constants K's.

The computer results are presented in Table A-6 for LOG $K_{(reaction)}$ and in Table A-7 for K's.

The last values of Table A-7 are hereafter used in Appendix B to calculate the equilibrium diagrams of the carbon-hydrogen system at high temperatures.

COMPUTER PROGRAM

```
      DIMENSION E(10,15),TEMP(50),TOTALP(9),RATIO(9),S(50),REVERS(50),FE
     1FMIN(50,15),DELTA(50,15),XOG10K(50,15),F(50,15),XOGK(20,50),QONSK(
     220,50),Q(20,50)
 2000 FORMAT(4E18.8)
 1001 FORMAT(6F12.1)
 1002 FORMAT(5F7.2)
 1003 FORMAT(8F9.1)
 1010 FORMAT (7E16.8, F8.1)
 2006 FORMAT(56HOCONSTANTS USED IN CALCULATING THE FREE ENERGY FUNCTIONS
     1)
 1008 FORMAT(13F8.5,F8.3,F8.1)
 1006 FORMAT(119HO   YH       YH2      YC2H     YC2H2    YC3H     YC4H     YC4
     1H2   YCH      YCH2     YC1      YC2      YC3      YSUM     C/H2    TEMP)
 3005 FORMAT(27HOCARBON TO HYDROGEN RATIO =,F8.3)
 1111 FORMAT(42H1CARBON-HYDROGEN SYSTEM,HOMOGENEOUS REGION)
 2007 FORMAT(120HO         A                B                C
     1 D              E                K                H              COMP)
 2050 FORMAT(59H1CALCULATIONS OF THE FREE ENERGY FUNCTIONS    - (F   -H   )
     1/RT)
 2003 FORMAT(105H1COMPONENTS ARE (1)H2 (2)H (3)C2H (4)C2H2 (5)C S (6)C1
     1(7)C2 (8)C3 (9)C3H (10)C4H (11)CH (12)CH2 (13)C4H2)
 2051 FORMAT(114HO           H2               H                C2H              C
     12H2            C S              C1               1/T          TEMP)
 2052 FORMAT(114H1           C2               C3               C3H              C
     14H            CH               CH2              C4H2         TEMP)
 1004 FORMAT(8F15.7)
 2004 FORMAT(42H1LOGARITHMS OF K FOR INDIVIDUAL COMPONENTS)
 2005 FORMAT(60HOLOG 10 K(COMP) = ( -(F -H )/RT - (DELTA H )/RT ) X 0.43
     14295)
 2008 FORMAT(113HO       LOG K H2         LOG K H          LOG K C2H        LOG
     1K C2H2       LOG K C S        LOG K C1         1/T          TEMP)
 2009 FORMAT(113H1       LOG K C2         LOG K C3         LOG K C3H        LOG
     1 K C4H       LOG K CH         LOG K CH2        LOG K C4H2   TEMP)
 2010 FORMAT(95H1CALCULATIONS OF THE EQUILIBRIUM CONSTANTS FOR THE FOLLO
     1WING REACTIONS (DATA OF BAUER AND DUFF))
 3000 FORMAT(31H1THIS IS A CHECK ON SUBROUTINES)
 2011 FORMAT(50HO                             C S = C1            K1)
 2012 FORMAT(50HO                            2C S = C2            K2)
 2013 FORMAT(50HO                            3C S = C3            K3)
 2014 FORMAT(50HO                       2C S + H2 = C2H2          K4)
 2015 FORMAT(50HO                              H2 = 2H            K5)
 2016 FORMAT(50HO                            C2H2 = C2H + H       K6)
 2017 FORMAT(50HO                        3C S + H = C3H           K7)
 2018 FORMAT(50HO                        4C S + H = C4H           K8)
 2019 FORMAT(50HO                           2 C2H = C4H2          K9)
 2020 FORMAT(51HO                              C3 = C2 + C1       K10)
 2021 FORMAT(51HO                              C2 = 2 C1          K11)
 2022 FORMAT(51HO                         C2 + H2 = C2H2          K12)
 2023 FORMAT(51HO                          C3 + H = C3H           K13)
 2024 FORMAT(51HO                 C2 + 2 C1 + H = C4H           K14)
 2025 FORMAT(51HO                          C1 + H = CH            K15)
 2026 FORMAT(51HO                         C1 + 2H = CH2           K16)
 2060 FORMAT(64H1LOGARITHMS OF THE EQUILIBRIUM CONSTANTS FOR THE ABOVE R
     1EACTIONS)
 2061 FORMAT(119HO      LOG K1           LOG K2           LOG K3           LOG K4
     1           LOG K5           LOG K6           LOG K7           LOG K8       TEMP)
 2062 FORMAT(119H1      LOG K9           LOG K10          LOG K11          LOG K1;
     1           LOG K13          LOG K14          LOG K15          LOG K16      TEMP)
 2063 FORMAT(46H1EQUILIBRIUM CONSTANTS FOR THE ABOVE REACTIONS)
 2064 FORMAT(119HO      K1               K2               K3               K4
     1           K5               K6               K7               K8           TEMP)
 2065 FORMAT(119H1      K9               K10              K11              K12
     1           K13              K14              K15              K16          TEMP)
 1005 FORMAT(8F14.7, F8.1)
 3006 FORMAT(8E14.6,F8.1)
 1000 FORMAT(44H1CARBON-HYDROGEN SYSTEM,HETEROGENEOUS REGION)
 2071 FORMAT(23HOTOTAL PRESSURE (ATM) =,F6.2)
 2072 FORMAT(118HO  Y H        Y H2       Y C2H      Y C2H2     Y C3H      Y C4H
     1  Y C4H2     Y C1       Y C2       Y C3       Y SUM        C/H2       TEMP)
 1007 FORMAT(11F9.5,F10.3,F10.1)
      READ 2000, ((E(I,J),I=1,8),J=1,13)
      READ 1001,(TEMP(L),L=1,42,1)
      READ 1002,(TOTALP(N),N=1,5,1)
      READ 1003,(RATIO(M),M=1,8,1)
      PRINT 2003
      PRINT 2006
      PRINT 2007
      PRINT 1010, ((E(I,J),I=1,8),J=1,13)
  101 CALL FREENE(E,S,TEMP,REVERS,FEFMIN,DELTA,XOG10K,8,13,42)
      PRINT 2050
      PRINT 2051
      PRINT 1004,((FEFMIN(L,J),J=1,6),REVERS(L),TEMP(L),L=1,42)
      PRINT 2052
      PRINT 1004,((FEFMIN(L,J),J=7,13),TEMP(L),L=1,42)
      PRINT 2004
      PRINT 2005
      PRINT 2008
      PRINT 1004,((XOG10K(L,J),J=1,6),REVERS(L),TEMP(L),L=1,42)
      PRINT 2009
      PRINT 1004,((XOG10K(L,J),J=7,13),TEMP(L),L=1,42)
      DO 25 J=1,13,1
      DO 25 L=1,42,1
      F(L,J) = XOG10K(L,J)
   25 CONTINUE
      PRINT 3000
      PRINT 2004
      PRINT 2005
      PRINT 2008
      PRINT 1004,((F(L,J),J=1,6),REVERS(L),TEMP(L),L=1,42)
      PRINT 2009
      PRINT 1004,((F(L,J),J=7,13),TEMP(L),L=1,42)
  102 CALL EQCTS(F,XOGK,QONSK,16,42,13)
      PRINT 2010
      PRINT 2011
      PRINT 2012
      PRINT 2013
      PRINT 2014
      PRINT 2015
      PRINT 2016
      PRINT 2017
      PRINT 2018
      PRINT 2019
```

```
      PRINT 2020
      PRINT 2021
      PRINT 2022
      PRINT 2023
      PRINT 2024
      PRINT 2025
      PRINT 2026
      PRINT 2060
      PRINT 2061
      PRINT 1005,((XOGK(K,L),K=1,8),TEMP(L),L=1,42)
      PRINT 2062
      PRINT 1005,((XOGK(K,L),K=9,16),TEMP(L),L=1,42)
      PRINT 2063
      PRINT 2064
      PRINT 3006,((QONSK(K,L),K=1.8).TEMP(L),L=1,42)
      PRINT 2065
      PRINT 3006,((QONSK(K,L),K=9,16),TEMP(L),L=1,42)
      DO 26 K=1,16,1
      DO 26 L=1,42,1
      Q(K,L) = QONSK(K,L)
   26 CONTINUE
      PRINT 3000
      PRINT 2063
      PRINT 2064
      PRINT 3006,((Q(K,L),K=1,8),TEMP(L),L=1,42,1)
      PRINT 2065
      PRINT 3006,((Q(K,L),K=9,16),TEMP(L),L=1,42,1)
   22 DO 29 N=1,5,1
      PRINT 1000
      PRINT 2071, TOTALP(N)
      PRINT 2072
   51 DO 29 L=1,42,1
      TP = TOTALP(N)
      A = (1. + Q(4,L))/Q(5,L) + Q(9,L)*((Q(6,L)*Q(4,L)/Q(5,L))**2)
      B = 1. + Q(4,L)*Q(6,L)/Q(5,L) + Q(7,L) + Q(8,L)
      C = Q(1,L) + Q(2,L) + Q(3,L) - TP
      IF (C)28,29,29
   28 PH = (-B + SQRTF(B**2 - 4.*A*C))/(2.*A)
      YH = PH/TP
      YH2 = ((PH**2)/Q(5,L))/TP
      YC2H = (Q(6,L)*Q(4,L)*PH/Q(5,L))/TP
      YC2H2 = (Q(4,L)*(PH**2)/Q(5,L))/TP
      YC3H = (Q(7,L)*PH)/TP
      YC4H = (Q(8,L)*PH)/TP
      YC4H2 = Q(9,L)*((Q(6,L)*Q(4,L)/Q(5,L))**2)*(PH**2)/TP
      YC1 = Q(1,L)/TP
      YC2 = Q(2,L)/TP
      YC3 = Q(3,L)/TP
      YSUM = YH + YH2 + YC2H + YC2H2 + YC3H + YC4H + YC4H2 + YC1 + YC2 +
     1YC3
      CARBON =  YC1 + 2.*(YC2 + YC2H + YC2H2) + 3.*(YC3 + YC3H) + 4.*(YC
     14H + YC4H2)
      HYDROG = YH2 + YC2H2 + YC4H2 + 0.5*(YH + YC2H + YC3H + YC4H)
      COVRH2 = CARBON/HYDROG
      PRINT 1007,YH,YH2,YC2H,YC2H2,YC3H,YC4H,YC4H2,YC1,YC2,YC3,YSUM,COVR
     1H2,TEMP(L)
   29 CONTINUE
   18 DO 39 N=1,5,1
   19 DO 39 M=1,8,1
      PRINT 1111
      PRINT 2071,TOTALP(N)
      PRINT 3005,RATIO(M)
      PRINT 1006
      X = 0.0000009091
      DO 39 L=11,42,1
      TP=TOTALP(N)
      R=RATIO(M)
   40 X=1.1*X
   50 A1=(1. + Q(5,L)*Q(16,L)*X + Q(12,L)*(X**2)/Q(11,L) + (Q(9,L)/Q(5,L
     1))*((Q(6,L)*Q(12,L)/Q(11,L))**2)*(X**4))/Q(5,L)
      B1=1. + Q(15,L)*X + Q(6,L)*Q(12,L)*(X**2)/(Q(5,L)*Q(11,L)) + Q(13,
     1L)*(X**3)/(Q(10,L)*Q(11,L)) + Q(14,L)*(X**4)/Q(11,L)
      C1=X + (X**2)/Q(11,L) + (X**3)/(Q(10,L)*Q(11,L)) - TP
      IF(C1)41,39,39
   41 Y1PH=(-B1 + SQRTF(B1**2 - 4.*A1*C1))/(2.*A1)
      AM=Q(12,L)*(X**2)/(Q(5,L)*Q(11,L)) + 3.*Q(9,L)*((Q(6,L)*Q(12,L)/(Q
     1(5,L)*Q(11,L)))**2)*(X**4) - 1./Q(5,L)
      BM=Q(6,L)*Q(12,L)*(X**2)/(Q(5,L)*Q(11,L)) + 2.*Q(13,L)*(X**3)/(Q(1
     10,L)*Q(11,L)) + 3.*Q(14,L)*(X**4)/Q(11,L) - 1.0
      CM=(X**2)/Q(11,L) + 2.*(X**3)/(Q(10,L)*Q(11,L)) + TP
      A2=A1*(R - 1.0) - AM
      B2 = B1*(R/2. - 1.) - BM
      C2 = -(C1 + CM)
      IF(A2)42,52,62
   42 IF(B2)80,80,43
   80 X=0.9*X
      GO TO 50
   43 Y2PH2 = (-B2 - SQRTF(B2**2 - 4.*A2*C2))/(2.*A2)
      IF(Y2PH2)46,46,44
   44 IF(Y2PH2 - TP)45,46,46
   45 Y2PH = Y2PH2
      GO TO 70
   52 IF(B2)40,40,53
   53 Y2PHA0 = -C2/B2
   54 Y2PH = Y2PHA0
      GO TO 70
   62 IF(B2)46,63,46
   63 Y2PHB0 = SQRTF(-C2/A2)
   64 Y2PH = Y2PHB0
      GO TO 70
   46 Y2PH1 = (-B2 + SQRTF(B2**2 - 4.*A2*C2))/(2.*A2)
   47 Y2PH = Y2PH1
   70 SUB = Y1PH - Y2PH
      IF(SUB)72,81,71
   71 IF(SUB-0.0005)81,81,73
   73 SUB1 = SUB
      X1=X
      GO TO 40
   72 IF(SUB+0.0005)74,81,81
   74 SUB2=SUB
      X2=X
      X=(X1*SUB2 - X2*SUB1)/(SUB2 - SUB1)
```

```
      GO TO 50
   81 YPH = (Y1PH + Y2PH)/2.
      YH = YPH/TP
      YH2 = ((YPH**2)/Q(5,L))/TP
      YC2H = (Q(6,L)*Q(12,L)*(X**2)*YPH/(Q(5,L)*Q(11,L)))/TP
      YC4H2=(Q(9,L)*((Q(6,L)*Q(12,L)/(Q(5,L)*Q(11,L)))**2)*(X**4)*(YPH**
     12))/TP
      YC2H2=(Q(12,L)*(X**2)*(YPH**2)/(Q(5,L)*Q(11,L)))/TP
      YC3H=(Q(13,L)*(X**3)*YPH/(Q(10,L)*Q(11,L)))/TP
      YC4H=(Q(14,L)*(X**4)*YPH/Q(11,L))/TP
      YCH=(Q(15,L)*X*YPH)/TP
      YCH2=(Q(16,L)*X*(YPH**2))/TP
      YC2=((X**2)/Q(11,L))/TP
      YC3=((X**3)/(Q(11,L)*Q(10,L)))/TP
      YC1=X/TP
      YSUM=YH + YH2 + YC2H + YC2H2 + YC3H + YC4H + YC4H2 + YCH + YCH2 +
     1YC1 + YC2 + YC3
      CARBON = YC1 + YCH + YCH2 + 2.*(YC2 + YC2H + YC2H2) + 3.*(YC3 + YC
     13H) + 4.*(YC4H + YC4H2)
      HYDROG = (YH + YCH + YC2H + YC3H + YC4H)/2. + YH2 + YCH2 + YC2H2 +
     1 YC4H2
      COVRH2 = CARBON/HYDROG
      PRINT 1008,YH,YH2,YC2H,YC2H2,YC3H,YC4H,YC4H2,YCH,YCH2,YC1,YC2,YC3,
     1YSUM,COVRH2,TEMP(L)
   39 CONTINUE
      CALL EXIT
      END(1,1,0,0,0,0,0,0,0,0,0,0,0,0,0)
```

```
      SUBROUTINE FREENE(U,T,TETA,SEVERS,PEFMIN,GELTA,ZOG10K,I,J,L)
      DIMENSION U(10,15),T(50),TETA(50),SEVERS(50),PEFMIN(50,15),GELTA(5
     10,15),ZOG10K(50,15)
      DO 20 L=1,42,1
      DO 20 J=1,13,1
      T(L) = TETA(L)
      SEVERS(L) = 1.0/T(L)
      PEFMIN(L,J) = U(1,J)*(LOGF(T(L)) - 1.) + U(2,J)*T(L) + U(3,J)*(T(L
     1)**2)/2. + U(4,J)*(T(L)**3)/3. + U(5,J)*(T(L)**4)/4. + U(6,J)
      GELTA(L,J) = (U(7,J)/T(L))/1.987
      ZOG10K(L,J) = (PEFMIN(L,J) - GELTA(L,J))*0.43429448
   20 CONTINUE
      RETURN
      END(1,0,0,0,0,0,0,0,0,0,0,0,0,0,0)
```

```
      SUBROUTINE EQCTS(D,ZOGK,CONSK,K,L,J)
      DIMENSION D(50,15),ZOGK(20,50),CONSK(20,50)
      DO 100 L=1,42,1
   99 Z=10.
    1 ZOGK(1,L) = D(L,6) - D(L,5)
      CONSK(1,L) = Z**ZOGK(1,L)
    2 ZOGK(2,L) = D(L,7) - 2.*D(L,5)
      CONSK(2,L) = Z**ZOGK(2,L)
    3 ZOGK(3,L) = D(L,8) - 3.*D(L,5)
      CONSK(3,L) = Z**ZOGK(3,L)
    4 ZOGK(4,L) = D(L,4) - D(L,1) - 2.*D(L,5)
      CONSK(4,L) = Z**ZOGK(4,L)
    5 ZOGK(5,L) = 2.*D(L,2) - D(L,1)
      CONSK(5,L) = Z**ZOGK(5,L)
    6 ZOGK(6,L) = D(L,3) + D(L,2) -D(L,4)
      CONSK(6,L) = Z**ZOGK(6,L)
    7 ZOGK(7,L) = D(L,9) -3.*D(L,5) -D(L,2)
      CONSK(7,L) = Z**ZOGK(7,L)
    8 ZOGK(8,L) = D(L,10) - 4.*D(L,5) - D(L,2)
      CONSK(8,L) = Z**ZOGK(8,L)
    9 ZOGK(9,L) = D(L,13) - 2.*D(L,3)
      CONSK(9,L) = Z**ZOGK(9,L)
   10 ZOGK(10,L) = D(L,6) + D(L,7) - D(L,8)
      CONSK(10,L) = Z**ZOGK(10,L)
   11 ZOGK(11,L) = 2.*D(L,6) - D(L,7)
      CONSK(11,L) = Z**ZOGK(11,L)
   12 ZOGK(12,L) = D(L,4) - D(L,1) - D(L,7)
      CONSK(12,L) = Z**ZOGK(12,L)
   13 ZOGK(13,L) = D(L,9) - D(L,2) -D(L,8)
      CONSK(13,L) = Z**ZOGK(13,L)
   14 ZOGK(14,L) = D(L,10) - D(L,7) - 2.*D(L,6) - D(L,2)
      CONSK(14,L) = Z**ZOGK(14,L)
   15 ZOGK(15,L) = D(L,11) - D(L,6) - D(L,2)
      CONSK(15,L) = Z**ZOGK(15,L)
   16 ZOGK(16,L) = D(L,12) - D(L,6) - 2.*D(L,2)
      CONSK(16,L) = Z**ZOGK(16,L)
  100 CONTINUE
      RETURN
      END(1,0,0,0,0,0,0,0,0,0,0,0,0,0,0)
```

TABLE A-3 .(COMPUTER OUTPUT)

COMPONENTS ARE (1)H2 (2)H (3)C2H (4)C2H2 (5)C S (6)C1 (7)C2 (8)C3 (9)C3H (10)C4H (11)CH (12)CH2 (13)C4H2

CONSTANTS USED IN CALCULATING THE FREE ENERGY FUNCTIONS

A	B	C	D	E	K	ΔH°_{0f}	COMP
0.32375731E 01	0.23187578E-03	0.50938301E-08	-0.39631803E-11	0.29310414E-15	-0.28803999E 01	0.	1.0
0.24999999E 01	0.	0.	0.	0.	-0.45931002E-00	0.51620000E 05	2.0
0.35134807E 01	0.17945357E-02	-0.44103585E-06	0.57630263E-10	-0.30599071E-14	0.46019890E 01	0.11669999E 06	3.0
0.39188681E 01	0.29099295E-02	-0.70821407E-06	0.88418587E-10	-0.44052944E-14	0.44387525E-00	0.54329000E 05	4.0
0.16176599E 01	0.38497601E-03	-0.32116701E-07	0.11281200E-11	0.	-0.86884999E 01	0.	5.0
0.26167393E 01	-0.10759307E-03	0.38601043E-07	-0.45084646E-11	0.18258099E-15	0.41143999E 01	0.16958000E 06	6.0
0.46082999E 01	-0.43094741E-03	0.25534049E-06	-0.50605532E-10	0.34887750E-14	-0.18514978E 01	0.19800000E 05	7.0
0.45770170E 01	0.11354603E-02	-0.20837176E-06	0.17096995E-10	-0.49578196E-15	-0.99026691E 00	0.18900000E 06	8.0
0.39647123E 01	0.31001513E-02	-0.75517813E-06	0.92928222E-10	-0.45250160E-14	0.37058850E 01	0.12710000E 06	9.0
0.58736851E 01	0.37016899E-02	-0.90964157E-06	0.11093365E-09	-0.52750488E-14	-0.34665898E 01	0.15400000E 06	10.0
0.28257000E 01	0.10263324E-02	-0.27358155E-06	0.37943584E-10	-0.20471105E-14	0.51903998E 01	0.14039999E 06	11.0
0.29730733E 01	0.19864158E-02	-0.43346947E-06	0.54597060E-10	-0.29521265E-14	0.50497741E 01	0.66800000E 05	12.0
0.63751955E 01	0.48240731E-02	-0.12354182E-05	0.15976494E-09	-0.81617652E-14	-0.81913174E 01	0.11130000E 06	13.0

CALCULATIONS OF THE EQUILIBRIUM CONSTANTS FOR THE FOLLOWING REACTIONS (DATA OF BAUER AND DUFF) (3)

C S = C1	K1
2C S = C2	K2
3C S = C3	K3
2C S + H2 = C2H2	K4
H2 = 2H	K5
C2H2 = C2H + H	K6
3C S + H = C3H	K7
4C S + H = C4H	K8
2 C2H = C4H2	K9
C3 = C2 + C1	K10
C2 = 2 C1	K11
C2 + H2 = C2H2	K12
C3 + H = C3H	K13
C2 + 2 C1 + H = C4H	K14
C1 + H = CH	K15
C1 + 2H = CH2	K16

TABLE A-4. (COMPUTER OUTPUT)

CALCULATIONS OF THE FREE ENERGY FUNCTIONS $-(F_T^\circ - H_0^\circ)/RT$

H2	H	C2H	C2H2	C S	C1	1/T	TEMP
18.9550464	16.0429456	30.6425729	30.9335327	2.6982423	21.2379642	0.0005000	2000.0
19.1358266	16.1649213	30.9246237	31.3039119	2.8095562	21.3610518	0.0004762	2100.0
19.3091805	16.2812212	31.1963034	31.6614430	2.9169239	21.4784193	0.0004545	2200.0
19.4757574	16.3923507	31.4583972	32.0070372	3.0206742	21.5905893	0.0004348	2300.0
19.6361237	16.4987497	31.7115979	32.3415022	3.1210945	21.6980155	0.0004167	2400.0
19.7907751	16.6008046	31.9565206	32.6655574	3.2184368	21.8010960	0.0004000	2500.0
19.9401503	16.6988564	32.1937146	32.9798512	3.3129240	21.9001813	0.0003846	2600.0
20.0846372	16.7932072	32.4236722	33.2849650	3.4047542	21.9955812	0.0003704	2700.0
20.2245808	16.8841264	32.6468401	33.5814281	3.4941034	22.0875719	0.0003571	2800.0
20.3602901	16.9718544	32.8636203	33.8697228	3.5811298	22.1763990	0.0003448	2900.0
20.4920418	17.0566082	33.0743804	34.1502881	3.6659759	22.2622833	0.0003333	3000.0
20.6200876	17.1385827	33.2794557	34.4235320	3.7487701	22.3454235	0.0003226	3100.0
20.7446523	17.2179546	33.4791536	34.6898246	3.8296293	22.4259987	0.0003125	3200.0
20.8659408	17.2948840	33.6737566	34.9495115	3.9086587	22.5041709	0.0003030	3300.0
20.9841402	17.3695161	33.8635249	35.2029119	3.9859551	22.5800867	0.0002941	3400.0
21.0994205	17.4419849	34.0486994	35.4503231	4.0616074	22.6538808	0.0002857	3500.0
21.2119386	17.5124123	34.2295041	35.6920233	4.1356964	22.7256758	0.0002778	3600.0
21.3218365	17.5809097	34.4061456	35.9282675	4.2082965	22.7955830	0.0002703	3700.0
21.4292469	17.6475801	34.5788174	36.1593008	4.2794770	22.8637052	0.0002632	3800.0
21.5342917	17.7125192	34.7476993	36.3853478	4.3493016	22.9301376	0.0002564	3900.0
21.6370823	17.7758136	34.9129581	36.6066217	4.4178288	22.9949667	0.0002500	4000.0
21.7377231	17.8375449	35.0747519	36.8233223	4.4851137	23.0582726	0.0002439	4100.0
21.8363116	17.8977888	35.2332268	37.0356364	4.5512077	23.1201296	0.0002381	4200.0
21.9329381	17.9566154	35.3885212	37.2437434	4.6161580	23.1806073	0.0002326	4300.0
22.0276847	18.0140891	35.5407634	37.4478073	4.6800086	23.2397685	0.0002273	4400.0
22.1206312	18.0702713	35.6900730	37.6479869	4.7428020	23.2976730	0.0002222	4500.0
22.2118511	18.1252184	35.8365650	37.8444290	4.8045763	23.3543761	0.0002174	4600.0
22.3014128	18.1789839	35.9803452	38.0372748	4.8653687	23.4099298	0.0002128	4700.0
22.3893809	18.2316175	36.1215129	38.2266560	4.9252136	23.4643815	0.0002083	4800.0
22.4758170	18.2831657	36.2601628	38.4126968	4.9841434	23.5177770	0.0002041	4900.0
22.5607784	18.3336725	36.3963823	38.5955153	5.0421885	23.5701578	0.0002000	5000.0
22.6443183	18.3831789	36.5302534	38.7752199	5.0993782	23.6215639	0.0001961	5100.0
22.7264891	18.4317243	36.6618538	38.9519172	5.1557399	23.6720324	0.0001923	5200.0
22.8073385	18.4793448	36.7912550	39.1257043	5.2112991	23.7215984	0.0001887	5300.0
22.8869133	18.5260751	36.9185257	39.2966738	5.2660807	23.7702942	0.0001852	5400.0
22.9652567	18.5719478	37.0437274	39.4649119	5.3201082	23.8181515	0.0001818	5500.0
23.0424111	18.6169944	37.1669197	39.6305013	5.3734041	23.8651996	0.0001786	5600.0
23.1184154	18.6612432	37.2881565	39.7935162	5.4259889	23.9114659	0.0001754	5700.0
23.1933079	18.7047224	37.4074888	39.9540277	5.4778832	23.9569757	0.0001724	5800.0
23.2671249	18.7474585	37.5249634	40.1121030	5.5291064	24.0017564	0.0001695	5900.0
23.3399010	18.7894762	37.6406221	40.2678027	5.5796765	24.0458295	0.0001667	6000.0
23.4116695	18.8307993	37.7545056	40.4211845	5.6296115	24.0892174	0.0001639	6100.0

C2	C3	C3H	C4H	CH	CH2	C4H2	TEMP
28.0952327	31.1199605	34.7962184	41.1638503	25.4410658	27.9144166	41.4614277	2000.0
28.3110588	31.4208629	35.1800208	41.6762037	25.6396656	28.1896579	42.0617399	2100.0
28.5173132	31.7099431	35.5505757	42.1700864	25.8304374	28.4557176	42.6408553	2200.0
28.7148695	31.9881537	35.9088101	42.6468396	26.0140014	28.7132671	43.2002749	2300.0
28.9044859	32.2563281	36.2555470	43.1076474	26.1909034	28.9628990	43.7413316	2400.0
29.0868220	32.5152001	36.5915208	43.5535669	26.3616266	29.2051401	44.2652140	2500.0
29.2624567	32.7654219	36.9173932	43.9855399	26.5266027	29.4404626	44.7729907	2600.0
29.4318991	33.0075727	37.2337584	44.4044218	26.6862180	29.6692891	45.2656283	2700.0
29.5955989	33.2421708	37.5411577	44.8109794	26.8408196	29.8920023	45.7440028	2800.0
29.7539575	33.4696851	37.8400841	45.2059164	26.9907219	30.1089489	46.2089128	2900.0
29.9073317	33.6905355	38.1309900	45.5898709	27.1362109	30.3204455	46.6610894	3000.0
30.0560422	33.9051070	38.4142900	45.9634304	27.2775464	30.5267808	47.1012073	3100.0
30.2003772	34.1137471	38.6903677	46.3271365	27.4149661	30.7282197	47.5298858	3200.0
30.3405960	34.3167725	38.9595766	46.6814857	27.5486896	30.9250066	47.9476986	3300.0
30.4769342	34.5144749	39.2222466	47.0269394	27.6789155	31.1173656	48.3551754	3400.0
30.6096065	34.7071238	39.4786820	47.3639278	27.8058307	31.3055060	48.7528176	3500.0
30.7388103	34.8949661	39.7291708	47.6928501	27.9296064	31.4896209	49.1410813	3600.0
30.8647220	35.0782294	39.9739780	48.0140777	28.0504005	31.6698885	49.5203986	3700.0
30.9875076	35.2571259	40.2133546	48.3279586	28.1683612	31.8464753	49.8911738	3800.0
31.1073201	35.4318528	40.4475360	48.6348209	28.2836258	32.0195408	50.2537847	3900.0
31.2243001	35.6025939	40.6767402	48.9349680	28.3963208	32.1892262	50.6085863	4000.0
31.3385785	35.7695179	40.9011755	49.2286887	28.5065668	32.3556690	50.9559097	4100.0
31.4502785	35.9327869	41.1210389	49.5162554	28.6144738	32.5189958	51.2960701	4200.0
31.5595143	36.0925522	41.3365130	49.7979212	28.7201469	32.6793265	51.6293626	4300.0
31.6663940	36.2489510	41.5477729	50.0739260	28.8236830	32.8367710	51.9560637	4400.0
31.7710192	36.4021192	41.7549801	50.3444986	28.9251733	32.9914346	52.2764349	4500.0
31.8734858	36.5521789	41.9582925	50.6098523	29.0247035	33.1434155	52.5907221	4600.0
31.9738872	36.6992502	42.1578555	50.8701897	29.1223526	33.2928047	52.8991599	4700.0
32.0723104	36.8434443	42.3538084	51.1257043	29.2181971	33.4396887	53.2019653	4800.0
32.1688399	36.9848661	42.5462804	51.3765745	29.3123066	33.5841479	53.4993453	4900.0
32.2635574	37.1236162	42.7353973	51.6229744	29.4047470	33.7262578	53.7914915	5000.0
32.3565407	37.2597880	42.9212747	51.8650627	29.4955795	33.8660889	54.0785890	5100.0
32.4478664	37.3934741	43.1040235	52.1029963	29.5848627	34.0037084	54.3608069	5200.0
32.5376072	37.5247593	43.2837481	52.3369179	29.6726506	34.1391754	54.6383066	5300.0
32.6258378	37.6537251	43.4605465	52.5669661	29.7589927	34.2725492	54.9112396	5400.0
32.7126265	37.7804499	43.6345086	52.7932668	29.8439369	34.4038815	55.1797452	5500.0
32.7980456	37.9050093	43.8057256	53.0159469	29.9275277	34.5332236	55.4439569	5600.0
32.8821626	38.0274739	43.9742761	53.2351184	30.0098047	34.6606197	55.7039962	5700.0
32.9650464	38.1479101	44.1402369	53.4508896	30.0908055	34.7861118	55.9599743	5800.0
33.0467634	38.2663851	44.3036804	53.6633615	30.1705663	34.9097404	56.2119989	5900.0
33.1273823	38.3829608	44.4646726	53.8726320	30.2491190	35.0315385	56.4601669	6000.0
33.2069697	38.4976988	44.6232762	54.0787883	30.3264930	35.1515398	56.7045660	6100.0

TABLE A-5. (COMPUTER OUTPUT)

LOGARITHMS OF K FOR INDIVIDUAL COMPONENTS

LOG 10 K(COMP) = $(-(F_T^\circ - H_0^\circ)/RT - (\text{DELTA } H_{0f}^\circ)/RT) \times 0.434295$

LOG K H2	LOG K H	LOG K C2H	LOG K C2H2	LOG K C S	LOG K C1	1/T	TEMP
8.2320719	1.3261244	0.5544615	7.4969738	1.1718317	-9.3088442	0.0005000	2000.0
8.3105837	1.6477282	1.2842612	7.9405555	1.2201748	-8.3728937	0.0004762	2100.0
8.3858703	1.9424460	1.9543471	8.3528547	1.2668039	-7.5196544	0.0004545	2200.0
8.4582138	2.2136828	2.5722615	8.7376198	1.3118621	-6.7384348	0.0004348	2300.0
8.5278600	2.4642840	3.1443062	9.0979953	1.3554741	-6.0203173	0.0004167	2400.0
8.5950242	2.6966471	3.6757894	9.4366404	1.3977493	-5.3578041	0.0004000	2500.0
8.6598971	2.9128070	4.1712151	9.7558222	1.4387846	-4.7445450	0.0003846	2600.0
8.7226470	3.1145021	4.6344302	10.0574850	1.4786659	-4.1751256	0.0003704	2700.0
8.7834237	3.3032269	5.0687433	10.3433083	1.5174698	-3.6449000	0.0003571	2800.0
8.8423615	3.4802735	5.4770138	10.6147517	1.5552649	-3.1498605	0.0003448	2900.0
8.8995805	3.6467653	5.8617283	10.8730891	1.5921131	-2.6865298	0.0003333	3000.0
8.9551901	3.8036833	6.2250588	11.1194410	1.6280701	-2.2518768	0.0003226	3100.0
9.0092878	3.9518887	6.5689123	11.3547939	1.6631868	-1.8432468	0.0003125	3200.0
9.0619628	4.0921403	6.8949698	11.5800232	1.6975089	-1.4583051	0.0003030	3300.0
9.1132962	4.2251095	7.2047191	11.7959075	1.7310783	-1.0949900	0.0002941	3400.0
9.1633618	4.3513929	7.4994829	12.0031432	1.7639336	-0.7514731	0.0002857	3500.0
9.2122277	4.4715226	7.7804409	12.2023548	1.7961101	-0.4261283	0.0002778	3600.0
9.2599558	4.5859740	8.0486482	12.3941028	1.8276399	-0.1175041	0.0002703	3700.0
9.3066036	4.6951737	8.3050531	12.5788958	1.8585532	0.1756995	0.0002632	3800.0
9.3522239	4.7995065	8.5505087	12.7571921	1.8888776	0.4546503	0.0002564	3900.0
9.3968652	4.8993185	8.7857856	12.9294093	1.9186386	0.7203997	0.0002500	4000.0
9.4405730	4.9949237	9.0115813	13.0959270	1.9478601	0.9738977	0.0002439	4100.0
9.4833895	5.0866069	9.2285297	13.2570920	1.9765643	1.2160043	0.0002381	4200.0
9.5253538	5.1746271	9.4372073	13.4132224	2.0047719	1.4475006	0.0002326	4300.0
9.5665017	5.2592201	9.6381396	13.5646082	2.0325019	1.6690965	0.0002273	4400.0
9.6068679	5.3406020	9.8318065	13.7115177	2.0597727	1.8814397	0.0002222	4500.0
9.6464843	5.4189699	10.0186489	13.8541967	2.0866009	2.0851223	0.0002174	4600.0
9.6853803	5.4945054	10.1990700	13.9928725	2.1130027	2.2806864	0.0002128	4700.0
9.7235844	5.5673748	10.3734406	14.1277550	2.1389930	2.4686285	0.0002083	4800.0
9.7611231	5.6377316	10.5421032	14.2590388	2.1645859	2.6494061	0.0002041	4900.0
9.7980214	5.7057174	10.7053723	14.3869036	2.1897946	2.8234395	0.0002000	5000.0
9.8343023	5.7714627	10.8635386	14.5115151	2.2146318	2.9911168	0.0001961	5100.0
9.8699887	5.8350890	11.0168718	14.6330299	2.2391093	3.1527965	0.0001923	5200.0
9.9051011	5.8967082	11.1656204	14.7515910	2.2632384	3.3088102	0.0001887	5300.0
9.9396600	5.9564246	11.3100159	14.8673326	2.2870298	3.4594649	0.0001852	5400.0
9.9736841	6.0143350	11.4502721	14.9803792	2.3104936	3.6050462	0.0001818	5500.0
10.0071918	6.0705298	11.5865884	15.0908475	2.3336397	3.7458191	0.0001786	5600.0
10.0402000	6.1250930	11.7191496	15.1988450	2.3564770	3.8820299	0.0001754	5700.0
10.0727254	6.1781030	11.8481282	15.3044726	2.3790144	4.0139086	0.0001724	5800.0
10.1047838	6.2296335	11.9736847	15.4078245	2.4012603	4.1416693	0.0001695	5900.0
10.1363900	6.2797530	12.0959680	15.5089879	2.4232227	4.2655126	0.0001667	6000.0
10.1675587	6.3285258	12.2151179	15.6080450	2.4449092	4.3856256	0.0001639	6100.0

LOG K C2	LOG K C3	LOG K C3H	LOG K C4H	LOG K CH	LOG K CH2	LOG K C4H2	TEMP
-9.4366206	-7.1394424	1.2218135	1.0475022	-4.2945544	4.8229082	5.8431637	2000.0
-8.3124969	-6.0252064	2.0499249	2.0714304	-3.4776620	5.2900710	6.6830810	2100.0
-7.2862020	-5.0055188	2.8121533	3.0144806	-2.7305916	5.7216438	7.4611377	2200.0
-6.3451384	-4.0683036	3.5167441	3.8867387	-2.0444095	6.1220404	8.1848537	2300.0
-5.4787956	-3.2034792	4.1705906	4.6966377	-1.4116593	6.4949530	8.8605310	2400.0
-4.6783339	-2.4025635	4.7795019	5.4512890	-0.8260661	6.8434950	9.4934937	2500.0
-3.9362651	-1.6583655	5.3484108	6.1567304	-0.2823111	7.1703158	10.0882739	2600.0
-3.2462035	-0.9647485	5.8815327	6.8181280	0.2241447	7.4776759	10.6487566	2700.0
-2.6026697	-0.3164442	6.3824946	7.4399247	0.6971992	7.7675251	11.1782925	2800.0
-2.0009343	0.2910999	6.8544347	8.0259690	1.1402189	8.0415510	11.6797892	2900.0
-1.4368944	0.8618339	7.3000838	8.5796088	1.5561274	8.3012228	12.1557832	3000.0
-0.9069720	1.3992076	7.7218288	9.1037732	1.9474757	8.5478258	12.6085005	3100.0
-0.4080337	1.9062436	8.1217680	9.6010379	2.3165004	8.7824905	13.0399010	3200.0
0.0626774	2.3856033	8.5017519	10.0736747	2.6651718	9.0062147	13.4517205	3300.0
0.5075965	2.8396403	8.8634216	10.5236984	2.9952303	9.2198830	13.8455006	3400.0
0.9288831	3.2704439	9.2082354	10.9529033	3.3082224	9.4242831	14.2226191	3500.0
1.3284594	3.6798747	9.5374973	11.3628910	3.6055246	9.6201191	14.5843081	3600.0
1.7080404	4.0695952	9.8523741	11.7550970	3.8883672	9.8080205	14.9316759	3700.0
2.0691640	4.4410965	10.1539158	12.1308125	4.1578538	9.9885546	15.2657216	3800.0
2.4132117	4.7957199	10.4430687	12.4912030	4.4149770	10.1622334	15.5873485	3900.0
2.7414286	5.1346751	10.7206876	12.8373209	4.6606309	10.3295187	15.8973768	4000.0
3.0549399	5.4590555	10.9875487	13.1701229	4.8956257	10.4908303	16.1965504	4100.0
3.3547655	5.7698541	11.2443582	13.4904788	5.1206943	10.6465493	16.4855497	4200.0
3.6418321	6.0679731	11.4917579	13.7991805	5.3365041	10.7970235	16.7649956	4300.0
3.9169832	6.3542332	11.7303355	14.0969518	5.5436624	10.9425697	17.0354562	4400.0
4.1809892	6.6293862	11.9606274	14.3844573	5.7427236	11.0834783	17.2974534	4500.0
4.4345550	6.8941183	12.1831276	14.6623051	5.9341950	11.2200156	17.5514662	4600.0
4.6783273	7.1490607	12.3982888	14.9310548	6.1185413	11.3524263	17.7979381	4700.0
4.9129001	7.3947921	12.6065284	15.1912231	6.2961896	11.4809350	18.0372758	4800.0
5.1388209	7.6318458	12.8082300	15.4432845	6.4675326	11.6057491	18.2698555	4900.0
5.3565947	7.8607138	13.0037502	15.6876802	6.6329317	11.7270598	18.4960253	5000.0
5.5666885	8.0818498	13.1934168	15.9248158	6.7927207	11.8450440	18.7161088	5100.0
5.7695349	8.2956756	13.3775347	16.1550701	6.9472083	11.9598655	18.9304037	5200.0
5.9655351	8.5025809	13.5563862	16.3787923	7.0966800	12.0716746	19.1391881	5300.0
6.1550637	8.7029274	13.7302338	16.5963092	7.2413999	12.1806124	19.3427200	5400.0
6.3384675	8.8970519	13.8993198	16.8079219	7.3816137	12.2868088	19.5412383	5500.0
6.5160726	9.0852685	14.0638731	17.0139146	7.5175496	12.3903850	19.7349663	5600.0
6.6881820	9.2678694	14.2241037	17.2145491	7.6494192	12.4914528	19.9241114	5700.0
6.8550807	9.4451269	14.3802085	17.4100704	7.7774193	12.5901166	20.1088643	5800.0
7.0170354	9.6172968	14.5323719	17.6007078	7.9017345	12.6864738	20.2894061	5900.0
7.1742975	9.7846179	14.6807643	17.7866762	8.0225357	12.7806140	20.4659035	6000.0
7.3271036	9.9473152	14.8255466	17.9681745	8.1399829	12.8726215	20.6385107	6100.0

TABLE A - 6 (COMPUTER OUTPUT)

LOGARITHMS OF THE ECUILIBRIUM CONSTANTS FOR THE ABOVE REACTIONS

LOG K1	LOG K2	LOG K3	LOG K4	LOG K5	LOG K6	LOG K7	LOG K8	TEMP
-10.4806759	-11.7802840	-10.6549376	-3.0787615	-5.5798230	-5.6163879	-3.6198060	-4.9659491	2000.0
-9.5930684	-10.7528464	-9.6857306	-2.8103777	-5.0151272	-5.0085661	-3.2583276	-4.4569969	2100.0
-8.7864583	-9.8198098	-8.8059305	-2.5666234	-4.5009783	-4.4560616	-2.9307045	-3.9951811	2200.0
-8.0502969	-8.9688627	-8.0038899	-2.3443183	-4.0308482	-3.9516755	-2.6325251	-3.5743926	2300.0
-7.3757913	-8.1897438	-7.2699015	-2.1408129	-3.5992921	-3.4894052	-2.3601156	-3.1895426	2400.0
-6.7555534	-7.4738325	-6.5958114	-1.9538825	-3.2017300	-3.0642039	-2.1103933	-2.8363555	2500.0
-6.1833296	-6.8138343	-5.9747193	-1.7816441	-2.8342830	-2.6718001	-1.8807500	-2.5112150	2600.0
-5.6537915	-6.2035353	-5.4007462	-1.6224937	-2.4936427	-2.3085527	-1.6689571	-2.2110378	2700.0
-5.1623698	-5.6376094	-4.8688535	-1.4750549	-2.1769698	-1.9713382	-1.4731418	-1.9331815	2800.0
-4.7051253	-5.1114640	-4.3746946	-1.3381394	-1.8818145	-1.6574645	-1.2916334	-1.5753640	2900.0
-4.2786429	-4.6211205	-3.9145054	-1.2107176	-1.6060500	-1.3645955	-1.1230207	-1.4356088	3000.0
-3.8799469	-4.1631123	-3.4850028	-1.0918893	-1.3478236	-1.0906991	-0.9660649	-1.2121906	3100.0
-3.5064336	-3.7344074	-3.0833169	-0.9808676	-1.1055104	-0.8339930	-0.8196813	-1.0035982	3200.0
-3.1558140	-3.3323404	-2.7069234	-0.8769574	-0.8776823	-0.5929132	-0.6829150	-0.8085012	3300.0
-2.8260683	-2.9545601	-2.3535945	-0.7795452	-0.6630772	-0.3660790	-0.5549227	-0.6257241	3400.0
-2.5154067	-2.5989842	-2.0213570	-0.6880858	-0.4605759	-0.1522675	-0.4349585	-0.4542242	3500.0
-2.2222384	-2.2637608	-1.7084555	-0.6020931	-0.2691824	0.0496087	-0.3223556	-0.2930721	3600.0
-1.9451440	-1.9472394	-1.4133247	-0.5211328	-0.0880078	0.2405194	-0.2165197	-0.1414367	3700.0
-1.6828538	-1.6479425	-1.1345631	-0.4448141	0.0837439	0.4213310	-0.1169176	0.0014259	3800.0
-1.4342274	-1.3645436	-0.8709130	-0.3727870	0.2467891	0.5928230	-0.0230706	0.1361859	3900.0
-1.1982390	-1.0958487	-0.6212408	-0.3047333	0.4017717	0.7556947	0.0654532	0.2634479	4000.0
-0.9739624	-0.8407804	-0.3845248	-0.2403662	0.5492743	0.9105779	0.1490447	0.3837587	4100.0
-0.7605600	-0.5983632	-0.1598390	-0.1794262	0.6898242	1.0580446	0.2280583	0.4976145	4200.0
-0.5572714	-0.3677117	0.0536574	-0.1216751	0.8239005	1.1986120	0.3028150	0.6054657	4300.0
-0.3634055	-0.1480206	0.2567275	-0.0668973	0.9519385	1.3327515	0.3736097	0.7077241	4400.0
-0.1783330	0.0614438	0.4500682	-0.0148956	1.0743361	1.4608908	0.4407074	0.8047646	4500.0
-0.0014787	0.2613531	0.6343156	0.0345106	1.1914556	1.5834221	0.5043550	0.8969315	4600.0
0.1676837	0.4523218	0.8100525	0.0814867	1.3036305	1.7007029	0.5647752	0.9845384	4700.0
0.3296354	0.6349141	0.9778131	0.1261846	1.4111651	1.8130603	0.6221746	1.0678763	4800.0
0.4848202	0.8096491	1.1380881	0.1687440	1.5143402	1.9207958	0.6767407	1.1472092	4900.0
0.6336449	0.9770055	1.2913300	0.2092930	1.6134133	2.0241860	0.7286490	1.2227845	5000.0
0.7764850	1.1374249	1.4379544	0.2479492	1.7086232	2.1234860	0.7780587	1.2948259	5100.0
0.9136871	1.2913163	1.5783476	0.2848226	1.8001894	2.2189307	0.8251177	1.3635437	5200.0
1.0455718	1.4390583	1.7128657	0.3200132	1.8883153	2.3107376	0.8699529	1.4291305	5300.0
1.1724352	1.5810042	1.8418381	0.3536131	1.9731892	2.3991078	0.9127199	1.4917655	5400.0
1.2945527	1.7174804	1.9655712	0.3857080	2.0549859	2.4842278	0.9535040	1.5516126	5500.0
1.4121794	1.8487931	2.0843493	0.4163762	2.1338679	2.5662706	0.9924240	1.6088258	5600.0
1.5255529	1.9752280	2.1984384	0.4456911	2.2099860	2.6453975	1.0295798	1.6635481	5700.0
1.6348942	2.0970519	2.3080837	0.4737184	2.2834806	2.7217585	1.0650623	1.7159098	5800.0
1.7404089	2.2145147	2.4135158	0.5005201	2.3544831	2.7954936	1.0989574	1.7660329	5900.0
1.8422900	2.3278521	2.5149499	0.5261526	2.4231160	2.8667331	1.1313433	1.8140324	6000.0
1.9407164	2.4372852	2.6125877	0.5506680	2.4894929	2.9355987	1.1622934	1.8600121	6100.0

LOG K9	LOG K10	LOG K11	LOG K12	LOG K13	LOG K14	LOG K15	LOG K16	TEMP
4.7342407	-11.6060224	-9.1810678	8.7015225	7.0351316	27.7756865	3.6881554	11.4795035	2000.0
4.1145586	-10.6601840	-8.4332905	7.9424686	6.4274030	25.4819860	3.2475035	10.3675082	2100.0
3.5524435	-9.8003376	-7.7531068	7.2531863	5.8752260	23.3975451	2.8466168	9.3564061	2200.0
3.0403306	-9.0152695	-7.1317312	6.6245444	5.3713649	21.4950635	2.4803424	8.4331095	2300.0
2.5719186	-8.2956336	-6.5618389	6.0489309	4.9097858	19.7517836	2.1443740	7.5867023	2400.0
2.1419148	-7.6335745	-6.0372744	5.5199500	4.4854181	18.1485839	1.8350909	6.8080058	2500.0
1.7458438	-7.0224446	-5.5528250	5.0321902	4.0939693	16.6692784	1.5494269	6.0892467	2600.0
1.3798963	-6.4565806	-5.1040477	4.5810415	3.7317791	15.3000803	1.2847582	5.4237972	2700.0
1.0408059	-5.9311256	-4.6871303	4.1625544	3.3957118	14.0291674	1.0388723	4.8059713	2800.0
0.7257617	-5.4418947	-4.2987867	3.7733245	3.0830613	12.8463507	0.8098059	4.2308645	2900.0
0.4323266	-4.9852580	-3.9361653	3.4104030	2.7914847	11.7427974	0.5958919	3.6942221	3000.0
0.1583829	-4.5580564	-3.5967815	3.0712230	2.5189379	10.7108154	0.3956692	3.1923361	3100.0
-0.0979235	-4.1575240	-3.2784599	2.7535397	2.2636356	9.7436763	0.2078584	2.7219599	3200.0
-0.3382190	-3.7812310	-2.9792875	2.4553829	2.0240084	8.8354671	0.0313366	2.2802393	3300.0
-0.5639375	-3.4270338	-2.6975765	2.1750149	1.7986718	7.9809724	-0.1348891	1.8646541	3400.0
-0.7763467	-3.0930339	-2.4318292	1.9108983	1.5863985	7.1755733	-0.2916976	1.4729704	3500.0
-0.9765737	-2.7775436	-2.1807159	1.6616677	1.3860999	6.4151655	-0.4398598	1.1032022	3600.0
-1.1656206	-2.4790588	-1.9430486	1.4261066	1.1968049	5.6960907	-0.5801027	0.7535766	3700.0
-1.3443847	-2.1962331	-1.7177651	1.2031283	1.0176455	5.0150759	-0.7130194	0.4225078	3800.0
-1.5136690	-1.9278579	-1.5039112	0.9917566	0.8478424	4.3691842	-0.8391798	0.1085702	3900.0
-1.6741943	-1.6728469	-1.3006293	0.7911154	0.6866940	3.7557746	-0.9590873	-0.1895179	4000.0
-1.8266122	-1.4307180	-1.1071444	0.6004142	0.5335695	3.1724638	-1.0731957	-0.4729147	4100.0
-1.9715097	-1.1990842	-0.9227569	0.4189370	0.3878973	2.6170977	-1.1819168	-0.7426686	4200.0
-2.1094191	-0.9786405	-0.7468310	0.2460365	0.2491576	2.0877202	-1.2856236	-0.9997312	4300.0
-2.2408230	-0.7681536	-0.5787903	0.0811233	0.1168821	1.5825557	-1.3846542	-1.2449669	4400.0
-2.3661597	-0.5669574	-0.4181099	-0.0763394	-0.0093608	1.0999869	-1.4793181	-1.4791652	4500.0
-2.4858315	-0.3744411	-0.2643105	-0.2268426	-0.1299606	0.6385357	-1.5695971	-1.7030464	4600.0
-2.6002018	-0.1900471	-0.1169544	-0.3708351	-0.2452773	0.1968493	-1.6566505	-1.9172709	4700.0
-2.7096055	-0.0132635	0.0243568	-0.5087295	-0.3556385	-0.2263086	-1.7398136	-2.1224430	4800.0
-2.8143508	0.1563812	0.1599913	-0.6409052	-0.4613474	-0.6320803	-1.8196052	-2.3191202	4900.0
-2.9147193	0.3193203	0.2902842	-0.7677125	-0.5626810	-1.0215108	-1.8962252	-2.5078144	5000.0
-3.0109684	0.4759554	0.4155450	-0.8894756	-0.6598957	-1.3955689	-1.9698588	-2.6889982	5100.0
-3.1033399	0.6266557	0.5360580	-1.0064937	-0.7532299	-1.7551468	-2.0406772	-2.8631090	5200.0
-3.1920528	0.7717644	0.6520852	-1.1190452	-0.8429028	-2.1010713	-2.1088383	-3.0305519	5300.0
-3.2773118	0.9116013	0.7638661	-1.2273911	-0.9291182	-2.4341090	-2.1744896	-3.1917017	5400.0
-3.3593059	1.0464618	0.8716249	-1.3317724	-1.0120671	-2.7549731	-2.2377675	-3.3469073	5500.0
-3.4382105	1.1766231	0.9755656	-1.4324169	-1.0919253	-3.0643259	-2.2987393	-3.4964937	5600.0
-3.5141878	1.3023425	1.0758778	-1.5295370	-1.1688586	-3.3627857	-2.3577037	-3.6407629	5700.0
-3.5873921	1.4238623	1.1727364	-1.6233336	-1.2430215	-3.6509305	-2.4145923	-3.7799979	5800.0
-3.6579633	1.5414078	1.2663032	-1.7139946	-1.3145584	-3.9292996	-2.4695583	-3.9144623	5900.0
-3,7260325	1.6551921	1.3567278	-1.8016995	-1.3836066	-4.1983995	-2.5227299	-4.0444044	6000.0
-3.7917252	1.7654139	1.4441476	-1.8866172	-1.4502944	-4.4587059	-2.5741584	-4.1700556	6100.0

TABLE A-7. (COMPUTER OUTPUT)

EQUILIBRIUM CONSTANTS FOR THE ABOVE REACTIONS

K1	K2	K3	K4	K5	K6	K7	K8	TEMP
0.330616E-10	0.165850E-11	0.221341E-10	0.834139E-03	0.263134E-05	0.241887E-05	0.239991E-03	0.108156E-04	2000.0
0.255230E-09	0.176666E-10	0.206191E-09	0.154747E-02	0.965768E-05	0.980469E-05	0.551661E-03	0.349143E-04	2100.0
0.163509E-08	0.151423E-09	0.156340E-08	0.271254E-02	0.315516E-04	0.349896E-04	0.117299E-02	0.101116E-03	2200.0
0.890642E-08	0.107433E-08	0.991084E-08	0.452566E-02	0.931434E-04	0.111770E-03	0.233064E-02	0.266445E-03	2300.0
0.420929E-07	0.646036E-08	0.537154E-07	0.723081E-02	0.251598E-03	0.324037E-03	0.436400E-02	0.646335E-03	2400.0
0.175569E-06	0.335867E-07	0.253623E-06	0.111203E-01	0.628449E-03	0.862574E-03	0.775545E-02	0.145762E-02	2500.0
0.655648E-06	0.153520E-06	0.105994E-05	0.165332E-01	0.146459E-02	0.212912E-02	0.131598E-01	0.308166E-02	2600.0
0.221926E-05	0.625842E-06	0.397424E-05	0.238510E-01	0.320891E-02	0.491414E-02	0.214305E-01	0.615123E-02	2700.0
0.688066E-05	0.230351E-05	0.135253E-04	0.334923E-01	0.665319E-02	0.106822E-01	0.336402E-01	0.116632E-01	2800.0
0.197185E-04	0.773635E-05	0.421993E-04	0.459051E-01	0.131276E-01	0.220057E-01	0.510936E-01	0.211172E-01	2900.0
0.526450E-04	0.239265E-04	0.121757E-03	0.615577E-01	0.247714E-01	0.431921E-01	0.753320E-01	0.366768E-01	3000.0
0.131842E-03	0.686891E-04	0.327339E-03	0.809302E-01	0.448928E-01	0.811523E-01	0.108127E-00	0.613493E-01	3100.0
0.311578E-03	0.184329E-03	0.825436E-03	0.104504E-00	0.784313E-01	0.146557E-00	0.151467E-00	0.991749E-01	3200.0
0.698532E-03	0.465221E-03	0.196371E-02	0.132752E-00	0.132531E-00	0.255321E-00	0.207532E-00	0.155417E-00	3300.0
0.149256E-02	0.111030E-02	0.443002E-02	0.166133E-00	0.217231E-00	0.430448E-00	0.278662E-00	0.236742E-00	3400.0
0.305206E-02	0.251777E-02	0.952013E-02	0.205076E-00	0.346277E-00	0.704259E 00	0.367317E-00	0.351379E-00	3500.0
0.599462E-02	0.544803E-02	0.195679E-01	0.249981E-00	0.538044E 00	0.112101E 01	0.476041E-00	0.509246E 00	3600.0
0.113463E-01	0.112917E-01	0.386078E-01	0.301208E-00	0.816568E 00	0.173988E 01	0.607408E 00	0.722043E 00	3700.0
0.207561E-01	0.224935E-01	0.733562E-01	0.359076E-00	0.121267E 01	0.263834E 01	0.763981E 00	0.100329E 01	3800.0
0.367936E-01	0.431973E-01	0.134613E-00	0.423851E-00	0.176518E 01	0.391582E 01	0.948264E 00	0.136831E 01	3900.0
0.633521E-01	0.801957E-01	0.239199E-00	0.495755E-00	0.252215E 01	0.569764E 01	0.116266E 01	0.183420E 01	4000.0
0.106179E-00	0.144284E-00	0.412549E-00	0.574955E 00	0.354221E 01	0.813913E 01	0.140943E 01	0.241968E 01	4100.0
0.173556E-00	0.252137E-00	0.692088E 00	0.661567E 00	0.489581E 01	0.114300E 02	0.169067E 01	0.314496E 01	4200.0
0.277159E-00	0.428833E-00	0.113151E 01	0.755657E 00	0.666654E 01	0.157984E 02	0.200824E 01	0.403149E 01	4300.0
0.433106E-00	0.711180E 00	0.180604E 01	0.857241E 00	0.895238E 01	0.215155E 02	0.236379E 01	0.510181E 01	4400.0
0.663234E 00	0.115198E 01	0.281883E 01	0.966283E 00	0.118669E 02	0.288995E 02	0.275872E 01	0.637918E 01	4500.0
0.996601E 00	0.182538E 01	0.430840E 01	0.108271E 01	0.155402E 02	0.383197E 02	0.319415E 01	0.788736E 01	4600.0
0.147124E 01	0.283349E 01	0.645732E 01	0.120639E 01	0.201201E 02	0.501999E 02	0.367092E 01	0.965025E 01	4700.0
0.213617E 01	0.431434E 01	0.950196E 01	0.133716E 01	0.257730E 02	0.650220E 02	0.418962E 01	0.116917E 02	4800.0
0.305366E 01	0.645133E 01	0.137432E 02	0.147484E 01	0.326844E 02	0.833289E 02	0.475051E 01	0.140349E 02	4900.0
0.430175E 01	0.948430E 01	[illegible]	0.161917E 01	0.410595E 02	0.105727E 03	0.535364E 01	[illegible]	5000.0
0.597702E 01	0.137222E 02	0.274129E 02	0.176990E 01	0.511238E 02	[illegible]	0.599872E 01	0.197153E 02	5100.0
0.819761E 01	0.195576E 02	0.378746E 02	0.192674E 01	0.631232E 02	0.165551E 03	0.568525E 01	0.230964E 02	5200.0
0.111064E 02	0.274826E 02	0.516257E 02	0.208936E 01	0.773242E 02	0.204521E 03	0.741247E 01	0.258615E 02	5300.0
0.148743E 02	0.381069E 02	0.694765E 02	0.225742E 01	0.940133E 02	0.250673E 03	0.817937E 01	0.310288E 02	5400.0
0.197039E 02	0.521771E 02	0.923785E 02	0.243057E 01	0.113497E 03	0.304949E 03	0.898471E 01	0.356133E 02	5500.0
0.258333E 02	0.705981E 02	0.121436E 03	0.260841E 01	0.136103E 03	0.368358E 03	0.982707E 01	0.406280E 02	5600.0
0.335392E 02	0.944557E 02	0.157920E 03	0.279056E 01	0.162176E 03	0.441975E 03	0.107048E 02	0.460838E 02	5700.0
0.431414E 02	0.125041E 03	[illegible]	[illegible]	[illegible]	0.526937E 03	0.116162E 02	[illegible]	5800.0
0.550058E 02	0.163876E 03	0.259129E 03	0.316607E 01	0.226195E 03	0.624444E 03	0.125591E 02	0.583489E 02	5900.0
0.695488E 02	0.212741E 03	0.327303E 03	0.335856E 01	0.264921E 03	0.735755E 03	0.135314E 02	0.651677E 02	6000.0
0.872401E 02	0.273707E 03	0.409815E 03	0.355360E 01	0.308669E 03	0.862181E 03	0.145309E 02	0.724456E 02	6100.0

K9	K10	K11	K12	K13	K14	K15	K16	TEMP
0.542301E 05	0.247730E-11	0.659071E-09	0.502947E 09	0.108425E 08	0.596603E 28	0.487714E 04	0.301650E 12	2000.0
0.130184E 05	0.218684E-10	0.368731E-08	0.875928E 08	0.267549E 07	0.303379E 26	0.176809E 04	0.233032E 11	2100.0
0.356815E 04	0.158366E-09	0.176560E-07	0.179137E 08	0.750284E 06	0.249772E 24	0.702452E 03	0.227199E 10	2200.0
0.109731E 04	0.965452E-09	0.738362E-07	0.421254E 07	0.235161E 06	0.312653E 22	0.302233E 03	0.271087E 09	2300.0
0.373180E 03	0.506252E-08	0.274259E-06	0.111926E 07	0.812429E 05	0.564655E 20	0.139436E 03	[illegible]	2400.0
0.138648E 03	0.232501E-07	0.917753E-06	0.331093E 06	0.305786E 05	0.140794E 19	0.684055E 02	0.642596E 07	2500.0
0.556985E 02	0.949633E-07	0.280011E-05	0.107694E 06	0.124156E 05	0.466958E 17	0.354345E 02	0.122814E 07	2600.0
0.239826E 02	0.349478E-06	0.786960E-05	0.381102E 05	0.539236E 04	0.199563E 16	0.192650E 02	0.265337E 06	2700.0
0.109851E 02	0.117186E-05	0.205527E-04	0.145397E 05	0.248721E 04	0.106947E 15	0.109363E 02	0.639692E 05	2800.0
0.531816E 01	0.361498E-05	0.502590E-04	0.593368E 04	0.121077E 04	0.702021E 13	0.545366E 01	0.170153E 05	2900.0
0.270599E 01	0.103453E-04	0.115834E-03	0.257278E 04	0.618706E 03	0.553091E 12	0.394359E 01	0.494563E 04	3000.0
0.144007E 01	0.276658E-04	0.253057E-03	0.117821E 04	0.330322E 03	0.513825E 11	0.248696E 01	0.155717E 04	3100.0
0.798135E 00	0.695787E-04	0.526672E-03	0.566943E 03	0.183500E 03	0.554212E 10	0.161383E 01	0.527181E 03	3200.0
0.458966E-00	0.165489E-03	0.104885E-02	0.285353E 03	0.105684E 03	0.684647E 09	0.107482E 01	0.190651E 03	3300.0
0.272937E-00	0.374082E-03	0.200643E-02	0.149629E 03	0.629030E 02	0.957133E 08	0.733012E 00	0.732241E 02	3400.0
0.167361E-00	0.807172E-03	0.369974E-02	0.814513E 02	0.385832E 02	0.149821E 08	0.510861E 00	0.297146E 02	3500.0
0.105542E-00	0.166900E-02	0.659605E-02	0.458847E 02	0.243276E 02	0.260115E 07	0.363187E-00	0.126824E 02	3600.0
0.682935E-01	0.331850E-02	0.114012E-01	0.266751E 02	0.157328E 02	0.496696E 06	0.262965E-00	0.565992E 01	3700.0
0.452497E-01	0.636454E-02	0.191529E-01	0.159635E 02	0.104147E 02	0.103532E 06	0.193634E-00	0.264550E 01	3800.0
0.306430E-01	0.118071E-01	0.313393E-01	0.981198E 01	0.704437E 01	0.233983E 05	0.144817E-00	0.128402E 01	3900.0
0.211741E-01	0.212399E-01	0.500462E-01	0.618181E 01	0.486065E 01	0.569868E 04	0.109879E-00	0.646371E 00	4000.0
0.149069E-01	0.371349E-01	0.781368E-01	0.398487E 01	0.341641E 01	0.148752E 04	0.844898E-01	0.336578E-00	4100.0
0.106780E-01	0.632289E-01	0.119466E-00	0.262384E 01	0.244285E 01	0.414093E 03	0.657784E-01	0.180855E-00	4200.0
0.777286E-02	0.105041E-00	0.179130E-00	0.176212E 01	0.177483E 01	0.122383E 03	0.518056E-01	0.100062E-00	4300.0
0.574351E-02	0.170548E-00	0.263760E-00	0.120538E 01	0.130883E 01	0.382433E 02	0.412426E-01	0.568896E-01	4400.0
0.430368E-02	0.271046E-00	0.381848E-00	0.838804E 00	0.978677E 00	0.125889E 02	0.331651E-01	0.331768E-01	4500.0
0.326715E-02	0.422240E-00	0.544114E 00	0.593140E 00	0.741378E 00	0.435046E 01	0.269217E-01	0.198132E-01	4600.0
0.251072E-02	0.645584E 00	0.763916E 00	0.425760E-00	0.568490E 00	0.157344E 01	0.220470E-01	0.120984E-01	4700.0
0.195162E-02	0.969921E 00	0.105769E 01	0.309935E-00	0.440922E-00	0.593870E 00	0.182048E-01	0.754323E-02	4800.0
0.153338E-02	0.143345E 01	0.144541E 01	0.228610E-00	0.345663E-00	0.233303E-00	0.151494E-01	0.479501E-02	4900.0
0.121697E-02	0.208603E 01	0.195112E 01	0.170721E-00	0.273728E-00	0.951676E-01	0.126992E-01	0.310589E-02	5000.0
0.975061E-03	0.299196E 01	0.260342E 01	0.128981E-00	0.218829E-00	0.402190E-01	0.107187E-01	0.204645E-02	5100.0
0.788243E-03	0.423307E 01	0.343604E 01	0.985159E-01	0.176510E-00	0.175733E-01	0.910590E-02	0.137054E-02	5200.0
0.642610E-03	0.591241E 01	0.448833E 01	0.760247E-01	0.143581E-00	0.792371E-02	0.778326E-02	0.932069E-03	5300.0
0.528066E-03	0.815833E 01	0.580585E 01	0.592392E-01	0.117729E-00	0.368037E-02	0.669130E-02	0.643130E-03	5400.0
0.437214E-03	0.111291E 02	0.744089E 01	0.465830E-01	0.972597E-01	0.175803E-02	0.578406E-02	0.449876E-03	5500.0
0.364577E-03	0.150184E 02	0.945291E 01	0.369473E-01	0.809235E-01	0.862331E-03	0.502575E-02	0.318791E-03	5600.0
0.306064E-03	0.200605E 02	0.119091E 02	0.295436E-01	0.677862E-01	0.433725E-03	0.438830E-02	0.228585E-03	5700.0
0.258588E-03	0.265376E 02	0.148846E 02	0.238049E-01	0.571450E-01	0.223393E-03	0.384953E-02	0.165960E-03	5800.0
0.219805E-03	0.347863E 02	0.184630E 02	0.193199E-01	0.484665E-01	0.117679E-03	0.339181E-02	0.121769E-03	5900.0
0.187918E-03	0.452056E 02	0.227367E 02	0.157870E-01	0.413422E-01	0.633287E-04	0.300103E-02	0.902809E-04	6000.0
0.161538E-03	0.582658E 02	0.278066E 02	0.129832E-01	0.354573E-01	0.347772E-04	0.265583E-02	0.675997E-04	6100.0

Appendix B

(1) Equilibrium Composition at High Temperatures

Reactions considered in the heterogeneous region:

C_s	$\longrightarrow$	C_1	$K1 = p_{C_1}$	(1)
$2C_s$	$\longrightarrow$	C_2	$K_2 = p_{C_2}$	(2)
$3C_s$	$\longrightarrow$	C_3	$K_3 = p_{C_3}$	(3)
$2C_s + H_2$	$\longrightarrow$	C_2H_2	$K_4 = p_{C_2H_2}/p_{H_2}$	(4)
H_2	$\longrightarrow$	$2H$	$K_5 = (p_H)^2/p_{H_2}$	(5)
C_2H_2	$\longrightarrow$	$C_2H + H$	$K_6 = p_{C_2H}\ p_H/p_{C_2H_2}$	(6)
$3C_s + H$	$\longrightarrow$	C_3H	$K_7 = p_{C_3H}/p_H$	(7)
$4C_s + H$	$\longrightarrow$	C_4H	$K_8 = p_{C_4H}/p_H$	(8)
$2C_2H$	$\longrightarrow$	C_4H_2	$K_9 = p_{C_4H_2}/(p_{C_2H})^2$	(9)

Reactions considered in the homogeneous region:

H_2	$\longrightarrow$	$2H$		(5)
C_2H_2	$\longrightarrow$	$C_2H + H$		(6)
$2C_2H$	$\longrightarrow$	C_4H_2		(9)
C_3	$\longrightarrow$	$C_1 + C_2$	$K_{10} = p_{C_1}\ p_{C_2}/p_{C_3}$	(10)
C_2	$\longrightarrow$	$2C_1$	$K_{11} = (p_{C_1})^2/p_{C_2}$	(11)
$C_2 + H_2$	$\longrightarrow$	C_2H_2	$K_{12} = p_{C_2H_2}/p_{C_2}\ p_{H_2}$	(12)
$C_3 + H$	$\longrightarrow$	C_3H	$K_{13} = p_{C_3H}/p_{C_3}\ p_H$	(13)
$C_2 + 2\ C_1 + H$	$\longrightarrow$	C_4H	$K_{14} = p_{C_4H}/p_{C_2}\ p_H(p_{C_1})^2$	(14)
$C_1 + H$	$\longrightarrow$	CH	$K_{15} = p_{CH}/p_{C_1}\ p_H$	(15)
$C_1 + 2H$	$\longrightarrow$	CH_2	$K_{16} = p_{CH_2}/p_{C_1}\ (p_H)^2$	(16)

Heterogeneous Region

By Dalton's law, the sum of partial pressures must equal the total pressure. In this region, the partial pressures can be reduced to terms involving the various equilibrium constants and the partial pressure of H atoms by manipulating the equations for K_1 to K_9. Collecting the terms containing a common power of p_H and rearranging, a quadratic equation results, with the partial pressure of H atoms to be determined

$$(p_H)^2 \left[\frac{1 + K_4}{K_5} + K_9 \left(\frac{K_6 K_4}{K_5}\right)^2\right] + (p_H) \left[1 + \frac{K_4 K_6}{K_5} + K_7 + K_8\right] + (K_1 + K_2 + K_3 - TP) = 0 \qquad (17)$$

where TP is the total pressure.

The solution of Eq. 17 is straightforward as it depends only on temperature at a fixed pressure. Once the partial pressure p_H is determined, all other component concentrations (mole fraction y) can be easily derived from the equilibrium constants and the value of p_H where applicable at the chosen temperature by inserting p_H in Eqs. 1 to 9 and dividing by the total pressure. The sum of mole fractions must also add up to unity.

The carbon to hydrogen ratio in this region is variable and depends on temperature. This can be expressed as:

$$\frac{C}{H_2} = \frac{y_{C_1} + 2\,(y_{C_2} + y_{C_2H} + y_{C_2H_2}) + 3\,(y_{C_3} + y_{C_3H}) + 4\,(y_{C_4H} + y_{C_4H_2})}{(y_{H_2} + y_{C_2H_2} + y_{C_4H_2}) + 0.5\,(y_H + y_{C_2H} + y_{C_3H} + y_{C_4H})} \qquad (18)$$

For the computer program discussed in Appendix A, four basic equations were set as follows:

$$A = \frac{1 + K_4}{K_5} + K_9 \left(\frac{K_4 K_6}{K_5}\right)^2 \qquad \text{positive} \qquad (19)$$

$$B = 1 + \frac{K_4 K_6}{K_5} + K_7 + K_8 \qquad \text{positive} \qquad (20)$$

$$C = K_1 + K_2 + K_3 - TP \qquad \text{negative} \qquad (21)$$

$$p_H = \frac{-B + \sqrt{B^2 - 4AC}}{2A} \qquad (22)$$

The computer loop was closed at the temperature for which the condition imposed on Eq. 21 could no longer be fulfilled, i.e., if C became positive, because this corresponds to an impossible case. Computer results for five different total pressures (0.1, 0.5, 1.0, 5.0, and 10.0 atm.) are presented in Table B-1.

Homogeneous Region

Two conditions must be fulfilled in this region; besides the condition that the sum of partial pressures must add up to the total pressure, the carbon to hydrogen ratio must also remain unchanged throughout the whole temperature range. From Eqs. 5, 6, 9 to 17, a quadratic equation in p_H can be obtained containing the partial pressure of C_1 as parameters (first condition):

$$(p_H)^2 \left[\frac{1}{K_5} + K_{16} (p_{C_1}) + \frac{K_{12}}{K_5 K_{11}} (p_{C_1})^2 + K_9 \left(\frac{K_6 K_{12}}{K_5 K_{11}}\right)^2 (p_{C_1})^4 \right]$$

$$+ (p_H) \left[1 + K_{15} (p_{C_1}) + \frac{K_6 K_{12}}{K_5 K_{11}} (p_{C_1})^2 + \frac{K_{13}}{K_{10} K_{11}} (p_{C_1})^3 + \frac{K_{14}}{K_{11}} (p_{C_1})^4 \right]$$

$$+ \left[p_{C_1} + (p_{C_1})^2 / K_{11} + (p_{C_1})^3 / K_{10} K_{11} - TP \right] = 0 \qquad (23)$$

For the computer program, p_H, was given the symbol Y1PH and p_{C_1} the symbol x, and Eq. 23 was labeled as follows:

$$A1 = {}^1/K_5 + K_{16} x + \frac{K_{12}}{K_5 K_{11}} x^2 + K_9 \left(\frac{K_6 K_{12}}{K_5 K_{11}}\right)^2 x^4 \qquad (24)$$

$$B1 = 1 + K_{15} x + \frac{K_6 K_{12}}{K_5 K_{11}} x^2 + \frac{K_{13}}{K_{10} K_{11}} x^3 + \frac{K_{14}}{K_{11}} x^4 \qquad (25)$$

$$C1 = x + \frac{x^2}{K_{11}} + \frac{x^3}{K_{10} K_{11}} - TP \quad \text{(negative)} \qquad (26)$$

$$Y1PH = \frac{- B1 + \sqrt{(B1)^2 - 4\,(A1)(C1)}}{2\,(A1)} \qquad (27)$$

Eq. 27 is the only root possible since A1 and B1 are always positive and C1 must always be negative, because the sum of partial pressures for carbon vapors cannot be larger than the total pressure.

The second condition concerns the carbon to hydrogen ratio and can be expressed by an equation similar to Eq. 18, but with partial pressures instead of mole fractions; this is converted later to mole fractions and serves to check the specified C/H_2 ratio.

Setting $R = C/H_2$ for the sake of simplicity and defining the following values

$$AM = \frac{K_{12}}{K_5 K_{11}} x^2 + 3 K_9 \left(\frac{K_6 K_{12}}{K_5 K_{11}}\right)^2 x^4 - \frac{1}{K_5} \tag{28}$$

$$BM = \frac{K_6 K_{12}}{K_5 K_{11}} x^2 + 2 \frac{K_{13}}{K_{10} K_{11}} x^3 + 3 \frac{K_{14}}{K_{11}} x^4 - 1 \tag{29}$$

$$CM = \frac{x^2}{K_{11}} + \frac{2 x^3}{K_{10} K_{11}} + TP \tag{30}$$

another quadratic expression containing also Eqs. 24, 25, and 26 results. The second equation is separated as before, for computer handling, to yield:

$$A2 = A1 \ (R - 1) - AM \tag{31}$$

$$B2 = B1 \ (\frac{R}{2} - 1) - BM \tag{32}$$

$$C2 = - (C1 + CM) \qquad \text{(negative)} \tag{33}$$

Here, however, two roots are possible, labeled Y2PH1 and Y2PH2, for the plus and minus signs:

$$Y2PH1 = \frac{- B2 + \sqrt{(B2)^2 - 4(A2)(C2)}}{2(A2)} \tag{34}$$

$$Y2PH2 = \frac{- B2 - \sqrt{(B2)^2 - 4(A2)(C2)}}{2(A2)} \tag{35}$$

Also two more roots are possible depending on whether A2 or B2 is equal to zero:

if B2 = 0, then we have

$$\text{Y2PHBO} = \sqrt{-\text{C2}/\text{A2}} \qquad (36)$$

and if A2 = 0, we get

$$\text{Y2PHAO} = -\text{C2}/\text{B2} \qquad (37)$$

The restrictions as to which root applies can be seen in the following diagram:

	A2 > 0	A2 < 0	A2 = 0
B2 > 0	Y2PH1	Y2PH1 Y2PH2	Y2PHAO
B2 < 0	Y2PH1	none	none
B2 = 0	Y2PHBO	none	none

Where two roots apply (B2 > 0 and A2 < 0), the negative root or the one larger than the total pressure must be rejected.

The procedure now consists in choosing a value of $p_{C_1} = x$ and trying to match Y1PH of Eq. 27 with one of the Y2PH roots of Eqs. 34, 35, 36, or 37. Trial and error calculations are involved, and a digital computer, such as the M.I.T. computer IBM 7090, is the most useful tool to get quick and accurate results. Once the two roots match, it is a simple procedure to obtain the other partial pressures from Eqs. 5, 6, 9 to 17. Mole fractions are again obtained by division with the total pressure and a check on the accuracy of the calculations is then performed by computing the sum of mole fractions that must add to unity and the carbon to hydrogen ratio from Eq. 18 that must be the same as the specified ratio R.

It was found necessary to set the initial value of x equal to 10^{-6} in order to get all the mole fractions at various pressures and C/H_2 ratios. Also the computations were obtained from 3,000°K up to 6,000°K, even though at a temperature below the sublimation point of carbon the values do not correspond to reality; they were useful, however, for determining the sublimation point of carbon under the assigned conditions, since curves drawn from both heterogeneous and homogeneous regions must meet at this point.

Computer results for the homogeneous region are presented in Table B-2 for the cases examined in this thesis. Other pertinent values can be obtained from the whole computer program input and output which are on file with Prof. Baddour or from a modification of the original program also on file.

(2) Quench Mechanism

The molecules, atoms and radicals of the equilibrium diagrams, as seen in section (1) of this appendix, were assumed to recombine in the following manner upon quenching of the gas mixture to room temperature:

All C_2H_2, H_2, and C_4H_2 present remain unchanged;

$$C_2H_{2(T)} \longrightarrow C_2H_2 \text{ (room temperature)}$$

$$H_{2(T)} \longrightarrow H_2 \text{ (room temperature}$$

$$C_4H_{2(T)} \longrightarrow C_4H_2 \text{ (room temperature)}$$

The C_2H radical combines with an H atom to yield more C_2H_2

$$C_2H + H \longrightarrow C_2H_2$$

The unused H radicals form molecular hydrogen

$$\text{H remaining} \longrightarrow 1/2\ H_2$$

The radicals C_3H, C_2H, CH and CH_2 go to solid carbon and molecular hydrogen

$$C_3H \longrightarrow 3\ C_s + 1/2\ H_2$$

$$C_4H \longrightarrow 4\ C_s + 1/2\ H_2$$

$$CH \longrightarrow C_s + 1/2\ H_2$$

$$CH_2 \longrightarrow C_s + H_2$$

It could be argued that CH could yield directly C_2H_2 by dimerization of the radical, but its concentration is so low as not to affect the resulting concentration of C_2H_2 in the quenched gas.

All carbon species, C_1, C_2, C_3 also form solid carbon:

$$C_1 \longrightarrow C_s$$

$$C_2 \longrightarrow 2\ C_s$$

$$C_3 \longrightarrow 3\ C_s$$

With this mechanism, the output gas would contain only C_2H_2 and H_2 and also a minute amount of C_4H_2 which does not contribute to more than about one half of one percent of the total. The calculated C_2H_2 concentrations are presented in the following tables (Tables B-3 to B-6) for various combinations of pressures and C/H_2 ratios.

<u>Example</u>: Pressure: 1.0 atm., C/H_2 ratio = 5.0, T = 3,900°K

C_2H_2		H_2	
0.01010	C_2H_2	0.02821	H_2
0.17715	$C_2H + H$	0.02300	remaining H
0.18725	total C_2H_2	0.08208	C_3H
		0.10883	C_4H
0,18725	C_2H_2	0.00096	C_4H_2
0.24579	$H_2 + C_4H_2$	0.00055	CH
0.43304	total gas	0.00216	CH_2
		0.24579	total $H_2 + C_4H_2$

$$\%C_2H_2 = \frac{0.18725}{0.43304} \times 100 = 43.3\%$$

TABLE B-I

CARBON-HYDROGEN SYSTEM,HETEROGENEOUS REGION

TOTAL PRESSURE (ATM) = 0.10

Y H	Y H2	Y C2H	Y C2H2	Y C3H	Y C4H	Y C4H2	Y C1	Y C2	Y C3	Y SUM	C/H2	TEMP
0.00511	0.99405	0.00000	0.00083	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	1.00000	0.002	2000.0
0.00977	0.98868	0.00002	0.00153	0.00001	0.00000	0.00000	0.00000	0.00000	0.00000	1.00000	0.003	2100.0
0.01758	0.97968	0.00005	0.00266	0.00002	0.00000	0.00000	0.00000	0.00000	0.00000	1.00000	0.006	2200.0
0.02999	0.96540	0.00016	0.00437	0.00007	0.00001	0.00000	0.00000	0.00000	0.00000	1.00000	0.009	2300.0
0.04873	0.94374	0.00045	0.00682	0.00021	0.00003	0.00001	0.00000	0.00000	0.00000	1.00000	0.016	2400.0
0.07572	0.91226	0.00116	0.01014	0.00059	0.00011	0.00002	0.00000	0.00000	0.00000	1.00000	0.026	2500.0
0.11277	0.86827	0.00271	0.01436	0.00148	0.00035	0.00004	0.00001	0.00000	0.00001	1.00000	0.043	2600.0
0.16113	0.80909	0.00589	0.01930	0.00345	0.00099	0.00008	0.00002	0.00001	0.00004	1.00000	0.071	2700.0
0.22075	0.73246	0.01187	0.02453	0.00743	0.00257	0.00015	0.00007	0.00002	0.00014	1.00000	0.121	2800.0
0.28926	0.63737	0.02226	0.02926	0.01478	0.00611	0.00026	0.00020	0.00008	0.00042	1.00000	0.209	2900.0
0.36076	0.52538	0.03872	0.03234	0.02718	0.01323	0.00041	0.00053	0.00024	0.00122	1.00000	0.364	3000.0
0.42502	0.40238	0.06218	0.03256	0.04596	0.02607	0.00056	0.00132	0.00069	0.00327	1.00000	0.624	3100.0
0.46836	0.27968	0.09146	0.02923	0.07094	0.04645	0.00067	0.00312	0.00184	0.00825	1.00000	1.040	3200.0
0.47760	0.17211	0.12214	0.02285	0.09912	0.07423	0.00068	0.00699	0.00465	0.01954	1.00000	1.653	3300.0
0.44583	0.09150	0.14677	0.01520	0.12424	0.10555	0.00059	0.01493	0.01110	0.04430	1.00000	2.490	3400.0
0.37451	0.04051	0.15620	0.00831	0.13757	0.13160	0.00041	0.03052	0.02518	0.09520	1.00000	3.643	3500.0
0.26852	0.01340	0.13985	0.00335	0.12783	0.13674	0.00021	0.05995	0.05448	0.19568	1.00000	5.584	3600.0
0.12951	0.00205	0.08312	0.00062	0.07867	0.09352	0.00005	0.11346	0.11292	0.38608	1.00000	11.660	3700.0

CARBON-HYDROGEN SYSTEM,HETEROGENEOUS REGION

TOTAL PRESSURE (ATM) = 0.50

Y H	Y H2	Y C2H	Y C2H2	Y C3H	Y C4H	Y C4H2	Y C1	Y C2	Y C3	Y SUM	C/H2	TEMP
0.00229	0.99688	0.00000	0.00083	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	1.00000	0.002	2000.0
0.00438	0.99407	0.00001	0.00154	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	1.00000	0.003	2100.0
0.00790	0.98938	0.00002	0.00268	0.00001	0.00000	0.00000	0.00000	0.00000	0.00000	1.00000	0.005	2200.0
0.01352	0.98192	0.00007	0.00444	0.00003	0.00000	0.00000	0.00000	0.00000	0.00000	1.00000	0.009	2300.0
0.02210	0.97056	0.00021	0.00702	0.00010	0.00001	0.00001	0.00000	0.00000	0.00000	1.00000	0.015	2400.0
0.03463	0.95390	0.00053	0.01061	0.00027	0.00005	0.00002	0.00000	0.00000	0.00000	1.00000	0.024	2500.0
0.05220	0.93027	0.00125	0.01538	0.00069	0.00016	0.00004	0.00000	0.00000	0.00000	1.00000	0.037	2600.0
0.07590	0.89771	0.00277	0.02141	0.00163	0.00047	0.00009	0.00000	0.00000	0.00001	1.00000	0.058	2700.0
0.10660	0.85401	0.00573	0.02860	0.00359	0.00124	0.00018	0.00001	0.00000	0.00003	1.00000	0.091	2800.0
0.14463	0.79675	0.01113	0.03657	0.00739	0.00305	0.00033	0.00004	0.00002	0.00008	1.00000	0.143	2900.0
0.18934	0.72363	0.02032	0.04454	0.01426	0.00694	0.00056	0.00011	0.00005	0.00024	1.00000	0.230	3000.0
0.23842	0.63312	0.03488	0.05124	0.02578	0.01463	0.00088	0.00026	0.00014	0.00065	1.00000	0.373	3100.0
0.28721	0.52587	0.05609	0.05496	0.04350	0.02848	0.00126	0.00062	0.00037	0.00165	1.00000	0.605	3200.0
0.32832	0.40668	0.08397	0.05399	0.06814	0.05103	0.00162	0.00140	0.00093	0.00393	1.00000	0.970	3300.0
0.35260	0.28616	0.11607	0.04754	0.09826	0.08347	0.00184	0.00299	0.00222	0.00886	1.00000	1.509	3400.0
0.35218	0.17910	0.14689	0.03673	0.12936	0.12375	0.00181	0.00610	0.00504	0.01904	1.00000	2.242	3500.0
0.32478	0.09802	0.16916	0.02450	0.15461	0.16539	0.00151	0.01199	0.01090	0.03914	1.00000	3.145	3600.0
0.27474	0.04622	0.17632	0.01392	0.16688	0.19837	0.00106	0.02269	0.02258	0.07722	1.00000	4.215	3700.0
0.20902	0.01801	0.16329	0.00647	0.15969	0.20971	0.00060	0.04151	0.04499	0.14671	1.00000	5.636	3800.0
0.13237	0.00496	0.12446	0.00210	0.12552	0.18113	0.00024	0.07359	0.08639	0.26923	1.00000	8.335	3900.0
0.04570	0.00041	0.05119	0.00021	0.05314	0.08383	0.00003	0.12670	0.16039	0.47840	1.00000	21.095	4000.0

CARBON-HYDROGEN SYSTEM,HETEROGENEOUS REGION

TOTAL PRESSURE (ATM) = 1.00

Y H	Y H2	Y C2H	Y C2H2	Y C3H	Y C4H	Y C4H2	Y C1	Y C2	Y C3	Y SUM	C/H2	TEMP
0.00162	0.99755	0.00000	0.00083	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	1.00000	0.002	2000.0
0.00310	0.99535	0.00000	0.00154	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	1.00000	0.003	2100.0
0.00559	0.99169	0.00002	0.00269	0.00001	0.00000	0.00000	0.00000	0.00000	0.00000	1.00000	0.005	2200.0
0.00958	0.98588	0.00005	0.00446	0.00002	0.00000	0.00000	0.00000	0.00000	0.00000	1.00000	0.009	2300.0
0.01568	0.97702	0.00015	0.00706	0.00007	0.00001	0.00001	0.00000	0.00000	0.00000	1.00000	0.015	2400.0
0.02461	0.96404	0.00038	0.01072	0.00019	0.00004	0.00002	0.00000	0.00000	0.00000	1.00000	0.023	2500.0
0.03721	0.94561	0.00089	0.01563	0.00049	0.00011	0.00004	0.00000	0.00000	0.00000	1.00000	0.036	2600.0
0.05434	0.92013	0.00198	0.02195	0.00116	0.00033	0.00009	0.00000	0.00000	0.00000	1.00000	0.055	2700.0
0.07677	0.88575	0.00413	0.02967	0.00258	0.00090	0.00019	0.00001	0.00000	0.00001	1.00000	0.083	2800.0
0.10503	0.84031	0.00808	0.03857	0.00537	0.00222	0.00035	0.00002	0.00001	0.00004	1.00000	0.128	2900.0
0.13913	0.78145	0.01493	0.04810	0.01048	0.00510	0.00060	0.00005	0.00002	0.00012	1.00000	0.198	3000.0
0.17814	0.70689	0.02606	0.05721	0.01926	0.01093	0.00098	0.00013	0.00007	0.00033	1.00000	0.310	3100.0
0.21968	0.61528	0.04290	0.06430	0.03327	0.02179	0.00147	0.00031	0.00018	0.00083	1.00000	0.489	3200.0
0.25937	0.50762	0.06633	0.06739	0.05383	0.04031	0.00202	0.00070	0.00047	0.00196	1.00000	0.770	3300.0
0.29082	0.38934	0.09574	0.06468	0.08104	0.06885	0.00250	0.00149	0.00111	0.00443	1.00000	1.195	3400.0
0.30665	0.27155	0.12790	0.05569	0.11264	0.10775	0.00274	0.00305	0.00252	0.00952	1.00000	1.800	3500.0
0.30140	0.16884	0.15698	0.04221	0.14348	0.15349	0.00260	0.00599	0.00545	0.01957	1.00000	2.585	3600.0
0.27475	0.09244	0.17633	0.02784	0.16688	0.19838	0.00212	0.01135	0.01129	0.03861	1.00000	3.507	3700.0
0.23159	0.04423	0.18092	0.01588	0.17693	0.23235	0.00148	0.02076	0.02249	0.07336	1.00000	4.541	3800.0
0.17828	0.01801	0.16763	0.00763	0.16905	0.24394	0.00086	0.03679	0.04320	0.13461	1.00000	5.823	3900.0
0.11892	0.00561	0.13318	0.00278	0.13826	0.21812	0.00038	0.06335	0.08020	0.23920	1.00000	7.994	4000.0
0.05456	0.00084	0.07209	0.00048	0.07691	0.13203	0.00008	0.10618	0.14428	0.41255	1.00000	14.993	4100.0

TABLE B-I (CONT'D)

CARBON-HYDROGEN SYSTEM,HETEROGENEOUS REGION

TOTAL PRESSURE (ATM) = 5.00

Y H	Y H2	Y C2H	Y C2H2	Y C3H	Y C4H	Y C4H2	Y C1	Y C2	Y C3	Y SUM	C/H2	TEMP
0.00072	0.99844	0.00000	0.00083	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	1.00000	0.002	2000.0
0.00139	0.99707	0.00000	0.00154	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	1.00000	0.003	2100.0
0.00251	0.99478	0.00001	0.00270	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	1.00000	0.005	2200.0
0.00430	0.99118	0.00002	0.00449	0.00001	0.00000	0.00000	0.00000	0.00000	0.00000	1.00000	0.009	2300.0
0.00704	0.98572	0.00007	0.00713	0.00003	0.00000	0.00001	0.00000	0.00000	0.00000	1.00000	0.015	2400.0
0.01109	0.97775	0.00017	0.01087	0.00009	0.00002	0.00002	0.00000	0.00000	0.00000	1.00000	0.023	2500.0
0.01683	0.96647	0.00040	0.01598	0.00022	0.00005	0.00005	0.00000	0.00000	0.00000	1.00000	0.034	2600.0
0.02470	0.95093	0.00090	0.02268	0.00053	0.00015	0.00010	0.00000	0.00000	0.00000	1.00000	0.050	2700.0
0.03518	0.92999	0.00189	0.03115	0.00118	0.00041	0.00020	0.00000	0.00000	0.00000	1.00000	0.073	2800.0
0.04867	0.90226	0.00375	0.04142	0.00249	0.00103	0.00037	0.00000	0.00000	0.00001	1.00000	0.106	2900.0
0.06551	0.86610	0.00703	0.05332	0.00493	0.00240	0.00067	0.00001	0.00000	0.00002	1.00000	0.154	3000.0
0.08578	0.81956	0.01255	0.06633	0.00928	0.00526	0.00113	0.00003	0.00001	0.00007	1.00000	0.224	3100.0
0.10922	0.76052	0.02133	0.07948	0.01654	0.01083	0.00182	0.00006	0.00004	0.00017	1.00000	0.328	3200.0
0.13494	0.68701	0.03451	0.09120	0.02801	0.02097	0.00273	0.00014	0.00009	0.00039	1.00000	0.485	3300.0
0.16119	0.59806	0.05306	0.09936	0.04492	0.03816	0.00384	0.00030	0.00022	0.00089	1.00000	0.719	3400.0
0.18516	0.49502	0.07723	0.10152	0.06801	0.06506	0.00499	0.00061	0.00050	0.00190	1.00000	1.062	3500.0
0.20307	0.38320	0.10576	0.09579	0.09667	0.10341	0.00590	0.00120	0.00109	0.00391	1.00000	1.549	3600.0
0.21097	0.27254	0.13540	0.08209	0.12815	0.15233	0.00626	0.00227	0.00226	0.00772	1.00000	2.200	3700.0
0.20634	0.17555	0.16120	0.06304	0.15764	0.20702	0.00588	0.00415	0.00450	0.01467	1.00000	2.997	3800.0
0.18962	0.10185	0.17829	0.04317	0.17981	0.25946	0.00487	0.00736	0.00864	0.02692	1.00000	3.876	3900.0
0.16416	0.05342	0.18385	0.02648	0.19086	0.30110	0.00358	0.01267	0.01604	0.04784	1.00000	4.767	4000.0
0.13415	0.02540	0.17723	0.01461	0.18907	0.32460	0.00234	0.02124	0.02886	0.08251	1.00000	5.683	4100.0
0.10260	0.01075	0.15848	0.00711	0.17347	0.32269	0.00134	0.03471	0.05043	0.13842	1.00000	6.783	4200.0
0.07081	0.00376	0.12680	0.00284	0.14220	0.28546	0.00062	0.05543	0.08577	0.22630	1.00000	8.554	4300.0
0.03878	0.00084	0.07990	0.00072	0.09167	0.19785	0.00018	0.08662	0.14224	0.36121	1.00000	13.035	4400.0
0.00586	0.00001	0.01378	0.00001	0.01616	0.03736	0.00000	0.13265	0.23040	0.56377	1.00000	68.563	4500.0

CARBON-HYDROGEN SYSTEM,HETEROGENEOUS REGION

TOTAL PRESSURE (ATM) = 10.00

Y H	Y H2	Y C2H	Y C2H2	Y C3H	Y C4H	Y C4H2	Y C1	Y C2	Y C3	Y SUM	C/H2	TEMP
0.00051	0.99865	0.00000	0.00083	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	1.00000	0.002	2000.0
0.00098	0.99747	0.00000	0.00154	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	1.00000	0.003	2100.0
0.00177	0.99552	0.00001	0.00270	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	1.00000	0.005	2200.0
0.00304	0.99244	0.00002	0.00449	0.00001	0.00000	0.00000	0.00000	0.00000	0.00000	1.00000	0.009	2300.0
0.00499	0.98779	0.00005	0.00714	0.00002	0.00000	0.00001	0.00000	0.00000	0.00000	1.00000	0.015	2400.0
0.00785	0.98103	0.00012	0.01091	0.00006	0.00001	0.00002	0.00000	0.00000	0.00000	1.00000	0.022	2500.0
0.01193	0.97148	0.00029	0.01606	0.00016	0.00004	0.00005	0.00000	0.00000	0.00000	1.00000	0.034	2600.0
0.01754	0.95838	0.00064	0.02286	0.00038	0.00011	0.00010	0.00000	0.00000	0.00000	1.00000	0.049	2700.0
0.02502	0.94079	0.00135	0.03151	0.00084	0.00029	0.00020	0.00000	0.00000	0.00000	1.00000	0.071	2800.0
0.03471	0.91761	0.00267	0.04212	0.00177	0.00073	0.00038	0.00000	0.00000	0.00000	1.00000	0.101	2900.0
0.04689	0.88749	0.00503	0.05463	0.00353	0.00172	0.00069	0.00001	0.00000	0.00001	1.00000	0.144	3000.0
0.06173	0.84885	0.00903	0.06870	0.00667	0.00379	0.00117	0.00001	0.00001	0.00003	1.00000	0.204	3100.0
0.07920	0.79985	0.01547	0.08359	0.01200	0.00786	0.00191	0.00003	0.00002	0.00008	1.00000	0.290	3200.0
0.09894	0.73856	0.02530	0.09805	0.02053	0.01538	0.00294	0.00007	0.00005	0.00020	1.00000	0.416	3300.0
0.12005	0.66339	0.03952	0.11021	0.03345	0.02842	0.00426	0.00015	0.00011	0.00044	1.00000	0.599	3400.0
0.14097	0.57392	0.05880	0.11770	0.05178	0.04954	0.00579	0.00031	0.00025	0.00095	1.00000	0.865	3500.0
0.15939	0.47215	0.08301	0.11803	0.07587	0.08117	0.00727	0.00060	0.00054	0.00196	1.00000	1.243	3600.0
0.17236	0.36381	0.11062	0.10958	0.10469	0.12445	0.00836	0.00113	0.00113	0.00386	1.00000	1.763	3700.0
0.17706	0.25854	0.13833	0.09283	0.13527	0.17765	0.00866	0.00208	0.00225	0.00734	1.00000	2.435	3800.0
0.17196	0.16752	0.16169	0.07100	0.16306	0.23530	0.00801	0.00368	0.00432	0.01346	1.00000	3.233	3900.0
0.15780	0.09873	0.17673	0.04895	0.18347	0.28944	0.00661	0.00634	0.00802	0.02392	1.00000	4.086	4000.0
0.13737	0.05328	0.18149	0.03063	0.19362	0.33240	0.00491	0.01062	0.01443	0.04125	1.00000	4.924	4100.0
0.11394	0.02652	0.17598	0.01754	0.19263	0.35832	0.00331	0.01736	0.02521	0.06921	1.00000	5.744	4200.0
0.08980	0.01210	0.16081	0.00914	0.18035	0.36204	0.00201	0.02772	0.04288	0.11315	1.00000	6.647	4300.0
0.06602	0.00487	0.13601	0.00417	0.15605	0.33680	0.00106	0.04331	0.07112	0.18060	1.00000	7.908	4400.0
0.04268	0.00154	0.10044	0.00148	0.11775	0.27228	0.00043	0.06632	0.11520	0.28188	1.00000	10.333	4500.0
0.01941	0.00024	0.05183	0.00026	0.06201	0.15312	0.00009	0.09966	0.18254	0.43084	1.00000	18.503	4600.0

TABLE B-2

CARBON-HYDROGEN SYSTEM,HOMOGENEOUS REGION

TOTAL PRESSURE (ATM) = 1.00

CARBON TO HYDROGEN RATIO = 0.500

YH	YH2	YC2H	YC2H2	YC3H	YC4H	YC4H2	YCH	YCH2	YC1	YC2	YC3	YSUM	C/H2	TEMP
0.13011	0.68340	0.03033	0.09135	0.03136	0.02250	0.00249	0.00004	0.00650	0.00008	0.00005	0.00039	0.99860	0.500	3000.0
0.17071	0.64911	0.03665	0.07709	0.03281	0.02255	0.00193	0.00007	0.00725	0.00015	0.00010	0.00058	0.99901	0.500	3100.0
0.21830	0.60758	0.04299	0.06403	0.03348	0.02201	0.00147	0.00011	0.00786	0.00031	0.00019	0.00084	0.99917	0.500	3200.0
0.27235	0.55968	0.04906	0.05233	0.03341	0.02100	0.00110	0.00017	0.00829	0.00059	0.00033	0.00115	0.99949	0.500	3300.0
0.33168	0.50643	0.05457	0.04205	0.03266	0.01962	0.00081	0.00026	0.00850	0.00106	0.00055	0.00157	0.99977	0.500	3400.0
0.39447	0.44938	0.05924	0.03318	0.03130	0.01797	0.00059	0.00037	0.00847	0.00183	0.00091	0.00205	0.99975	0.500	3500.0
0.45851	0.39074	0.06284	0.02570	0.02946	0.01617	0.00042	0.00051	0.00820	0.00307	0.00143	0.00264	0.99969	0.500	3600.0
0.52140	0.33292	0.06522	0.01955	0.02725	0.01430	0.00029	0.00069	0.00772	0.00501	0.00220	0.00332	0.99987	0.500	3700.0
0.58049	0.27787	0.06622	0.01457	0.02475	0.01242	0.00020	0.00089	0.00707	0.00793	0.00328	0.00409	0.99978	0.500	3800.0
0.63368	0.22748	0.06573	0.01064	0.02202	0.01055	0.00013	0.00112	0.00630	0.01222	0.00477	0.00493	0.99958	0.500	3900.0
0.67960	0.18312	0.06370	0.00760	0.01913	0.00873	0.00009	0.00137	0.00547	0.01833	0.00671	0.00579	0.99963	0.500	4000.0
0.71741	0.14530	0.06005	0.00529	0.01613	0.00697	0.00005	0.00162	0.00463	0.02673	0.00914	0.00658	0.99991	0.500	4100.0
0.74670	0.11388	0.05476	0.00358	0.01306	0.00529	0.00003	0.00186	0.00381	0.03782	0.01197	0.00716	0.99992	0.500	4200.0
0.76795	0.08846	0.04798	0.00233	0.01005	0.00377	0.00002	0.00206	0.00305	0.05177	0.01496	0.00737	0.99978	0.500	4300.0
0.78227	0.06836	0.04015	0.00146	0.00727	0.00248	0.00001	0.00221	0.00238	0.06836	0.01772	0.00710	0.99976	0.500	4400.0
0.79106	0.05273	0.03191	0.00087	0.00490	0.00148	0.00000	0.00228	0.00180	0.08684	0.01975	0.00633	0.99995	0.500	4500.0
0.79553	0.04072	0.02400	0.00050	0.00305	0.00080	0.00000	0.00227	0.00133	0.10594	0.02063	0.00518	0.99994	0.500	4600.0
0.79732	0.03160	0.01711	0.00027	0.00176	0.00039	0.00000	0.00218	0.00096	0.12424	0.02021	0.00389	0.99993	0.500	4700.0
0.79771	0.02469	0.01165	0.00014	0.00095	0.00017	0.00000	0.00204	0.00067	0.14055	0.01868	0.00271	0.99997	0.500	4800.0
0.79752	0.01946	0.00764	0.00007	0.00049	0.00007	0.00000	0.00186	0.00047	0.15418	0.01645	0.00177	0.99999	0.500	4900.0
0.79724	0.01548	0.00489	0.00004	0.00024	0.00003	0.00000	0.00167	0.00033	0.16502	0.01396	0.00110	0.99999	0.500	5000.0
0.79692	0.01242	0.00308	0.00002	0.00012	0.00001	0.00000	0.00148	0.00023	0.17330	0.01154	0.00067	0.99978	0.500	5100.0
0.79695	0.01006	0.00193	0.00001	0.00006	0.00000	0.00000	0.00130	0.00016	0.17964	0.00939	0.00040	0.99990	0.500	5200.0
0.79703	0.00822	0.00121	0.00000	0.00003	0.00000	0.00000	0.00114	0.00011	0.18437	0.00757	0.00024	0.99993	0.500	5300.0
0.79720	0.00676	0.00077	0.00000	0.00001	0.00000	0.00000	0.00100	0.00008	0.18791	0.00608	0.00014	0.99996	0.500	5400.0
0.79740	0.00560	0.00049	0.00000	0.00001	0.00000	0.00000	0.00088	0.00005	0.19057	0.00488	0.00008	0.99997	0.500	5500.0
0.79762	0.00467	0.00031	0.00000	0.00000	0.00000	0.00000	0.00077	0.00004	0.19258	0.00392	0.00005	0.99998	0.500	5600.0
0.79784	0.00393	0.00020	0.00000	0.00000	0.00000	0.00000	0.00068	0.00003	0.19412	0.00316	0.00003	0.99999	0.500	5700.0
0.79805	0.00332	0.00013	0.00000	0.00000	0.00000	0.00000	0.00060	0.00002	0.19529	0.00256	0.00002	0.99999	0.500	5800.0
0.79825	0.00282	0.00009	0.00000	0.00000	0.00000	0.00000	0.00053	0.00002	0.19620	0.00208	0.00001	1.00000	0.500	5900.0
0.79842	0.00241	0.00006	0.00000	0.00000	0.00000	0.00000	0.00047	0.00001	0.19691	0.00171	0.00001	1.00000	0.500	6000.0
0.79859	0.00207	0.00004	0.00000	0.00000	0.00000	0.00000	0.00042	0.00001	0.19747	0.00140	0.00000	1.00000	0.500	6100.0

CARBON-HYDROGEN SYSTEM,HOMOGENEOUS REGION

TOTAL PRESSURE (ATM) = 1.00

CARBON TO HYDROGEN RATIO = 1.000

YH	YH2	YC2H	YC2H2	YC3H	YC4H	YC4H2	YCH	YCH2	YC1	YC2	YC3	YSUM	C/H2	TEMP
0.11734	0.55586	0.04834	0.13132	0.06646	0.06339	0.00632	0.00005	0.00702	0.00010	0.00009	0.00092	0.99721	0.999	3000.0
0.15421	0.52971	0.05794	0.11011	0.06863	0.06241	0.00484	0.00008	0.00782	0.00021	0.00018	0.00135	0.99749	0.999	3100.0
0.19747	0.49718	0.05767	0.09118	0.06954	0.06032	0.00366	0.00013	0.00849	0.00041	0.00032	0.00192	0.99829	0.999	3200.0
0.24663	0.45896	0.07715	0.07452	0.06924	0.05734	0.00273	0.00020	0.00896	0.00077	0.00057	0.00265	0.99973	1.000	3300.0
0.30020	0.41485	0.08572	0.05978	0.06758	0.05348	0.00201	0.00031	0.00917	0.00139	0.00096	0.00358	0.99903	1.000	3400.0
0.35704	0.36813	0.09331	0.04730	0.06505	0.04926	0.00146	0.00044	0.00915	0.00242	0.00158	0.00472	0.99985	1.000	3500.0
0.41467	0.31958	0.09934	0.03675	0.06158	0.04467	0.00104	0.00061	0.00887	0.00407	0.00251	0.00610	0.99978	1.000	3600.0
0.47099	0.27166	0.10362	0.02805	0.05742	0.03996	0.00073	0.00082	0.00836	0.00664	0.00387	0.00775	0.99987	1.000	3700.0
0.52367	0.22613	0.10588	0.02102	0.05268	0.03519	0.00051	0.00107	0.00766	0.01056	0.00582	0.00965	0.99984	1.000	3800.0
0.57071	0.18452	0.10589	0.01543	0.04744	0.03041	0.00034	0.00135	0.00684	0.01634	0.00852	0.01180	0.99960	1.000	3900.0
0.61087	0.14796	0.10351	0.01110	0.04180	0.02565	0.00023	0.00165	0.00594	0.02464	0.01213	0.01408	0.99957	1.000	4000.0
0.64338	0.11686	0.09859	0.00779	0.03582	0.02095	0.00014	0.00197	0.00504	0.03616	0.01674	0.01630	0.99973	1.000	4100.0
0.66796	0.09113	0.09105	0.00532	0.02961	0.01636	0.00009	0.00227	0.00416	0.05156	0.02225	0.01815	0.99992	1.000	4200.0
0.68471	0.07033	0.08102	0.00351	0.02336	0.01205	0.00005	0.00253	0.00334	0.07124	0.02834	0.01922	0.99970	1.000	4300.0
0.69479	0.05392	0.06913	0.00223	0.01743	0.00827	0.00003	0.00273	0.00261	0.09518	0.03435	0.01917	0.99984	1.000	4400.0
0.69910	0.04119	0.05624	0.00136	0.01219	0.00521	0.00001	0.00284	0.00199	0.12252	0.03938	0.01782	0.99994	1.000	4500.0
0.69892	0.03143	0.04346	0.00079	0.00794	0.00299	0.00001	0.00286	0.00147	0.15210	0.04252	0.01532	0.99981	1.000	4600.0
0.69605	0.02408	0.03197	0.00044	0.00482	0.00156	0.00000	0.00279	0.00107	0.18175	0.04324	0.01217	0.99995	1.000	4700.0
0.69166	0.01856	0.02247	0.00024	0.00274	0.00075	0.00000	0.00264	0.00076	0.20962	0.04154	0.00898	0.99995	1.000	4800.0
0.68694	0.01444	0.01521	0.00013	0.00147	0.00033	0.00000	0.00244	0.00053	0.23430	0.03798	0.00621	0.99999	1.000	4900.0
0.68247	0.01134	0.01000	0.00006	0.00076	0.00014	0.00000	0.00221	0.00037	0.25502	0.03333	0.00407	0.99978	1.000	5000.0
0.67877	0.00901	0.00646	0.00003	0.00038	0.00006	0.00000	0.00198	0.00026	0.27190	0.02840	0.00258	0.99983	1.000	5100.0
0.67577	0.00723	0.00413	0.00002	0.00019	0.00002	0.00000	0.00176	0.00018	0.28523	0.02368	0.00160	0.99980	1.000	5200.0
0.67348	0.00587	0.00264	0.00001	0.00009	0.00001	0.00000	0.00155	0.00012	0.29567	0.01948	0.00097	0.99989	1.000	5300.0
0.67172	0.00480	0.00169	0.00000	0.00005	0.00000	0.00000	0.00137	0.00009	0.30372	0.01589	0.00059	0.99992	1.000	5400.0
0.67040	0.00396	0.00108	0.00000	0.00002	0.00000	0.00000	0.00120	0.00006	0.30994	0.01291	0.00036	0.99995	1.000	5500.0
0.66941	0.00329	0.00070	0.00000	0.00001	0.00000	0.00000	0.00106	0.00004	0.31475	0.01048	0.00022	0.99997	1.000	5600.0
0.66867	0.00276	0.00046	0.00000	0.00001	0.00000	0.00000	0.00093	0.00003	0.31847	0.00852	0.00014	0.99998	1.000	5700.0
0.66811	0.00232	0.00030	0.00000	0.00000	0.00000	0.00000	0.00083	0.00002	0.32137	0.00694	0.00008	0.99999	1.000	5800.0
0.66770	0.00197	0.00020	0.00000	0.00000	0.00000	0.00000	0.00073	0.00002	0.32364	0.00567	0.00005	0.99999	1.000	5900.0
0.66739	0.00168	0.00014	0.00000	0.00000	0.00000	0.00000	0.00065	0.00001	0.32543	0.00466	0.00003	0.99999	1.000	6000.0
0.66716	0.00144	0.00009	0.00000	0.00000	0.00000	0.00000	0.00058	0.00001	0.32684	0.00384	0.00002	1.00000	1.000	6100.0

TABLE B-2 (CONT'D)

CARBON-HYDROGEN SYSTEM,HOMOGENEOUS REGION

TOTAL PRESSURE (ATM) = 1.00

CARBON TO HYDROGEN RATIO = 2.500

YH	YH2	YC2H	YC2H2	YC3H	YC4H	YC4H2	YCH	YCH2	YC1	YC2	YC3	YSUM	C/H2	TEMP
0.08603	0.29876	0.07566	0.15069	0.15200	0.21184	0.01549	0.00005	0.00552	0.00015	0.00020	0.00285	0.99924	2.499	3000.0
0.11358	0.28735	0.09004	0.12601	0.15491	0.20459	0.01167	0.00009	0.00616	0.00031	0.00037	0.00413	0.99921	2.499	3100.0
0.14578	0.27097	0.10472	0.10416	0.15578	0.19563	0.00875	0.00014	0.00670	0.00060	0.00068	0.00582	0.99973	2.500	3200.0
0.18202	0.24998	0.11900	0.08483	0.15439	0.18486	0.00650	0.00022	0.00705	0.00112	0.00119	0.00803	0.99919	2.499	3300.0
0.22146	0.22577	0.13250	0.06817	0.15120	0.17317	0.00479	0.00033	0.00723	0.00201	0.00202	0.01085	0.99949	2.500	3400.0
0.26270	0.19929	0.14449	0.05390	0.14613	0.16052	0.00349	0.00047	0.00719	0.00350	0.00332	0.01442	0.99941	2.500	3500.0
0.30428	0.17208	0.15454	0.04195	0.13948	0.14735	0.00252	0.00065	0.00695	0.00592	0.00531	0.01884	0.99987	2.500	3600.0
0.34445	0.14530	0.16197	0.03206	0.13121	0.13351	0.00179	0.00088	0.00653	0.00971	0.00827	0.02421	0.99989	2.500	3700.0
0.38178	0.12019	0.16632	0.02407	0.12146	0.11911	0.00125	0.00115	0.00598	0.01550	0.01254	0.03055	0.99990	2.500	3800.0
0.41506	0.09760	0.16706	0.01771	0.11024	0.10407	0.00086	0.00145	0.00533	0.02407	0.01849	0.03770	0.99963	2.500	3900.0
0.44365	0.07804	0.16386	0.01276	0.09769	0.08850	0.00057	0.00177	0.00463	0.03638	0.02645	0.04530	0.99960	2.500	4000.0
0.46716	0.06161	0.15637	0.00898	0.08397	0.07256	0.00036	0.00211	0.00393	0.05345	0.03656	0.05261	0.99967	2.500	4100.0
0.48543	0.04813	0.14454	0.00614	0.06947	0.05674	0.00022	0.00243	0.00325	0.07620	0.04861	0.05858	0.99976	2.500	4200.0
0.49846	0.03727	0.12878	0.00406	0.05485	0.04182	0.00013	0.00272	0.00262	0.10527	0.06187	0.06200	0.99985	2.500	4300.0
0.50636	0.02864	0.11002	0.00259	0.04099	0.02873	0.00007	0.00294	0.00205	0.14065	0.07500	0.06185	0.99991	2.500	4400.0
0.50939	0.02187	0.08975	0.00158	0.02879	0.01822	0.00003	0.00307	0.00156	0.18148	0.08625	0.05775	0.99975	2.499	4500.0
0.50826	0.01662	0.06985	0.00093	0.01896	0.01062	0.00002	0.00309	0.00116	0.22610	0.09396	0.05031	0.99988	2.500	4600.0
0.50378	0.01261	0.05184	0.00052	0.01169	0.00568	0.00001	0.00302	0.00084	0.27204	0.09688	0.04082	0.99973	2.499	4700.0
0.49722	0.00959	0.03692	0.00028	0.00680	0.00282	0.00000	0.00287	0.00059	0.31690	0.09495	0.03102	0.99996	2.500	4800.0
0.48967	0.00734	0.02535	0.00015	0.00376	0.00130	0.00000	0.00266	0.00041	0.35832	0.08883	0.02220	0.99998	2.500	4900.0
0.48212	0.00566	0.01694	0.00008	0.00200	0.00057	0.00000	0.00242	0.00029	0.39486	0.07991	0.01513	0.99996	2.500	5000.0
0.47522	0.00442	0.01110	0.00004	0.00103	0.00024	0.00000	0.00217	0.00020	0.42596	0.06969	0.00992	0.99999	2.500	5100.0
0.46925	0.00349	0.00719	0.00002	0.00052	0.00010	0.00000	0.00193	0.00014	0.45147	0.05932	0.00633	0.99976	2.499	5200.0
0.46429	0.00279	0.00464	0.00001	0.00026	0.00004	0.00000	0.00171	0.00009	0.47235	0.04971	0.00397	0.99987	2.499	5300.0
0.46026	0.00225	0.00299	0.00001	0.00013	0.00002	0.00000	0.00151	0.00007	0.48899	0.04118	0.00247	0.99988	2.499	5400.0
0.45704	0.00184	0.00194	0.00000	0.00007	0.00001	0.00000	0.00133	0.00005	0.50223	0.03390	0.00153	0.99992	2.500	5500.0
0.45448	0.00152	0.00126	0.00000	0.00003	0.00000	0.00000	0.00117	0.00003	0.51269	0.02781	0.00095	0.99995	2.500	5600.0
0.45245	0.00126	0.00083	0.00000	0.00002	0.00000	0.00000	0.00103	0.00002	0.52096	0.02279	0.00059	0.99996	2.500	5700.0
0.45085	0.00106	0.00055	0.00000	0.00001	0.00000	0.00000	0.00092	0.00002	0.52750	0.01869	0.00037	0.99998	2.500	5800.0
0.44959	0.00089	0.00037	0.00000	0.00001	0.00000	0.00000	0.00081	0.00001	0.53270	0.01537	0.00024	0.99998	2.500	5900.0
0.44859	0.00076	0.00025	0.00000	0.00000	0.00000	0.00000	0.00072	0.00001	0.53683	0.01267	0.00015	0.99999	2.500	6000.0
0.44780	0.00065	0.00017	0.00000	0.00000	0.00000	0.00000	0.00064	0.00001	0.54013	0.01049	0.00010	0.99999	2.500	6100.0

CARBON-HYDROGEN SYSTEM,HOMOGENEOUS REGION

TOTAL PRESSURE (ATM) = 1.00

CARBON TO HYDROGEN RATIO = 5.000

YH	YH2	YC2H	YC2H2	YC3H	YC4H	YC4H2	YCH	YCH2	YC1	YC2	YC3	YSUM	C/H2	TEMP
0.04453	0.08004	0.07982	0.08228	0.22893	0.45549	0.01724	0.00004	0.00211	0.00022	0.00040	0.00831	0.99939	4.999	3000.0
0.05895	0.07741	0.09485	0.06890	0.23250	0.43750	0.01296	0.00006	0.00237	0.00044	0.00076	0.01194	0.99863	4.999	3100.0
0.07562	0.07291	0.11043	0.05698	0.23425	0.41944	0.00973	0.00010	0.00257	0.00085	0.00138	0.01688	1.00115	5.001	3200.0
0.09410	0.06681	0.12545	0.04623	0.23242	0.39740	0.00722	0.00016	0.00269	0.00159	0.00243	0.02337	0.99988	5.000	3300.0
0.11401	0.05984	0.13971	0.03700	0.22817	0.37399	0.00533	0.00024	0.00274	0.00288	0.00413	0.03181	0.99985	5.000	3400.0
0.13489	0.05255	0.15250	0.02921	0.22111	0.34822	0.00389	0.00035	0.00272	0.00502	0.00682	0.04248	0.99976	5.000	3500.0
0.15638	0.04545	0.16318	0.02276	0.21110	0.31965	0.00281	0.00048	0.00263	0.00849	0.01091	0.05549	0.99934	4.999	3600.0
0.17833	0.03894	0.17130	0.01756	0.19834	0.28844	0.00200	0.00065	0.00250	0.01388	0.01690	0.07069	0.99954	4.999	3700.0
0.20062	0.03319	0.17616	0.01339	0.18264	0.25428	0.00140	0.00085	0.00234	0.02201	0.02528	0.08741	0.99958	4.999	3800.0
0.22316	0.02821	0.17715	0.01010	0.16416	0.21766	0.00096	0.00109	0.00216	0.03381	0.03647	0.10443	0.99937	4.999	3900.0
0.24575	0.02394	0.17391	0.00750	0.14351	0.17997	0.00064	0.00136	0.00197	0.05036	0.05067	0.12015	0.99973	4.999	4000.0
0.26782	0.02025	0.16593	0.00546	0.12123	0.14253	0.00041	0.00165	0.00176	0.07271	0.06767	0.13249	0.99989	5.000	4100.0
0.28854	0.01700	0.15321	0.00387	0.09833	0.10725	0.00025	0.00193	0.00153	0.10176	0.08668	0.13951	0.99988	5.000	4200.0
0.30683	0.01412	0.13629	0.00265	0.07612	0.07611	0.00014	0.00219	0.00130	0.13804	0.10637	0.13978	0.99995	5.000	4300.0
0.32157	0.01155	0.11625	0.00174	0.05587	0.05051	0.00008	0.00241	0.00107	0.18142	0.12479	0.13274	0.99998	5.000	4400.0
0.33183	0.00928	0.09472	0.00109	0.03867	0.03115	0.00004	0.00254	0.00084	0.23099	0.13973	0.11908	0.99997	5.000	4500.0
0.33725	0.00732	0.07362	0.00065	0.02518	0.01778	0.00002	0.00259	0.00064	0.28497	0.14925	0.10073	0.99998	5.000	4600.0
0.33817	0.00568	0.05461	0.00037	0.01543	0.00939	0.00001	0.00254	0.00047	0.34078	0.15202	0.08025	0.99972	4.997	4700.0
0.33545	0.00437	0.03888	0.00020	0.00895	0.00463	0.00000	0.00242	0.00034	0.39597	0.14824	0.06052	0.99998	5.000	4800.0
0.33047	0.00334	0.02672	0.00011	0.00495	0.00214	0.00000	0.00224	0.00023	0.44776	0.13870	0.04333	0.99999	5.000	4900.0
0.32444	0.00256	0.01786	0.00005	0.00264	0.00094	0.00000	0.00204	0.00016	0.49433	0.12524	0.02968	0.99994	4.999	5000.0
0.31827	0.00198	0.01172	0.00003	0.00137	0.00040	0.00000	0.00182	0.00011	0.53479	0.10986	0.01964	0.99999	5.000	5100.0
0.31265	0.00155	0.00760	0.00001	0.00070	0.00017	0.00000	0.00162	0.00008	0.56865	0.09411	0.01264	0.99978	4.997	5200.0
0.30767	0.00122	0.00491	0.00001	0.00035	0.00007	0.00000	0.00143	0.00005	0.59679	0.07935	0.00801	0.99987	4.998	5300.0
0.30351	0.00098	0.00317	0.00000	0.00018	0.00003	0.00000	0.00126	0.00004	0.61957	0.06612	0.00502	0.99987	4.998	5400.0
0.30008	0.00079	0.00205	0.00000	0.00009	0.00001	0.00000	0.00111	0.00003	0.63792	0.05469	0.00313	0.99992	4.999	5500.0
0.29731	0.00065	0.00134	0.00000	0.00005	0.00000	0.00000	0.00098	0.00002	0.65258	0.04505	0.00196	0.99994	4.999	5600.0
0.29508	0.00054	0.00088	0.00000	0.00002	0.00000	0.00000	0.00086	0.00001	0.66428	0.03705	0.00123	0.99996	4.999	5700.0
0.29330	0.00045	0.00058	0.00000	0.00001	0.00000	0.00000	0.00076	0.00001	0.67360	0.03048	0.00077	0.99997	5.000	5800.0
0.29187	0.00038	0.00039	0.00000	0.00001	0.00000	0.00000	0.00067	0.00001	0.68104	0.02512	0.00049	0.99998	5.000	5900.0
0.29073	0.00032	0.00026	0.00000	0.00000	0.00000	0.00000	0.00060	0.00001	0.68699	0.02076	0.00032	0.99999	5.000	6000.0
0.28982	0.00027	0.00018	0.00000	0.00000	0.00000	0.00000	0.00053	0.00000	0.69176	0.01721	0.00020	0.99999	5.000	6100.0

TABLE B-2 (CONT'D)

CARBON-HYDROGEN SYSTEM,HOMOGENEOUS REGION

TOTAL PRESSURE (ATM) = 1.00

CARBON TO HYDROGEN RATIO = 7.500

YH	YH2	YC2H	YC2H2	YC3H	YC4H	YC4H2	YCH	YCH2	YC1	YC2	YC3	YSUM	C/H2	TEMP
0.00712	0.00205	0.03956	0.00652	0.19975	0.69958	0.00424	0.00001	0.00010	0.00038	0.00124	0.04532	1.00587	7.503	3000.0
0.01054	0.00248	0.04934	0.00641	0.20624	0.66182	0.00351	0.00002	0.00013	0.00075	0.00220	0.05922	1.00265	7.501	3100.0
0.01524	0.00296	0.06057	0.00630	0.21196	0.62608	0.00293	0.00003	0.00017	0.00141	0.00375	0.07578	1.00720	7.505	3200.0
0.02162	0.00353	0.07272	0.00616	0.21397	0.58106	0.00243	0.00006	0.00023	0.00253	0.00612	0.09363	1.00405	7.504	3300.0
0.02995	0.00413	0.08569	0.00596	0.21382	0.53550	0.00200	0.00010	0.00029	0.00440	0.00965	0.11348	1.00497	7.505	3400.0
0.04067	0.00478	0.09865	0.00570	0.20951	0.48334	0.00163	0.00015	0.00036	0.00736	0.01464	0.13353	1.00031	7.500	3500.0
0.05383	0.00539	0.11136	0.00535	0.20286	0.43249	0.00131	0.00023	0.00044	0.01195	0.02164	0.15490	1.00174	7.503	3600.0
0.06977	0.00596	0.12268	0.00492	0.19218	0.37813	0.00103	0.00034	0.00052	0.01878	0.03094	0.17508	1.00032	7.501	3700.0
0.08837	0.00644	0.13189	0.00442	0.17827	0.32359	0.00079	0.00049	0.00059	0.02869	0.04297	0.19371	1.00021	7.501	3800.0
0.10943	0.00678	0.13799	0.00386	0.16116	0.26930	0.00058	0.00068	0.00066	0.04261	0.05793	0.20906	1.00003	7.500	3900.0
0.13242	0.00695	0.14013	0.00326	0.14141	0.21685	0.00042	0.00090	0.00070	0.06158	0.07578	0.21971	1.00009	7.500	4000.0
0.15649	0.00691	0.13761	0.00265	0.11978	0.16778	0.00028	0.00115	0.00071	0.08663	0.09604	0.22405	1.00008	7.500	4100.0
0.18045	0.00665	0.13016	0.00205	0.09737	0.12378	0.00018	0.00141	0.00070	0.11861	0.11776	0.22090	1.00002	7.500	4200.0
0.20281	0.00617	0.11807	0.00152	0.07549	0.08641	0.00011	0.00166	0.00065	0.15803	0.13941	0.20973	1.00005	7.500	4300.0
0.22197	0.00550	0.10229	0.00106	0.05550	0.05665	0.00006	0.00188	0.00057	0.20483	0.15907	0.19105	1.00043	7.505	4400.0
0.23678	0.00472	0.08430	0.00069	0.03844	0.03457	0.00003	0.00203	0.00048	0.25797	0.17428	0.16588	1.00018	7.502	4500.0
0.24642	0.00391	0.06605	0.00042	0.02504	0.01959	0.00001	0.00209	0.00038	0.31577	0.18325	0.13704	0.99997	7.500	4600.0
0.25097	0.00313	0.04928	0.00025	0.01535	0.01031	0.00001	0.00208	0.00029	0.37576	0.18483	0.10758	0.99983	7.497	4700.0
0.25118	0.00245	0.03519	0.00014	0.00891	0.00506	0.00000	0.00199	0.00021	0.43531	0.17916	0.08041	0.99999	7.500	4800.0
0.24859	0.00189	0.02420	0.00007	0.00492	0.00234	0.00000	0.00185	0.00015	0.49139	0.16705	0.05727	0.99972	7.493	4900.0
0.24419	0.00145	0.01619	0.00004	0.00262	0.00103	0.00000	0.00168	0.00010	0.54254	0.15086	0.03924	0.99995	7.499	5000.0
0.23940	0.00112	0.01062	0.00002	0.00136	0.00044	0.00000	0.00151	0.00007	0.58693	0.13232	0.02596	0.99975	7.493	5100.0
0.23462	0.00087	0.00689	0.00001	0.00069	0.00018	0.00000	0.00133	0.00005	0.62481	0.11362	0.01677	0.99985	7.495	5200.0
0.23037	0.00069	0.00444	0.00000	0.00035	0.00008	0.00000	0.00118	0.00003	0.65612	0.09592	0.01064	0.99983	7.495	5300.0
0.22670	0.00055	0.00287	0.00000	0.00018	0.00003	0.00000	0.00103	0.00002	0.68175	0.08006	0.00669	0.99988	7.496	5400.0
0.22366	0.00044	0.00186	0.00000	0.00009	0.00001	0.00000	0.00091	0.00002	0.70243	0.06631	0.00419	0.99991	7.497	5500.0
0.22117	0.00036	0.00121	0.00000	0.00005	0.00001	0.00000	0.00080	0.00001	0.71903	0.05469	0.00262	0.99994	7.498	5600.0
0.21915	0.00030	0.00079	0.00000	0.00002	0.00000	0.00000	0.00070	0.00001	0.73230	0.04503	0.00164	0.99996	7.499	5700.0
0.21754	0.00025	0.00053	0.00000	0.00001	0.00000	0.00000	0.00062	0.00001	0.74290	0.03708	0.00104	0.99997	7.499	5800.0
0.21624	0.00021	0.00035	0.00000	0.00001	0.00000	0.00000	0.00055	0.00000	0.75138	0.03058	0.00065	0.99998	7.499	5900.0
0.21519	0.00017	0.00024	0.00000	0.00000	0.00000	0.00000	0.00049	0.00000	0.75818	0.02528	0.00042	0.99998	7.500	6000.0
0.21435	0.00015	0.00016	0.00000	0.00000	0.00000	0.00000	0.00044	0.00000	0.76364	0.02097	0.00027	0.99999	7.500	6100.0

CARBON-HYDROGEN SYSTEM,HOMOGENEOUS REGION

TOTAL PRESSURE (ATM) = 1.00

CARBON TO HYDROGEN RATIO = 15.000

YH	YH2	YC2H	YC2H2	YC3H	YC4H	YC4H2	YCH	YCH2	YC1	YC2	YC3	YSUM	C/H2	TEMP
0.00032	0.00000	0.00635	0.00005	0.06074	0.40328	0.00011	0.00000	0.00000	0.00072	0.00445	0.30883	0.78484	11.655	3000.0
0.00050	0.00001	0.00822	0.00005	0.06447	0.38816	0.00010	0.00000	0.00000	0.00140	0.00774	0.39118	0.86182	12.795	3100.0
0.00094	0.00001	0.01158	0.00007	0.07144	0.37210	0.00011	0.00000	0.00000	0.00248	0.01166	0.41552	0.88592	13.140	3200.0
0.00146	0.00002	0.01473	0.00008	0.07514	0.35370	0.00010	0.00001	0.00000	0.00439	0.01838	0.48775	0.95576	14.254	3300.0
0.00233	0.00002	0.01886	0.00010	0.07918	0.33359	0.00010	0.00001	0.00000	0.00740	0.02730	0.54021	1.00912	15.160	3400.0
0.00417	0.00005	0.02538	0.00015	0.08540	0.31213	0.00011	0.00002	0.00001	0.01166	0.03675	0.53095	1.00679	15.123	3500.0
0.00706	0.00009	0.03291	0.00021	0.08997	0.28788	0.00011	0.00005	0.00001	0.01793	0.04874	0.52365	1.00863	15.163	3600.0
0.01163	0.00017	0.04160	0.00028	0.09294	0.26078	0.00012	0.00008	0.00002	0.02678	0.06291	0.50777	1.00508	15.101	3700.0
0.01838	0.00028	0.05080	0.00035	0.09346	0.23088	0.00012	0.00014	0.00003	0.03905	0.07960	0.48835	1.00142	15.030	3800.0
0.02759	0.00043	0.05952	0.00042	0.09093	0.19874	0.00011	0.00022	0.00005	0.05573	0.09911	0.46785	1.00072	15.017	3900.0
0.03959	0.00062	0.06689	0.00046	0.08529	0.16525	0.00009	0.00034	0.00008	0.07781	0.12097	0.44315	1.00054	15.014	4000.0
0.05435	0.00083	0.07185	0.00048	0.07669	0.13170	0.00008	0.00049	0.00011	0.10622	0.14439	0.41300	1.00018	15.005	4100.0
0.07110	0.00103	0.07337	0.00046	0.06565	0.09982	0.00006	0.00066	0.00013	0.14186	0.16846	0.37798	1.00058	15.019	4200.0
0.08893	0.00119	0.07101	0.00040	0.05317	0.07127	0.00004	0.00085	0.00015	0.18507	0.19120	0.33687	1.00015	15.006	4300.0
0.10603	0.00126	0.06478	0.00032	0.04048	0.04757	0.00002	0.00103	0.00015	0.23586	0.21091	0.29167	1.00008	15.004	4400.0
0.12076	0.00123	0.05559	0.00023	0.02882	0.02948	0.00001	0.00117	0.00014	0.29334	0.22535	0.24388	1.00002	15.001	4500.0
0.13178	0.00112	0.04486	0.00015	0.01916	0.01690	0.00001	0.00126	0.00012	0.35585	0.23273	0.19614	1.00008	15.005	4600.0
0.13861	0.00095	0.03415	0.00009	0.01191	0.00896	0.00000	0.00129	0.00010	0.42091	0.23192	0.15121	1.00010	15.007	4700.0
0.14166	0.00078	0.02469	0.00005	0.00697	0.00442	0.00000	0.00125	0.00007	0.48555	0.22290	0.11158	0.99992	14.994	4800.0
0.14171	0.00061	0.01710	0.00003	0.00387	0.00205	0.00000	0.00117	0.00005	0.54711	0.20709	0.07904	0.99986	14.988	4900.0
0.13981	0.00048	0.01147	0.00002	0.00207	0.00090	0.00000	0.00107	0.00004	0.60347	0.18665	0.05400	0.99997	14.998	5000.0
0.13721	0.00037	0.00753	0.00001	0.00107	0.00038	0.00000	0.00096	0.00003	0.65283	0.16370	0.03572	0.99980	14.980	5100.0
0.13424	0.00029	0.00488	0.00000	0.00055	0.00016	0.00000	0.00085	0.00002	0.69515	0.14064	0.02310	0.99987	14.986	5200.0
0.13149	0.00022	0.00314	0.00000	0.00028	0.00007	0.00000	0.00075	0.00001	0.73035	0.11884	0.01468	0.99983	14.982	5300.0
0.12901	0.00018	0.00202	0.00000	0.00014	0.00003	0.00000	0.00066	0.00001	0.75930	0.09930	0.00924	0.99989	14.987	5400.0
0.12693	0.00014	0.00131	0.00000	0.00007	0.00001	0.00000	0.00057	0.00001	0.78274	0.08234	0.00579	0.99991	14.990	5500.0
0.12520	0.00012	0.00085	0.00000	0.00004	0.00000	0.00000	0.00050	0.00000	0.80152	0.06798	0.00363	0.99994	14.993	5600.0
0.12379	0.00009	0.00056	0.00000	0.00002	0.00000	0.00000	0.00044	0.00000	0.81675	0.05601	0.00228	0.99995	14.995	5700.0
0.12265	0.00008	0.00037	0.00000	0.00001	0.00000	0.00000	0.00039	0.00000	0.82886	0.04616	0.00144	0.99997	14.996	5800.0
0.12174	0.00007	0.00025	0.00000	0.00001	0.00000	0.00000	0.00035	0.00000	0.83857	0.03809	0.00092	0.99998	14.997	5900.0
0.12100	0.00006	0.00017	0.00000	0.00000	0.00000	0.00000	0.00031	0.00000	0.84636	0.03151	0.00059	0.99998	14.998	6000.0
0.12040	0.00005	0.00011	0.00000	0.00000	0.00000	0.00000	0.00027	0.00000	0.85262	0.02614	0.00038	0.99999	14.999	6100.0

TABLE B-2 (CONT'D)

CARBON-HYDROGEN SYSTEM,HOMOGENEOUS REGION

TOTAL PRESSURE (ATM) = 0.10

CARBON TO HYDROGEN RATIO = 5.000

YH	YH2	YC2H	YC2H2	YC3H	YC4H	YC4H2	YCH	YCH2	YC1	YC2	YC3	YSUM	C/H2	TEMP
0.12299	0.06106	0.11913	0.03392	0.25119	0.36739	0.00384	0.00008	0.00118	0.00158	0.00216	0.03301	0.99753	4.998	3000.0
0.15112	0.05087	0.13261	0.02469	0.24003	0.33354	0.00253	0.00012	0.00115	0.00323	0.00412	0.04808	0.99210	4.992	3100.0
0.18028	0.04144	0.14357	0.01766	0.22489	0.29737	0.00165	0.00018	0.00108	0.00629	0.00752	0.06798	0.98992	4.989	3200.0
0.21028	0.03336	0.15115	0.01245	0.20562	0.25815	0.00105	0.00026	0.00099	0.01171	0.01308	0.09252	0.99062	4.988	3300.0
0.24136	0.02682	0.15506	0.00869	0.18336	0.21762	0.00066	0.00037	0.00089	0.02085	0.02167	0.12077	0.99812	4.997	3400.0
0.27176	0.02133	0.15176	0.00586	0.15464	0.17117	0.00039	0.00049	0.00078	0.03531	0.03371	0.14748	0.99467	4.989	3500.0
0.30158	0.01690	0.14349	0.00386	0.12535	0.12817	0.00022	0.00063	0.00066	0.05730	0.04977	0.17085	0.99877	4.997	3600.0
0.32794	0.01317	0.12837	0.00242	0.09488	0.08808	0.00011	0.00076	0.00054	0.08861	0.06887	0.18389	0.99765	4.991	3700.0
0.34882	0.01003	0.10876	0.00144	0.06720	0.05575	0.00005	0.00089	0.00042	0.13113	0.08978	0.18497	0.99923	4.996	3800.0
0.36181	0.00742	0.08610	0.00080	0.04369	0.03171	0.00002	0.00097	0.00031	0.18511	0.10933	0.17141	0.99868	4.991	3900.0
0.36587	0.00531	0.06365	0.00041	0.02604	0.01619	0.00001	0.00100	0.00022	0.24969	0.12458	0.14645	0.99942	4.995	4000.0
0.36176	0.00369	0.04371	0.00019	0.01410	0.00732	0.00000	0.00098	0.00014	0.32112	0.13197	0.11413	0.99914	4.991	4100.0
0.35175	0.00253	0.02808	0.00009	0.00699	0.00296	0.00000	0.00091	0.00009	0.39457	0.13031	0.08132	0.99959	4.995	4200.0
0.33918	0.00173	0.01699	0.00004	0.00319	0.00107	0.00000	0.00081	0.00005	0.46357	0.11996	0.05294	0.99954	4.994	4300.0
0.32680	0.00119	0.00984	0.00001	0.00136	0.00036	0.00000	0.00071	0.00003	0.52355	0.10392	0.03190	0.99967	4.995	4400.0
0.31626	0.00084	0.00554	0.00001	0.00056	0.00011	0.00000	0.00060	0.00002	0.57210	0.08571	0.01809	0.99985	4.998	4500.0
0.30813	0.00061	0.00307	0.00000	0.00022	0.00003	0.00000	0.00051	0.00001	0.60917	0.06820	0.00984	0.99981	4.997	4600.0
0.30208	0.00045	0.00170	0.00000	0.00009	0.00001	0.00000	0.00042	0.00001	0.63680	0.05308	0.00524	0.99990	4.998	4700.0
0.29772	0.00034	0.00095	0.00000	0.00004	0.00000	0.00000	0.00036	0.00000	0.65694	0.04080	0.00275	0.99993	4.999	4800.0
0.29458	0.00027	0.00054	0.00000	0.00001	0.00000	0.00000	0.00030	0.00000	0.67159	0.03120	0.00146	0.99996	4.999	4900.0
0.29231	0.00021	0.00031	0.00000	0.00001	0.00000	0.00000	0.00025	0.00000	0.68225	0.02386	0.00078	0.99997	5.000	5000.0
0.29067	0.00017	0.00018	0.00000	0.00000	0.00000	0.00000	0.00021	0.00000	0.69004	0.01829	0.00042	0.99998	5.000	5100.0
0.28947	0.00013	0.00011	0.00000	0.00000	0.00000	0.00000	0.00018	0.00000	0.69578	0.01409	0.00023	0.99999	5.000	5200.0
0.28858	0.00011	0.00006	0.00000	0.00000	0.00000	0.00000	0.00016	0.00000	0.70003	0.01092	0.00013	0.99999	5.000	5300.0
0.28882	0.00009	0.00004	0.00000	0.00000	0.00000	0.00000	0.00014	0.00000	0.70024	0.00845	0.00007	0.99784	4.963	5400.0
0.28743	0.00007	0.00002	0.00000	0.00000	0.00000	0.00000	0.00012	0.00000	0.70561	0.00669	0.00004	0.99999	5.000	5500.0
0.28756	0.00006	0.00002	0.00000	0.00000	0.00000	0.00000	0.00010	0.00000	0.70576	0.00527	0.00002	0.99880	4.979	5600.0
0.28766	0.00005	0.00001	0.00000	0.00000	0.00000	0.00000	0.00009	0.00000	0.70589	0.00418	0.00001	0.99789	4.964	5700.0
0.28655	0.00004	0.00001	0.00000	0.00000	0.00000	0.00000	0.00008	0.00000	0.70991	0.00339	0.00001	0.99999	5.000	5800.0
0.28662	0.00004	0.00000	0.00000	0.00000	0.00000	0.00000	0.00007	0.00000	0.70997	0.00273	0.00001	0.99943	4.990	5900.0
0.28667	0.00003	0.00000	0.00000	0.00000	0.00000	0.00000	0.00006	0.00000	0.71001	0.00222	0.00000	0.99900	4.983	6000.0
0.28672	0.00003	0.00000	0.00000	0.00000	0.00000	0.00000	0.00005	0.00000	0.71004	0.00181	0.00000	0.99866	4.977	6100.0

CARBON-HYDROGEN SYSTEM,HOMOGENEOUS REGION

TOTAL PRESSURE (ATM) = 10.00

CARBON TO HYDROGEN RATIO = 5.000

YH	YH2	YC2H	YC2H2	YC3H	YC4H	YC4H2	YCH	YCH2	YC1	YC2	YC3	YSUM	C/H2	TEMP
0.01282	0.06631	0.04499	0.13350	0.18059	0.50283	0.05478	0.00002	0.00245	0.00003	0.00008	0.00228	1.00065	5.001	3000.0
0.01781	0.07064	0.05548	0.12175	0.18923	0.49547	0.04433	0.00003	0.00300	0.00006	0.00015	0.00322	1.00116	5.001	3100.0
0.02401	0.07351	0.06695	0.10969	0.19624	0.48552	0.03578	0.00005	0.00358	0.00012	0.00026	0.00445	1.00016	5.000	3200.0
0.03151	0.07490	0.07934	0.09790	0.20201	0.47470	0.02889	0.00007	0.00415	0.00022	0.00046	0.00607	1.00023	5.000	3300.0
0.04032	0.07483	0.09236	0.08651	0.20625	0.46223	0.02328	0.00012	0.00469	0.00039	0.00077	0.00813	0.99989	5.000	3400.0
0.05042	0.07340	0.10579	0.07573	0.20897	0.44838	0.01873	0.00018	0.00517	0.00068	0.00127	0.01074	0.99946	4.999	3500.0
0.06172	0.07081	0.11943	0.06576	0.21039	0.43379	0.01505	0.00026	0.00558	0.00116	0.00202	0.01401	0.99998	5.000	3600.0
0.07410	0.06724	0.13286	0.05658	0.21018	0.41761	0.01206	0.00037	0.00590	0.00190	0.00315	0.01803	0.99997	5.000	3700.0
0.08736	0.06294	0.14582	0.04829	0.20844	0.40011	0.00962	0.00051	0.00613	0.00303	0.00481	0.02291	0.99997	5.000	3800.0
0.10134	0.05818	0.15797	0.04088	0.20513	0.38112	0.00765	0.00070	0.00625	0.00474	0.00716	0.02873	0.99985	5.000	3900.0
0.11587	0.05323	0.16904	0.03438	0.20031	0.36067	0.00605	0.00092	0.00627	0.00723	0.01045	0.03557	0.99999	5.000	4000.0
0.13079	0.04829	0.17868	0.02871	0.19384	0.33841	0.00476	0.00119	0.00622	0.01080	0.01492	0.04338	0.99998	5.000	4100.0
0.14602	0.04355	0.18656	0.02383	0.18573	0.31424	0.00372	0.00152	0.00609	0.01579	0.02086	0.05207	0.99997	5.000	4200.0
0.16152	0.03913	0.19239	0.01967	0.17597	0.28811	0.00288	0.00189	0.00590	0.02260	0.02852	0.06138	0.99997	5.000	4300.0
0.17725	0.03509	0.19584	0.01613	0.16456	0.26010	0.00220	0.00232	0.00567	0.03172	0.03814	0.07093	0.99995	5.000	4400.0
0.19318	0.03145	0.19661	0.01314	0.15158	0.23052	0.00166	0.00279	0.00540	0.04362	0.04982	0.08018	0.99997	5.000	4500.0
0.20925	0.02818	0.19442	0.01062	0.13722	0.19989	0.00123	0.00331	0.00510	0.05879	0.06353	0.08845	0.99999	5.000	4600.0
0.22529	0.02523	0.18904	0.00848	0.12173	0.16895	0.00090	0.00386	0.00477	0.07768	0.07899	0.09504	0.99995	5.000	4700.0
0.24108	0.02255	0.18041	0.00669	0.10552	0.13869	0.00064	0.00442	0.00441	0.10061	0.09570	0.09927	1.00000	5.000	4800.0
0.25627	0.02009	0.16859	0.00519	0.08910	0.11010	0.00044	0.00496	0.00402	0.12773	0.11287	0.10058	0.99994	5.000	4900.0
0.27045	0.01781	0.15397	0.00394	0.07306	0.08423	0.00029	0.00546	0.00361	0.15896	0.12951	0.09869	0.99997	5.000	5000.0
0.28317	0.01569	0.13713	0.00292	0.05801	0.06186	0.00018	0.00589	0.00318	0.19392	0.14444	0.09361	0.99999	5.000	5100.0
0.29402	0.01370	0.11891	0.00211	0.04450	0.04350	0.00011	0.00621	0.00275	0.23191	0.15653	0.08575	0.99999	5.000	5200.0
0.30268	0.01185	0.10032	0.00148	0.03296	0.02925	0.00006	0.00641	0.00232	0.27200	0.16483	0.07583	0.99999	5.000	5300.0
0.30901	0.01016	0.08239	0.00102	0.02356	0.01881	0.00004	0.00647	0.00192	0.31305	0.16880	0.06477	0.99999	5.000	5400.0
0.31306	0.00864	0.06596	0.00068	0.01630	0.01160	0.00002	0.00641	0.00156	0.35391	0.16833	0.05353	0.99999	5.000	5500.0
0.31510	0.00729	0.05161	0.00044	0.01094	0.00689	0.00001	0.00623	0.00125	0.39350	0.16381	0.04292	1.00000	5.000	5600.0
0.31547	0.00614	0.03961	0.00028	0.00716	0.00396	0.00000	0.00597	0.00098	0.43096	0.15595	0.03350	1.00000	5.000	5700.0
0.31462	0.00515	0.02993	0.00018	0.00460	0.00222	0.00000	0.00564	0.00076	0.46565	0.14568	0.02556	1.00000	5.000	5800.0
0.31293	0.00433	0.02235	0.00011	0.00290	0.00122	0.00000	0.00528	0.00059	0.49723	0.13391	0.01914	1.00000	5.000	5900.0
0.31075	0.00365	0.01655	0.00007	0.00181	0.00066	0.00000	0.00490	0.00046	0.52555	0.12148	0.01412	1.00000	5.000	6000.0
0.30835	0.00308	0.01219	0.00004	0.00113	0.00035	0.00000	0.00453	0.00035	0.55063	0.10904	0.01030	1.00000	5.000	6100.0

Table B-3

Maximum Calculated Vol. % C_2H_2 in
Quenched Gas at One Atm. Pressure

T, °K	Hetero. region	Homogeneous region for C/H_2 ratios of 0.5	1.0	2.5	5.0	7.5	10.0	15.0
2500	1.12	-	-	-	-	-	-	-
2700	2.46	-	-	-	-	-	-	-
2900	4.96	-	-	-	-	-	-	-
3100	9.53	-	-	-	-	-	-	-
3300	17.0	12.42	-	-	-	-	-	
3500	27.9	12.47	20.1	-	-	-	-	
3700	38.5	12.56	20.7	34.2	-	-	-	
3900	43.2	12.79	20.7	35.5	43.3	-	-	
4100	42.9	11.73	20.0	35.5	45.4	46.5	46.2	42.7
4300		9.87	17.7	32.6	43.8	46.2	49.0	49.4
4500		6.95	13.5	26.2	37.5	41.5	44.2	46.7
4700		3.90	8.1	17.3	25.4	29.2	32.0	34.7
4900		1.90	4.3	9.3	14.3	17.1	18.6	20.5
5100		0.7	2.9	4.5	6.9	8.2	9.2	10.2
5300			1.0	1.9	3.1	3.6	4.1	4.6
5500			0.6	1.0	1.3	1.7	1.8	1.9

Table B-4

Maximum Calculated Vol. % C_2H_2 in
Quenched Gas at 0.1 Atm. Pressure

		Homogeneous region for C/H_2 ratios of					
T, °K	Hetero. region	0.5	1.0	2.5	5.0	10.0	15.0
2500	1.2	-	-	-	-	-	-
2700	2.8	-	-	-	-	-	-
2900	6.2	-	-	-	-	-	-
3100	13.3	11.3	-	-	-	-	-
3300	24.9	11.5	18.7	-	-	-	-
3500	36.7	11.3	18.6	31.5	-	-	-
3700	43.0	9.9	16.6	29.7	38.9	42.7	-
3900		6.8	12.3	23.4	32.0	38.0	40.6
4100		3.3	7.0	14.1	20.1	25.6	27.7
4300		1.2	2.9	6.4	9.1	12.1	13.5
4500		0.3	0.9	2.2	3.4	4.5	5.1
4700				0.8	1.2	1.5	1.7
4900							
5100							
5300							
5500							

Table B-5

Maximum Calculated Vol. % C_2H_2 in Quenched Gas at 10.0 Atm. Pressure

T, °K	Hetero. region	Homogeneous region for C/H_2 ratios of 0.5	1.0	2.5	5.0	10.0	15.0
2600	1.6	-	-	-	-	-	-
2800	3.3	-	-	-	-	-	-
3000	6.1	-	-	-	-	-	-
3200	10.5	-	-	-	-	-	-
3400	16.8	14.4	-	-	-	-	-
3600	25.2	13.7	21.8	-	-	-	-
3800	34.3	13.3	21.4	-	-	-	-
4000	40.4	13.2	21.5	35.2	-	-	-
4200	41.8	13.2	22.1	36.9	42.6	-	-
4400	39.3	13.2	22.3	38.5	46.2	-	-
4600	37.7	12.8	22.2	39.3	49.1	42.7	37.8
4800	36.2	11.9	21.2	38.9	50.7	50.5	47.9
5000		10.3	19.0	36.4	49.6	53.5	54.2
5200		8.0	15.7	31.5	44.5	52.7	54.2
5400		5.6	11.6	24.4	35.5	44.4	47.7
5600		3.4	7.6	17.0	24.9	32.6	36.0
5800		1.9	4.5	10.6	16.3	21.3	23.5
6000		1.0	2.5	6.2	9.8	12.8	14.2

Table B-6

Maximum Calculated Vol. % C_2H_2 in Quenched Gas at 0.5 and 5.0 Atm. Pressure, for a C/H_2 = 5.0 in the homogeneous regions

	Heterogeneous region		Homogeneous region	
T, °K	0.5 atm.	5.0 atm.	0.5 atm.	5.0 atm.
2600	1.7	1.7	-	-
2800	3.6	3.5	-	-
3000	7.3	6.4	-	-
3200	14.1	11.1	-	-
3400	24.7	18.0	-	-
3600	36.5	27.4	-	-
3800	42.8	36.5	42.6	-
4000	43.7	41.6	43.6	-
4200		41.7	39.8	44.7
4400		39.2	30.0	47.9
4600			17.9	49.2
4800			8.7	47.6
5000			3.7	40.9
5200			1.5	30.9
5400				20.2
5600				11.8
5800				6.4
6000				3.3

Appendix C

Experimental Results

Explanation of Symbols for Tables C-1 and C-2

P.P	-	probe plugged
S.S.	-	small sample, poor sample
S.F.	-	slow feed rate of the anode
L.A.	-	lots of air in the sampling bottle, air leak
F.F.	-	fast feed rate of the anode
M.E.	-	methane and ethylene concentrations in output gas
S.P.W.	-	sampling procedure wrong
V	-	voltage
I	-	current
P	-	power
C.V.R.	-	carbon vaporization rate
A.F.B.	-	air-free basis
A	-	specific energy, kw-hr/lb C_2H_2
β	-	coefficient of volume expansion
A.O.	-	arc out for specified time
S	-	sampling made sideways
EXT	-	extrapolated from C.V.R. curve and flow rate
Note:		Hydrogen: Series A, B, C: 1/4 in. graphite anodes, probes 5/16 in. o.d.; series X: 3/8 in. graphite anodes, probes 3/8 in. o.d. Methane: Series D, E, Y, and Z: 3/8 in. graphite anodes, probes 3/8 in. o.d.

Table C-1

Hydrogen Runs

Run No.	V volts	I amps	P kw	CVR gm/min.	probe position	sample size ml	C/H_2 ratio (feed)	$\%C_2H_2$ (AFB)	β	A $\frac{\text{kw-hr}}{\text{lb } C_2H_2}$	Remarks
H_2 flow rate: 3.0 lit./min., 19 g. probe (0.043 in. i.d.)											
A-II-1	84	160	13.4	-	1 1/2	75	-	7.7	~ 1	407	1/4" anode
III-1	90	180	16.1	0.645	1 1/4	15	0.43	8.8		428	for series
-2	77	220	17.7	-	7/8	20	-	17.1		238	A
-3	70	260	18.1	4.88	1	25	3.25	8.9		473	
A-IV-1	72	255	18.5	3.47	1	10	2.33	7.1		413	
-2	62	300	18.6	-	1	5	-	-		-	missed
-3	85	200	17.0	3.95	1	55	2.65	7.3		545	
-4	75	200	15.0	4.32	7/8	25	2.9	14.9		236	
-5	85	180	15.2	4.47	1/2	30	3.0	9.9		359	P.P.
-6	75	220	16.4	5.45	1/2	5	3.65	4.6		827	P.P.
-7	65	250	16.2	7.43	3/4	25	4.97	16.7		227	
-8	70	260	18.2	8.3	3/4	25	5.55	14.4		295	
-9	70	275	19.2	7.6	5/8	15	5.1	15.1		375	
-10	70	320	22.4	8.7	1	25	5.85	12.6		525	
-11	75	310	23.2	10.2	1/2	5	6.83	-		-	S.S.
-12	70	320	22.4	9.85	1/2	20	6.6	16.8		393	
-13	75	335	25	-	1/2	25	-	-		475	S.F.

Table C-1 (cont'd)

Run No.	V volts	I amps	P kw	CVR gm/min.	Probe Position	Sample Size ml	C/H_2 ratio (AFB)	$\%C_2H_2$ (AFB)	β	A $\frac{\text{kw-hr}}{\text{lb } C_2H_2}$	Remarks
H_2 flow rate: 3.0 lit./min., 14 g probe (0.063 in. i.d.)											
B-I-1	42	170	7.2	3.89	1/2	55	2.6	17.4	~1	122	
-2	53	225	11.9	5.26		100	3.55	19.4		143	
-3	65	260	17.2	6.9		25	4.63	23.6		171	
-4	73	300	22.0	8.1		5	5.43	6.3		595	S.S.
-5	62	310	19.3	8.7		5	5.82	12.4		264	S.S.
-6	62	310	19	6.77		25	4.55	23.2		193	
-7	62	310	19.2	8.7		25	5.83	21.6		208	
-8	70	320	22.4	9.6		50	6.42	25.5		205	
-9	72	350	25.0	10.2		100	6.85	24.9		234	
-10	73	317	23.5	9.4		7	6.3	10.7		512	S.S.
-11	70	350	24.4	10.2		20	6.85	18.1		595	S.F.

Table C-1 (cont'd)

Run No.	V Volts	I amps	P kw	CVR gm/min.	Probe Position in.	Sample Size ml	C/H_2 ratio	$\%C_2H_2$ (AFB)	β	A $\frac{\text{kw-hr}}{\text{lb.}C_2H_2}$	Remarks
	H_2 flow rate: 1.5 lit./min.; series B: 19 g probe; series C: 0.100 in. probe										
B-II-1	40	140	5.6	2.34	1/2	5	3.14	7.3	~1	358	S.S.
-2	45	130	5.7	2.25		100	3.0	15.9		167	
-3	46	165	7.6	3.43		100	4.6	19.1		186	
-4	47	160	7.5	3.42		50	4.3	13.35		262	
-5	45	172	7.8	3.6		25	4.8	14.5		251	
-6	49	172	8.4	3.85		200	5.15	14.3		275	
C-I-1	43	130	5.4	2.25	1	100	3.02	14.2	~1	229	L.A.
-2	39	135	5.4	2.52	1/2	100	3.4	11.9		212	L.A.
-3	45	170	7.6	3.65		100	4.9	16.8		211	L.A.
-4	52	220	11.4	5.1		100	6.85	16.7		321	L.A., S.F.
-5	50	230	11.5	6.93		25	9.3	16.9		320	S.S., P.P. F.F.
-6	65	265	16.6	7.62		100	10.2	25.9		300	
-7	62	305	18.9	8.85		100	11.85	22.4		395	
-8	65	300	19.4	8.82		100	11.83	19.6		465	
-9	74	320	23.6	10.0		100	13.4	22.9		482	

Table C-1 (cont'd)

Run No.	V volts	I amps	P kw	CVR gm/min.	Probe Position in.	Sample Size ml	C/H_2 ratio	$\%C_2H_2$ (AFB)	β	A $\frac{\text{kw-hr}}{\text{lb.}C_2H_2}$	Remarks
				H_2 flow rate: 6.0 lit./min.; probe: 0.100 in. i.d.							
X-I-1	58	170	9.85	3.02	1 1/2	100	1.35	13.25	~1	116	4.5 lit./min.
-2	51	170	8.65	2.80	2	↓	0.94	10.9	↓	92.5	0.9% ME
-3	50	290	14.5	6.75	↓	↓	2.26	14.25	↓	119	0.6% ME
-4	70	305	21.2	6.8	↓	↓	2.28	17.7	↓	140.5	0.4% ME
-5	63	420	26.4	12?	↓	↓	4?	14.1	↓	218	S.P.W.
-6	60	395	23.8	13.25	↓	↓	4.41	25.7	↓	108	
-7	55	480	26.4	15.5	↓	↓	5.2	19.6	↓	257	S.P.W.
-8	54	500	27.0	16.1	↓		5.36	26.2		121	
				H_2 flow rate: 10.0 lit./min.; probe: 0.100 in. i.d.							
X-II-1	45	180	8.1	2.92	3	100	0.59	9.2	~1	62.2	
-2	44	290	12.8	6.75	↓	↓	1.35	14.9	↓	60.7	
-3	54	850	18.9	9.0	↓	↓	1.81	17.4	↓	78.1	0.95% ME
-4	54	470	25.4	14.0	↓	↓	2.82	17.0	↓	105	0.6% ME
-5	59	490	28.9	11.85	↓	↓	2.38	19.6	↓	140	0.5% ME
				H_2 flow rate: 16.0 lit./min.; probe: 0.100 in. i.d.							
X-III-1	50	520	26	13.7	4	100	1.84	18.3	.991	66.5	15 lit./min.
-2	52	510	26.5	15.45	5	100	1.94	20.0	.985	59.0	1.7% ME
-3	50	270	13.5	4.15	5	40	.52	7.2	.995	82	0.7% ME
-4	50	310	15.5	7.12	5	100	.90	14.7	.986	46.9	1.5% ME

Table C-2

Methane Runs

Run No.	V volts	I amps	P kw	CVR gm/min.	Probe Position in.	Sample Size ml	C/H_2 ratio (feed)	$\%C_2H_2$ (AFB)	β	A $\frac{\text{kw-hr}}{\text{lb.}C_2H_2}$	Remarks
CH_4 flow rate: 1.5 lit./min.; probe: 0.100 in. i.d. (I), 0.135 (II)											
D-I-3	62	292	18.1	9.12	1	100	6.58	28.8	1.82	160	
-4	50	320	16.0	10.3	2	100	7.4	23.4	1.83	175	
-5	72	260	18.7	8.67	1	20	6.35	35.2	1.66	150	
-6	58	290	16.6	8.39	1/2	20	6.12	28.8	1.49	181	P.P.
-7	60	300	18.0	6.95	1	100	5.15	23.1	1.91	191	
-8	50	360	18.0	11.65		50	8.3	39.2	1.87	123	
-9	64	400	25.6	13.1		40	9.27	39.1	1.85	162	
-10	56	430	24.0	15.2		45	10.7	31.3	1.82	198	
-11	54	430	23.1	15.25		10	10.7	-	-	-	P.P., S.S.
D-II-1	50	110	5.5	1.41	1 1/2	100	1.45	9.8	1.84	142	less water
-2	46	170	7.8	3.06	1 1/2	100	2.55	10.5	1.89	184	through
-3	57	160	9.1	2.85	1	100	2.41	14.3	1.89	156	probe than
-5	54	310	16.8	8.7	1 1/2	100	6.33	15.8	1.93	285	usual
-6	30	180	5.5	3.46	1	100	2.81	9.6	1.92	141	L.A.
-7	60	280	16.8	6.70	1	100	4.99	31.7	1.93	128	A.O. 8 sec.
-8	75	290	21.7	9.40		100	6.8	35.5	1.92	149	P.P.
-9	66	380	25.0	12.8		25	9.1	37.6		162	
-10	55	380	20.8	12.2		100	8.65	34.5		147	
-11	58	440	26.5	15.4		100	10.8	23.2		277	S.P.W.
-12	55	460	25.3	16.3		30	11.45	52.0	1.93	118	P.P.

Table C-2 (cont'd)

Run No.	V volts	I amps	P kw	CVR gm/min.	Probe Position in.	Sample Size ml	C/H_2 ratio (feed)	$\%C_2H_2$ (AFB)	β	A $\frac{kw\text{-}hr}{lb.C_2H_2}$	Remarks
CH_4 flow rate: 1.5 lit./min.; probe: 0.135 in.i.d.											
D-III-1	68	180	12.2	4.5	3/4-S	100	3.5	6.2	1.85	500	L.A.
-2	34	230	7.8	4.4	3/8-S		3.4	5.2	1.81	386	L.A.
-3	40	220	8.8	4.6	1/4-S		3.6	7.1	1.90	307	L.A.
D-IV-1	62	160	9.9	2.81	1		2.4	12.5	1.85	200	
-2	50	210	10.5	4.71			3.6	8.8	1.99	200	L.A.
-3	60	290	17.4	8.7			6.3	20.7	1.93	204	
CH_4 flow rate: 0.75 lit./min.; probe: 0.135 in.i.d.											
E-I-1	45	175	17.9	3.1	1	100	4.6	7.7	1.90	505	L.A.
-2	42	220	9.2	5.3		60	7.6	15.3	1.92	295	L.A.
-3	70	280	19.6	7.4		60	10.3	44.7	1.92	214	
E-II-1	48	210	10.1	5.0			7.2	6.6	1.93	740	L.A.
-2	52	275	14.3	8.7			12.2	-	-	-	L.A.
-3	66	290	19.1	9.7			13.4	40.6	1.92	228	
-4	73	310	22.8	10.2			14.2	35.0		316	P.P.
-5	72	370	26.6	12.8			17.7	38.2		340	
-6	67	440	27.1	14.6			20.1	32.6		406	P.P.
-7	63	460	28.0	16.1			22.1	40.0		340	P.P.

Table C-2 (cont'd)

Run No.	V volts	I amps	P kw	CVR gm/min.	Probe Position in.	Sample Size ml	C/H_2 ratio (feed)	%C_2H_2 (AFB)	β	A $\frac{\text{kw-hr}}{\text{lb.}C_2H_2}$	Remarks
CH_4 flow rate: 5.0 lit./min.; probe: 0.100 in. i.d.											
Y-I-1	45	320	14.4	4.92	5	100	1.486	16.3	1.91	65	1.15% ME
-2	55	330	18.1	9.45		50	2.39	17.7	1.91	75	1.35% ME
-3	50	300	15.0	7.55		50	2.01	12.8	1.90	86	1.65% ME
-4	56	220	12.5	5.76		30	1.65	14.0	1.89	66	2.2% ME
-5	50	150	7.5	1.55		20	0.81	7.3	1.88	76	2.9% ME
-9	80	400	32.0	ext		100	4.3	20.4	1.92	114	1.0% ME
-10	55	470	25.9	ext			3.5	18.6	1.92	102	
-11	57	435	24.7	14.55			3.4	20.2	1.90	90	2.0% ME
-12	55	500	27.5	ext			3.7	19.5	1.88	105	2.5% ME
-13	70	450	31.5	ext			4.2	12.4	1.90	189	1.7% ME,S.P.W.
CH_4 flow rate: 8.0 lit./min.; probe: 0.100 in. i.d.											
Y-II-1	52	310	16.1	8.82	5	20	1.62	6.8	1.88	111	P.P.,2.9% ME
-2	52	350	18.2	7.8	5	5	1.47	6.8	1.85	127	P.P., 4.3% ME
CH_4 flow rate: 12.0 lit./min.; probe 0.100 in. i.d.											
Z-I-1	55	510	28.0	ext	5	100	1.86	20.4	1.91	42	0.75% ME
-2	55	510	28.0				1.86	20.6	1.91	42	0.6%ME
-4	50	340	17.0				1.24	12.1	1.92	43	1.6% ME
-5	70	170	11.9				0.95	12.6	1.92	29	2.6% ME
-6	40	250	10.0				0.84	10.4	1.92	29	0.6% ME

Appendix D

Calculations Pertaining to the C - CH_4 System

The following reactions are considered:

(A) $2C_1 + H_2 \longrightarrow C_2H_2$ (at T)

(B) $2CH_4$ (298°K) $\longrightarrow 2\ CH_4$ (at T)

(C) $2\ CH_4$ (at T) $\longrightarrow C_2H_2 + 3\ H_2$

the heat given off in reaction (A) serving to bring methane to reaction temperature by reaction (B) and to crack the CH_4 to acetylene and hydrogen, by reaction (C).

From thermodynamics, the heat of reaction for each reaction is

$$\Delta H^\circ_R = (\Delta H^\circ_{Tf})_{products} - (\Delta H^\circ_{Tf})_{reactants} \quad (1)$$

The heat of formation of each species can be calculated by means of the relation

$$\Delta H^\circ_{Tf} = \Delta H^\circ_{of} + \Delta\ (H^\circ_T - H^\circ_o) \quad (2)$$

provided the thermodynamic functions $\frac{H^\circ_T - H^\circ_o}{RT}$ or $H^\circ_T - H^\circ_o$ are available.

Since most of the tabulated thermodynamic functions in the literature(28) are available only up to 1,500°K, the missing values had to be extended to 4,000°K by the method of Bauer and Duff. Using the constants of this last work, the function $\frac{H^\circ_T - H^\circ_o}{RT}$ could be calculated from the expression(3).

$$\frac{H^\circ_T - H^\circ_o}{RT} = a + bT + cT^2 + dT^3 + eT^4 \quad (3)$$

where a, b, c, d, e are the constants listed in Table A-3.

For methane, not included in this table, the following values apply:

$$a = 2.1142316$$

$$b = 4.6999314 \times 10^{-3}$$

$$c = -1.1162007 \times 10^{-6}$$

$$d = 1.3638225 \times 10^{-10}$$

$$e = -6.6735613 \times 10^{-15}$$

$$k = 7.2880040$$

$$\Delta H^\circ_{of} = -15.987 \text{ kcal/mole}$$

Example: Methane, 2,500°K

From Eq. 3, $\frac{H^\circ_T - H^\circ_o}{RT} = 8.774$, $RT = 4967$

$$H^\circ_T - H^\circ_o = 43.5 \text{ kcal.}$$

If one now considers the CH_4 formation from the elements

$$C_s + 2\ H_2 \longrightarrow CH_4$$

the heat of formation at any temperature can be calculated from Eq. 2. Values of $(H^\circ_T - H^\circ_o)$ for $C_s + 2\ H_2$ can be obtained from Rossini(28) and this is equal to 49.55 kcal. at 2,500°K. Then the heat of formation of methane at 2,500°K is

$$\Delta H^\circ_{Tf} = -15.987 + (43.5 - 49.55) = -22.04 \text{ kcal.}$$

Table D-1 shows ΔH°_{Tf} for CH_4 and C_2H_2 and the sensible heat $(H^\circ_T - H^\circ_o)$ for CH_4 calculated in such a way; values for C_1, H_2, H, and C_s were taken directly from Rossini(28).

The heat of reaction for reactions (A), (B), and (C) was calculated by using Eq. 1. The overall reaction, however, is obtained by adding up all three separate reactions and dividing by two to get

$$C_1 + CH_4 \longrightarrow C_2H_2 + H_2$$

Equilibrium limitation on reaction (C) below 2,000°K was taken into account as the yield cannot be 100%. Also $(H_{298} - H_o^\circ)$ for CH_4 is 2.4 kcal at 25°C for results from room temperature.

Example: T = 2,500°K

ΔH_R° (reaction A): 51.38 - 2 (171.09) = - 290.80 kcal

(reaction B): 41.1 x 2 = 82.2 kcal

(reaction C): 51.38 + 2 (22.04) = 94.46 kcal

$$\Delta H_R^\circ \text{ (overall reaction)} = \frac{-113.14}{2} = -56.57 \text{ kcal}$$

To get $\Delta H_R^\circ = 0$, we must take 0.611 ΔH_R° of reaction A to match exactly the sum of ΔH_R°'s for reactions (B) and (C), or $C_1/CH_4 = 0.611$ and $C/H_2 = 0.805$. The overall reaction can be represented stoichiometrically by

$$0.611\ C_1 + CH_4 \longrightarrow 0.805\ C_2H_2 + 1.195\ H_2$$

which gives 40.3 % C_2H_2 in the product gas.

Results of similar calculations are presented in Table D-2 for the temperature range 1,500 to 4,000°K. At 1,500°K and 1,650°K, the yields of reaction (C) are 70% and 95% respectively.

Table D-1

Heats of Formation, ΔH°_{Tf}, and CH_4 sensible heat in kcal. for the temperature range 1,500 - 4,500°K

T, °K	1,500	1,650	2,000	2,500	3,000	3,500	4,000
C_2H_2	52.55	52.33	52.10	51.38	50.48	49.46	48.46
H	53.72	53.87	54.22	54.61	54.93	55.19	55.40
C_1	172.1	171.95	171.64	171.09	170.47	169.84	169.16
CH_4	-22.06	-22.16	-22.16	-22.04	-21.89	-21.85	-21.85
H_2	0	0	0	0	0	0	0
CH_4 sensible heat ($H^\circ_T - H^\circ_o$)	18.73	21.75	31.95	43.5	55.5	67.7	80.1

<u>Table D-2</u>

Overall heat of reaction, carbon vapor requirement and calculated % C_2H_2 for null reaction heat for the temperature range 1,500-4,000°K

T, °K	1,500*	1,650*	2,000	2,500	3,000	3,500	4,000
ΔH°_R kcal/mole C_2H_2	-95.65	-80.56	-67.83	-56.57	-45,00	-33.28	-21.15
C_1/CH_4	0.345	0.447	0.535	0.611	0.690	0.770	0.855
C/H_2	0.672	0.723	0.767	0.805	0.845	0.885	0.927
% C_2H_2	30.8	34.9	38.4	40.3	42.2	44.2	46.4
	70% yield	95% yield					

* Equilibrium limitation on reaction (C) taken into account

Appendix E

(1) Calculation of the Coefficient of Volume Expansion, β, from Gas Analyses

This development follows the scheme used by Drahny[10].

Suppose that for methane cracking the following reactions are possible, and, by analysis of output gases from a high temperature zone, correct:

$$2\ CH_4 \longrightarrow C_2H_2 + 3\ H_2$$

$$2\ CH_4 \longrightarrow C_2H_4 + 2\ H_2$$

$$CH_4 \longrightarrow C + 2\ H_2$$

the unreacted methane is not changed

$$CH_4 \longrightarrow CH_4$$

and any diluent gas is not lost by side reactions

$$R \longrightarrow R$$

With these assumptions, we can apply stoichiometric considerations that can be used to relate the concentration of individual substances before and after reaction and hence the coefficient of volume expansion, β.

Material Balance

Assume that, of the total moles of original gas,

(1) N_a moles of CH_4 are cracked to C_2H_2 and H_2

$$N_a\ (CH_4) \longrightarrow \frac{1}{2} N_a\ (C_2H_2) + \frac{3}{2} N_a\ (H_2)$$

(2) N_e to C_2H_4 and H_2

$$N_e\ (CH_4) \longrightarrow \frac{1}{2} N_e\ (C_2H_4) + N_e\ (H_2)$$

(3) N_c to C and H_2

$$N_c\ (CH_4) \longrightarrow N_c\ (C) + 2\ N_c\ (H_2)$$

(4) N_m moles remain unchanged

$$N_m\ (CH_4) \longrightarrow N_m\ (CH_4)$$

(5) All N_p moles of diluent are unaffected

$$N_p\ (R) \longrightarrow N_p\ (R)$$

The total number of moles of CH_4 is

$$N_t = N_a + N_e + N_c + N_m \tag{1}$$

Adding all equations and substituting for N_c the value computed from Equation 1, we obtain

$$N_t\ (CH_4) + N_p\ (R) \longrightarrow \frac{1}{2} N_a\ (C_2H_2) + \frac{1}{2} N_e\ (C_2H_4) + N_m\ (CH_4)$$
$$+ (N_t - N_a - N_e - N_m)\ (C) + (2\ N_t - \frac{1}{2} N_a - N_e - 2\ N_m)\ (H_2) + N_p (R) \tag{2}$$

Volume Balance

Since the solid carbon does not contribute to the volume of the gas, we can pass from the material balance to volume balance by adding up those constituents other than carbon

$$N_t + N_p \longrightarrow 2\ N_t + N_p - \frac{1}{2} N_e - N_m \tag{3}$$

and obtain the coefficient of volume expansion by the ratio of the right-hand side to the left hand side of Eq. 3.

$$\beta = 1 + \frac{N_t - 1/2\ N_e - N_m}{N_t + N_p} \tag{4}$$

Concentration Balance

Since the volume concentrations of individual components are determined by gas analysis, in the feed gas, methane concentration is

$$t = \frac{N_t}{N_t + N_p} \tag{5}$$

and diluent concentration

$$p = \frac{N_p}{N_t + N_p} \tag{6}$$

In the product gas (primed symbols), we define the analyzed concentrations by the following: C_2H_2 concentration:

$$a' = \frac{1/2\ N_a}{2\ N_t - 1/2\ N_e - N_m + N_p} \tag{7}$$

C_2H_4 concentration

$$e' = \frac{1/2\ N_e}{2\ N_t - 1/2\ N_e - N_m + N_p} \tag{8}$$

Unchanged CH_4

$$m' = \frac{N_m}{2\ N_t - 1/2\ N_e - N_m + N_p} \tag{9}$$

H_2 concentration

$$h' = \frac{2\ N_t - 1/2\ N_a - N_e - 2\ N_m}{2\ N_t - 1/2\ N_e - N_m + N_p} \tag{10}$$

Diluent concentration

$$p' = \frac{N_p}{2\ N_t - 1/2\ N_e - N_m + N_p} \tag{11}$$

We can then perform the concentration balance as follows

$$t + p = 1 \tag{12}$$

$$a' + e' + m' + h' + p' = 1 \tag{13}$$

It is possible to recalculate the concentrations of the components in the output gas to the original volume by means of the coefficient β, if consideration is given to their physical meaning and thus a methane balance is obtained.

Note that the concentration $m = \beta m'$ takes no part in the reaction, only $t - m = t - \beta m'$ is cracked. Of this, a CH_4 concentration, $2a = 2\beta a'$ goes to C_2H_2, $2e = 2\ \beta e'$ to C_2H_4 and $c = t - m - 2a - 2e = t - \beta\ (m' - 2a' - 2e')$ to carbon

$$t \begin{cases} \nearrow \text{unchanged: } m \\ \searrow \text{cracked: } (t - m) \begin{cases} \nearrow \text{to } C_2H_2\text{: } 2a \\ \rightarrow \text{to } C_2H_4\text{: } 2e \\ \searrow \text{to carbon: } c \end{cases} \end{cases} \tag{14}$$

Hydrogen Balance

To obtain the relationship between the analysed concentrations and the coefficient of volume expansion we set from Eq. 12

$$p = 1 - t = \beta p' \tag{15}$$

which can be written as

$$p' = \frac{1 - t}{\beta} \tag{16}$$

and we substitute this last equation into Eq. 13.

$$\beta = \frac{1 - t}{1 - m' - h' - a' - e'} \tag{17}$$

Another independent relation for β can be obtained from its definition, Eq. 4, after substituting for the different concentrations, giving

$$\beta = 1 + t - e - m \tag{18}$$

or with the determined actual concentrations in the output gas for e' and m'

$$\beta = \frac{1 + t}{1 + e' + m'} \tag{19}$$

This can be modified further, by manipulating Eqs. 17 and 19 to get new relations for β. Eliminating the fractions in Eqs. 17 and 19 and adding up the two resulting equations, the following results

$$\beta = \frac{1}{1 - \frac{a' + h'}{2}} \tag{20}$$

By subtracting, one obtains

$$\beta = \frac{4\ t}{4\ m' + 2\ e' + 2\ a' + 2\ h'} \tag{21}$$

But Eq. 21 is exactly the hydrogen balance, i.e., the ratio of the number of H atoms in the methane feed gas (numerator) to the number of H atoms in the output gas (denominator). This last equation is most useful for determining the coefficient of volume expansion, since all concentrations can be easily determined by gas chromatography, for instance.

Example: Run D - II - 10

Feed gas: CH_4, commercial grade 95% minimum purity (taken here as being 96.6% CH_4)

Gas Analysis:	H_2	64.7%
	CH_4	0.4%
	C_2H_4	0.4%
	C_2H_2	34.5%

$$\beta = \frac{4 \times .966}{2(.647 + .345) + 4(.004 + .004)} = 1.92$$

Carbon-Hydrogen System

If a similar stoichiometric development is applied to reactions of carbon with hydrogen regarding C_2H_2, C_2H_4, CH_4 formation and unreacted H_2, carbon and diluent, the same Eq. 21 reduced by one half because of H_2 feed instead of CH_4 and still represented by an hydrogen balance results and can be applied directly to the concentrations determined by gas analysis to calculate the coefficient of volume expansion.

Example: Run X - I - 8

Feed gas: H_2, commercial grade, 99.98% purity (taken as 100% H_2)

Output gas:	H_2	73.45%
	CH_4	0.2%
	C_2H_4	0.15%
	C_2H_2	26.2%

$$\beta = \frac{2.0}{2(.7345 + .262) + 4(.002 + .0015)} = 0.996$$

(2) Calculation of the Efficiency of Carbon Utilization for Acetylene Production, Ω.

The efficiency of carbon utilization for C_2H_2 production, Ω, is defined here as the fraction of carbon in the feed that is converted to acetylene in the product gas. The constant quantity that serves as a basis for calculation is the amount of hydrogen which remains unchanged through the various processes taking place under the action of the electric arc.

$$\Omega = \frac{C/H_2 \text{ in product gas}}{C/H_2 \text{ in the feed}} \tag{22}$$

The carbon to hydrogen ratio in the feed can be determined by the loss in weight of the anode after a run.

$$(C/H_2)_{\text{feed}} = k\frac{W}{G} \tag{23}$$

where W is the weight loss of carbon from the anode in g/min. and G is the flow rate of feed gas in liters/min. at 70°F and atmospheric pressure. k is a constant taking care of the conversion factors to get C/H_2 in mole/mole.

For H_2 feed and consumable graphite anode

$$(C/H_2)_{H_2 \text{ feed}} = 2.01\frac{W}{G}\ \frac{\text{mole C}}{\text{mole } H_2} \tag{24}$$

and for methane feed

$$(C/H_2)_{CH_4 \text{ feed}} = 0.5 + 1.005\frac{W}{G} \tag{25}$$

If the output gas is assumed to contain only acetylene and hydrogen, which is true for most cases, then the carbon to hydrogen ratio can be represented by

$$(C/H_2)_{gas} = 2a'/a' + h' \approx 2a' \qquad (26)$$

since ethylene and methane concentrations do not amount to more than about 2% in all runs.

Then, by definition,

$$\Omega = 2a'/2.01 \frac{W}{G} \quad (H_2 \text{ feed}) \qquad (27)$$

$$\Omega = 2a'/0.5 + 1.005 \frac{W}{G} \ (CH_4 \text{ feed}) \qquad (28)$$

Examples

Run D-II-10: CH_4 feed

$$(C/H_2)_{feed} = 0.5 + 1.005 \times \frac{12.2}{1.5} = 8.65$$

$$(C/H_2)_{gas} = 2 \times 0.345 = 0.690$$

$$\Omega = \frac{0.690}{8.65} = 0.08$$

Run X-I-8: H_2 feed

$$(C/H_2)_{feed} = 2.01 \times \frac{16.1}{6.0} = 5.36$$

$$(C/H_2)_{gas} = 2 \times 0.262 = 0.524$$

$$\Omega = \frac{0.524}{5.36} = 0.098$$

Results for Ω covering both H_2 and CH_4 feeds are tabulated in Table E-1.

Table E-1

Efficiency of carbon utilization for acetylene production, averaged over the specified number of runs

Feed: H_2

G, lit./min	Ω ave.	Probe Size	No. of Runs
1.5	0.053	0.100"	9
3.0	0.062	0.043" (19g)	10
3.0	0.083	0.063" (14 g)	13
6.0	0.125	0.100"	7
10.1	0.202	0.100"	5
16.0	0.270	0.100"	3

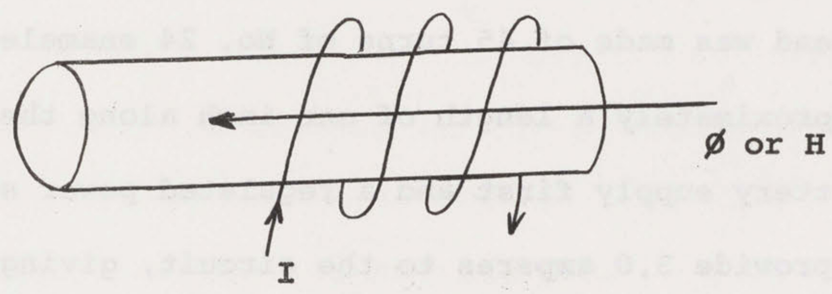
Feed: CH_4

G, lit./min	Ω ave.	Probe Size	No. of Runs
0.75	0.051	0.135" (8 g)	6
1.5	0.0875	0.100"	8
1.5	0.101	0.135"	9
5.0	0.133	0.100"	10
12.0	0.230	0.100"	5

Appendix F

Magnetic Circuit Relations

A current passing through a wire wound in the form of a coil generates a magnetic field in a direction parallel to the axis of the coil. The actual field vector can be determined according to the usual convention by wrapping the right hand around the coil in the direction of the current flow and choosing that direction where the thumb points.



The flux, Ø, expressed as Maxwell or lines is related to the current, I, flowing through the wire by

$$\text{Ø} = \frac{1.26\ N\ I}{R'}$$

where N is the number of turns of wire and R' is the reluctance of the circuit. For nonmagnetic material as air and other gases, the reluctance is given by

$$R' = \frac{l'}{A}$$

where l' is the length of the magnetic circuit in cm and A the area of the circuit in sq. cm. The flux is often expressed in amperes-turns as a measure of the quantity N I.

The magnetic field whose strength is given in gauss is the number of lines per unit area, or

$$H = \frac{\emptyset}{A} = \frac{1.26\ N\ I}{R'A}$$

For the case of nonmagnetic material, which is assumed here because no data exist for plasmas, the field expression reverts to

$$H = \frac{1.26\ N\ I}{l'} \quad \text{(gauss)}$$

The coil wrapped around the reactor at the location of the cathode end was made of 45 turns of No. 24 enameled copper wire over approximately a length of one inch along the reactor outside walls. A battery supply first and a regulated power supply later on was used to provide 3.0 amperes to the circuit, giving 135 amperes-turns for the value of N I. Converting l' to cm, this gave for the value of H

$$H = \frac{1.26 \times 135}{2.5} = 68 \text{ gauss}$$

This value of H was carefully chosen in view of the following considerations:

When the electrons leaving the cathode strike the anode, they travel in a magnetic field which is at right angle with the electron path; they are then subjected to a centrifugal force which tends to bend their path and which is balanced by the force generated in the magnetic field, i.e.,

$$\frac{M_e v^2}{r} = H\ e\ v$$

where M_e is the electron mass, v is the speed of the electrons in cm/sec., r the radius of curvature in cm and e, the electronic charge in e.m.u.

The speed of the electrons is determined by the potential existing between the anode and cathode, as the kinetic energy of the electrons is related to the potential energy by

$$\frac{M_e v^2}{2} = V_A e$$

where V_A is the arc voltage. In most experiments performed in the high intensity arc, the voltage was varied between 40 and 70 volts, giving

$$v = \sqrt{\frac{2 V_A e}{M_e}} = 5.94 \times 10^7 \sqrt{V_A}$$

Thus, the speed of the electrons was calculated as

$$v = (3.75 \text{ to } 5) \times 10^8 \text{ cm/sec.}$$

giving in turn for the radius of curvature

$$r = \frac{M_e v^2}{H e v} = \frac{M_e v}{H e}$$

or

$$r = \frac{9.1 \times 10^{-28} \times (3.75 \text{ to } 5) \times 10^8}{68 \times 1.6 \times 10^{-20}}$$

$$r = 0.314 \text{ to } 0.418 \text{ cm}$$

or approximately 1/8 to 3/16 in.

But this is exactly of the same order of magnitude as the gap spacing between the anode and cathode, as shown in section Apparatus and Procedure and shown in the details of the reactor.

Should the magnetic field have been too large, the radius of curvature would have become so small as to focus the electrons instead of bending their path; on the other hand, should it have been too small, no bending would have occurred. Thus, a magnetic field of 70 gauss was adequate to induce swirling of the electrons and provide additional mixing of the plasma.

Appendix G

Gas Chromatography Analysis

The quenched gas from the arc zone was analyzed with a Perkin Elmer Fractometer Model 154. A one-meter silica gel column was held at a constant temperature of 125°C under a pressure of 10 psi with helium carrier gas. The variables of the unit, temperature and pressure, were fixed at the above values after a number of trials to determine the best operating conditions that would allow separation of all components together with good sensitivity. Components like hydrogen, air, carbon monoxide and methane have approximately the same retention time, but the recorder chart speed was increased threefold over the normal speed. This gave enough separation between the different peaks to enable identification of all components. As hydrogen gives a weak double peak with helium as carrier gas, its concentration was obtained by assuming that the remainder of the gas, after identification of all other components, was hydrogen. Verification of this assumption was made by running several samples through the fractometer with argon gas as carrier gas, which gave good separation and strong peaks for H_2, air, CO and CH_4. It might be mentioned that operation with only one carrier gas (helium) was really an advantage, since no waiting period was necessary for the stabilization of the unit after change of the carrier gas.

The chromatography apparatus was calibrated by mixing H_2, air, CO, CH_4, C_2H_6, C_2H_4, CO_2, and C_2H_2 in definite proportions in a gas mixing apparatus, running the different mixtures (covering the whole range of concentrations for each component) through the chromatograph and reading the peak height on the recorder chart. The peak heights were sharp enough as not to warrant taking the area under the curves as a measure of concentrations. The peak heights were all related to concentrations as determined in the mixing apparatus by a straight line. For ease of actual determination of an unknown sample, the peak height was reduced to a standard value giving one percent of a given component for an attenuation of 1/1, thus gas concentrations were determined by dividing the peak heights read on the chart by the peak height giving one percent of the gas.

Since the peak heights and retention times change a little over the months, the last determinations are given in Table G-1.

Table G-1

Gas Chromatography Determinations. Carrier gas: helium; Pressure: 10 psi; Temperature: 125°C; Detector voltage: 4.0 volts; sensitivity attenuation: 1.

Component	Time for maximum of peak to appear	Peak height for 1% concentration *
H_2	46 - 50 sec.	-
air	58 sec.	13.7
CO	1 min. 3 sec.	12.8
CH_4	1 min. 11 sec.	10.3
C_2H_6	2 min. 6 sec.	7.1
CO_2	2 min. 38 sec.	5.77
C_2H_4	2 min. 53 sec.	6.0
C_2H_2	5 min. 2 sec.	2.08

* Note: Peak heights given in standard chart graduation.

NOMENCLATURE

A	-	specific energy, kw-hr/lb.C_2H_2
a'	-	acetylene concentration in product gas, volume %
CVR	-	carbon vaporization rate, gm./min.
E_o	-	excitation energy, ev
e	-	electronic charge, e.m.u.
F	-	free energy, kcal.
G	-	gas flow rate, lit./min.
H	-	enthalpy, kcal.
I	-	current, amperes
k	-	constant
K	-	equilibrium constant
n	-	concentration for atoms, ions and electrons
P	-	power, kw
p	-	partial pressure, atm.
R	-	universal gas constant
r	-	radial distance, cm
t	-	time, sec.
U	-	ionization energy, ev.
V	-	voltage, volts
x	-	ionized fraction
y	-	mole fraction

Greek Symbols

α	-	emissivity
β	-	coefficient of volume expansion
π	-	total pressure, atm.
σ	-	radiation constant
Ω	-	efficiency of carbon utilization for C_2H_2 production

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BIOGRAPHICAL NOTE

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