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SURVEY OF THE LITERATURE ON THE CARBON-HYDROGEN SYSTEM

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SURVEY OF THE LITERATURE ON THE CARBON-HYDROGEN SYSTEM

R. A. Krakowski and D. R. Olander

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SURVEY OF THE LITERATURE ON THE CARBON-HYDROGEN SYSTEM

by R. A. Krakowski and D. R. Olander

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ABSTRACT

The literature on the carbon-hydrogen system up to ca 1968 is reviewed. The thermodynamics and heterogeneous kinetics of the reaction, the adsorption of hydrogen on graphite, and the evaporation of graphite are considered.

I. INTRODUCTION

The hydrogenation of carbon to gaseous hydrocarbons has been of interest to chemists for many years. Because of the relative simplicity of the reacting species, this reaction presents an ideal system in which heterogeneous reaction kinetics could be examined. The possibility of incorporating this reaction network into production process for cheap BTU gases by gasification of the carbons with a water-hydrogen mixture provided the first practical impetus for kinetic investigation of this system. These early works generally employed bed or packed tube type reactor systems. The exact form of the carbon was not known, the sample purity was not controlled, surface areas were measured with crude techniques or not at all, and reaction rates were measured by sample weight loss techniques. The purpose of these experiments was generally to explore the possibility of producing cheap industrial heating gases; obtaining reaction kinetic data was secondary. The few works carried out at the turn of the century which were of a truly scientific nature generally were concerned with attainment of thermodynamic equilibrium within the carbon-hydrogen system. The goals of such investigations were 1) experimental determination and verification of thermodynamic data, 2) attainment of conditions which would give maximum permissible yields of certain valuable hydrocarbons. These works will be briefly reviewed later in this section.

With the advent of modern process techniques for economical production of high grade graphites, applications of carbon to more

sensitive, critical, high temperature areas were considered. When these graphites were employed in direct contact with gases at high temperature, prediction of the chemical behavior of the resultant gas-graphite system became imperative. In particular, the gas-cooled reactor program required a critical evaluation of carbon stability in atmospheres of helium, carbon monoxide, hydrogen, and air. Above 650°C corrosion of vital structural parts of the reactor may become serious.^{1,2,3,4} Air has been found to be compatible with graphite components (Windscale Reactors, Oak Ridge X-10, Brookhaven Graphite Research Reactor) below 200°C; at 300°C-500°C, CO₂ has proven successful (Calder Hall Reactor, Advanced Gas-Cooled Reactor); hydrogen, nitrogen or helium appear to be promising for very high temperatures, 800°C (High Temperature Gas-Cooled Reactor, Dragon Reactor). As reactor operating temperatures are pushed to higher and higher values, compatibility of the various gas-graphite systems become increasingly critical.

At the other extreme of very low temperatures, the recombination of interstellar hydrogen atoms on the graphite grains which constitute interstellar dust has been suggested as a source of interstellar molecular hydrogen^{5,6}.

In addition to corrosive reaction between graphite and the surrounding atmosphere, evolution of gases from the bulk of the graphite structure becomes a concern at high operating temperatures. For example, when graphite is used as an anode in a mercury vapor rectifier, the release of gaseous species (H₂, CO, hydrocarbons) results in adverse effects on tube life and operation. Hydrogen outgassed from graphite reactor components and moderator is known

to induce embrittlement of zirconium fuel element cladding. Hydrocarbons evolved from high temperature zones of the reactor can migrate to cooler parts of the system, crack, and deposit soot on critical surfaces. When graphite is employed as a high temperature crucible, both outgassed species and gaseous reaction products may seriously contaminate melts. The nuclear rocket program serves as a final case-in-point for the necessity of studies of gas-graphite systems. Typically, a nuclear rocket of the Kiwi prototype consists of a graphite moderated core through which flows considerable quantities of high temperature hydrogen propellant. In addition to outright surface corrosion of flow channels and exit nozzles (which may be serious in long term operations), accelerated crack growth in critical components by a stress-corrosion mechanism greatly amplifies the damage.

Two major problems are associated with the kinetic study of the heterogeneous reaction of graphite with hydrogen. First, the variety of graphitic forms of carbon (i.e., the degree of crystallinity and purity) has made chemical reaction characteristics highly specific to the sample employed. Second, the products of hydrogen-graphite reaction are in such low concentrations and are formed at such slow rates that common analytical techniques are of marginal utility. In addition, many of the primary reaction products are unstable free radicals, which are destroyed before analysis.

An excellent monograph by Ubbelohde and Lewis⁷ gives a good summary of the physical properties of graphite, crystallographic causes for the great variance in physical and chemical properties

of graphite, and observed characteristics of the chemical transformation of graphite to volatile products, (particularly by oxidation). These aspects will not be considered in any great detail. However it must be emphasized that any future kinetic study should pay proper due to the physico-chemical characteristics of samples used in the investigation, and attempts should be made to correlate kinetic data with these characteristics.

There has been a wide variety of corrosion rate experiments performed on graphite, in which sample weight loss is recorded as a function of gas flow velocity, sample shape, temperature, and a host of other variables. In general, these "engineering-type" investigations will not be treated in this review, for although they are of prime importance to preliminary component design and feasibility studies, the information they yield does not illuminate the fundamental processes involved.

This review is divided into four basic topics. First, the thermodynamic aspects of the hydrogen-graphite system will be presented. A brief review of equilibrium experiments performed will be included. This section will be followed by a discussion of kinetic aspects of the reaction of hydrogen with graphitized and non-graphitized carbons. The third topic will cover a number of important investigations of hydrogen adsorption on graphite at high temperatures (900-1500°C). The last section will consider direct evaporation of carbon species from graphitic surfaces. Since carbon sublimation becomes an important corrosion mechanism at elevated temperatures (> 2000°C), gaseous carbon may contribute to the overall hydrocarbon yield via homogeneous, gas-phase reactions.

II. THERMODYNAMICS OF THE CARBON-HYDROGEN REACTION

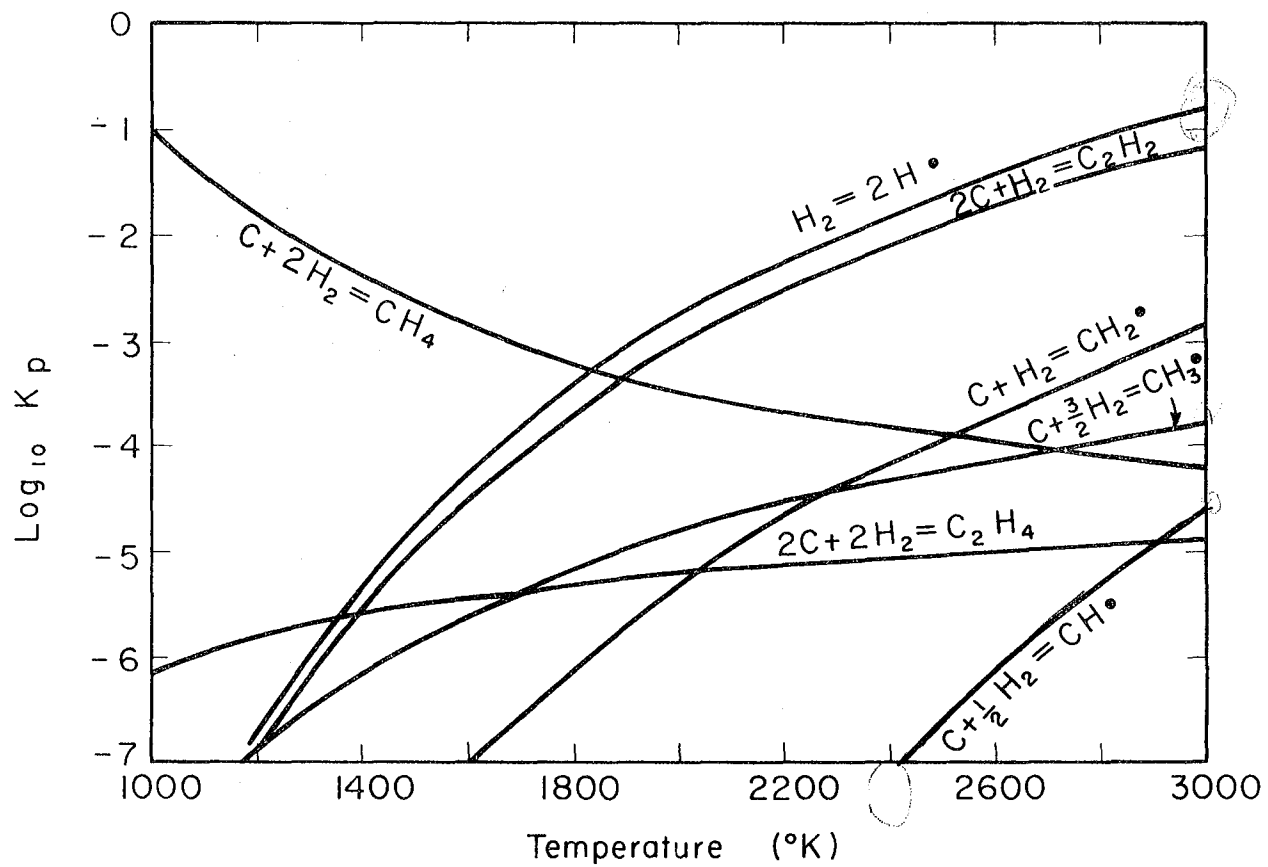
Methane is a major product of the carbon-hydrogen reaction above 800°C, and like most exothermic compounds it decreases in stability with increasing temperature. The stability of the unsaturated reaction products, such as acetylene and ethylene, on the other hand, increases with temperature. These trends may be seen from Fig. 1, where the equilibrium constants calculated from spectroscopic data for the species of interest have been plotted against temperature.⁸

The effect of total pressure on the yield of gaseous product C_nH_{2m} formed by the reaction $nC + mH_2 = C_nH_{2m}$ is given by,

$$\text{mole fraction } C_nH_{2m} = K_p P^{m-1}$$

where P is the total pressure (approximately equal to the pressure of H_2) and K_p is the equilibrium constant in terms of partial pressure. An increase in pressure will increase the thermodynamic yield of the hydrocarbon, with the exception of acetylene, which theoretically shows no pressure dependence.

The first recorded work on the thermodynamic behavior of this reaction was carried out by Bertholet.⁹ This pioneering experiment was performed under three different conditions: 1) retort carbon was heated to approximately 1200°C in a porcelain tube, and a stream of hydrogen gas was allowed to pass over the carbon. 2) a series of electric sparks originating from carbon electrodes was initiated in a hydrogen atmosphere, 3) an electric arc was struck between carbon electrodes within an atmosphere of hydrogen. Acetylene was the only reaction species investigated, and only the



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Fig. 1 Equilibrium Constants in the Carbon-Hydrogen System

third of the above experiments yielded this product. The primary results of this investigation are expressed by the words of Bertholet. "Quant á l'hydrogene, toutes ses combinaisons avec le carbon, extraites jusque lá de produits organique se detruisaient précisement sous l'influence d'une temperature range; il semblait des lors chimerique de chercher á les former directment"

Although analytical techniques available for identification of reaction products and temperature have been vastly improved since this early investigation, there has not been much improvement upon Bertholet's basic experimental procedure. The lack of accurate product analysis led Bone and Jerdan^{10,11} to re-examine Bertholet's experiment under more controlled conditions. Though no acetylene was observed under Bertholet's first experimental condition, Bone and Jerdan did observe 1% methane evolved from the various sugar carbons reacted at 1200°C. The electric arc experiments yield both methane and acetylene. Equilibrium was also approached from the gas side; it was observed that the same equilibrium state resulted when the electric arc was struck in an atmosphere of either methane or acetylene under similar conditions. These kinds of studies were extended by Bone and Coward^{12,13} to further investigate the synthesis of methane from chars.

Equilibrium was also approached both from the hydrogen side and the hydrocarbon side by Coward and Fairlie¹⁴, who measured an equilibrium concentration of 0.1% methane over heated carbons. The methane concentration was observed to decrease with increase in the reaction temperature from 1000 to 1100°C in accordance to thermodynamic prediction.

Pring^{15,16,17} investigated hydrogen reaction with sugar charcoal, retort carbon, and Acheson graphite in the temperature range 1200-2000°C. In all cases CO and CH₄ were observed, but acetylene and ethylene were observed only for retort carbon in the higher temperature ranges. Increases in hydrogen over-pressure (up to 200 atm) did not increase the methane yield. The methane concentration was noted to increase with temperature above 1500°C with the formation of acetylene taking place above 1850°C. The increase in CH₄ concentration was attributed to decomposition of acetylene. Equilibrium was obtained at a faster rate when platinum was deposited on the carbon surface¹⁸. The effects of catalysts on the reduction of carbon have held the attention of other early works.¹⁹⁻²¹ In these investigations various catalysts were employed to arrive at equilibrium within shorter times. Berl and Bemman²² and Randall and Mohammad²³ report experimental results on the hydrogen-methane-carbon system. Important experimental evidence obtained prior to the 1930's is summarized and compared by these latter investigators.

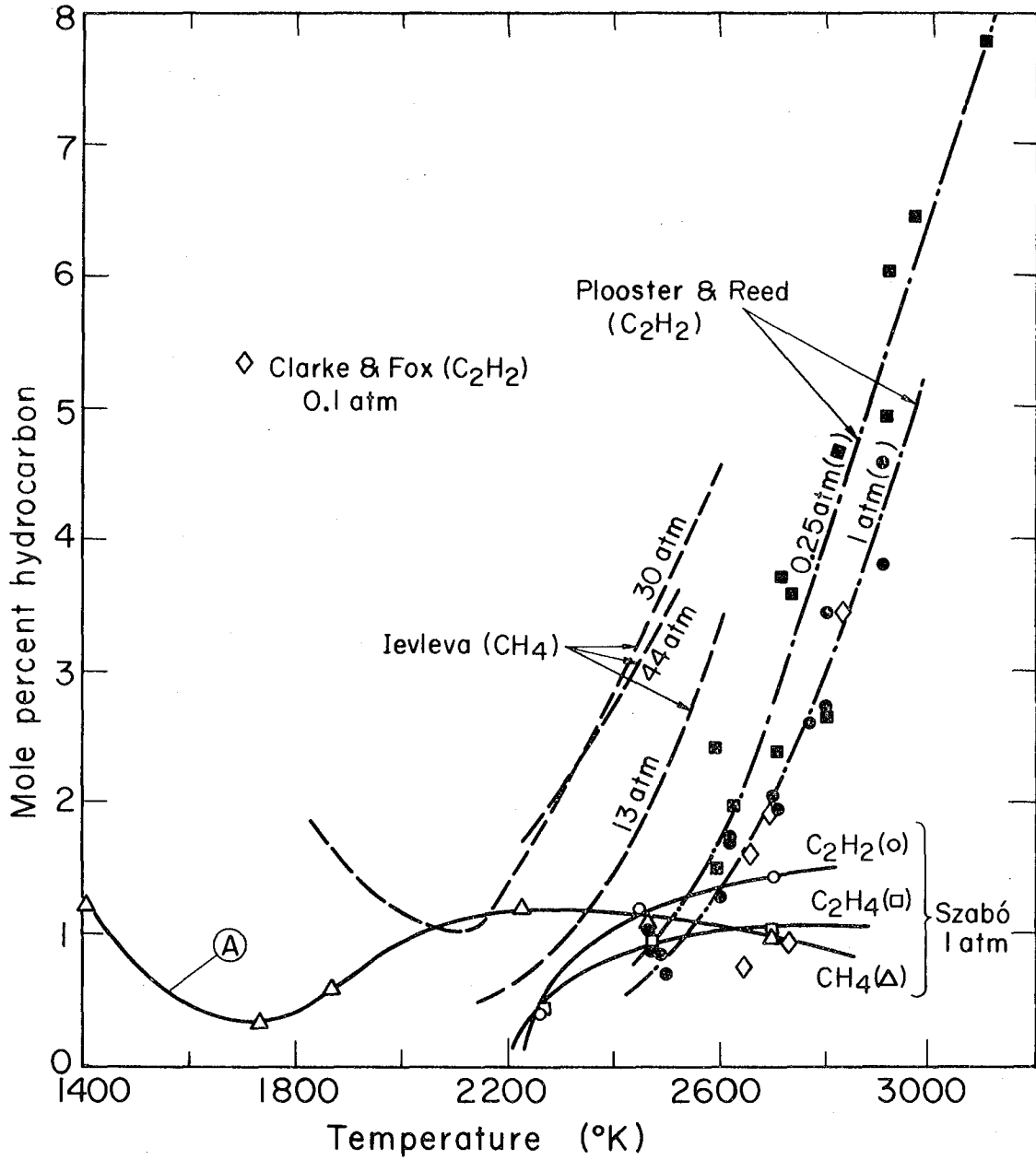
In 1950, Szabó²⁴ examined the carbon-hydrogen system over the temperature range of 1100 to 2600°C and in the range of pressures from 1/2 to 1 atm. Szabó notes that most of the previous work on this system employed rather primitive techniques and defective thermodynamic considerations. The effects of decrease in surface activity with time, catalytic effects, and wall effects were either not considered or accounted for in a manner which violated basic thermodynamic principles.

Szabó used a carbon arc glow maintained in a pure hydrogen atmosphere and a reactor designed to minimize the surface and wall

effects. Reaction products generated in this constant volume system were frozen out as swiftly as possible, and the equilibrium was approached from both sides. Schwab and Pieteck²⁵ studied the decomposition of methane on a catalytic thread and concluded that only methane which actually collided with the hot, solid surface undergoes decomposition. This result, along with the fact that no soot separated out on parts of the apparatus, formed the basis for Szabo's conclusion that the reaction which accounts for the consumption of methane is heterogeneous.

For purposes of analysis, Szabo divided the reactor system into two zones: 1) the reaction or hot zone, which was considered to be a molecular monolayer around the carbon filament, and 2) the cool zone, which consisted of the bulk of the reactor. The very large temperature gradient that existed between the carbon and the bulk of the reactor gave impetus to this two zone concept. Using this model it was assumed that (i) the reaction temperature is that of the carbon filament, and (ii) the reaction which formed the methane or the CH_2 species takes place in the hot zone. The overall system is a dynamic one, i.e., a flow system in which the hold-up time in the reaction zone is quite short (small volume of the reaction zone), and the delay in the reaction zone is less than or commensurate with the reaction time. Under these conditions gases flow around the system and change in composition until a stationary state is established. It is this state which is eventually measured in equilibrium experiments.

The "equilibrium" methane concentrations vs temperature is given by curve A on Fig. 2. Each point on this curve was obtained



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Fig. 2. Experimental Measurements of the Carbon-Hydrogen Equilibrium

by three methods: (i) approach of equilibrium from the hydrogen side, (ii) approach of equilibrium from the methane side, (iii) use of a lower initial hydrogen pressure followed by a normalization to 760 mm. These three methods, which gave good agreement and indicated attainment of equilibrium, were then averaged. The behavior of the methane concentration with temperature indicated in Fig. 2 cannot be explained by a simple equilibrium argument, since thermodynamically the methane becomes monotonically less stable with increase in temperature. Comparison of these experimental "equilibrium" values with those calculated from the equilibrium constants of Fig. 1 shows that the theoretical equilibrium concentrations are about a third of the values obtained in Szabo's work.

Invoking an argument based on a diffusion effect, the three fold discrepancy between these data and thermodynamic predictions can be explained. However such an argument does not explain the increase in methane concentration above 1700°K. Therefore, the idea of classical, segregated equilibrium cannot be applied, and recourse to explanations which are based on postulated reaction mechanisms must be made. Though the exothermic methane molecule is unstable at high temperatures, the lower hydrides (i.e., CH, CH₂ and CH₃) are formed with the absorption of heat. Therefore, high temperature favors the stability of these species. A possible explanation for the minimum at 1700°K in the methane concentration vs temperature curve may be through some mechanism whereby the lower hydrides are formed in the thermodynamically favorable atmosphere at the hot carbon filament and then react

further with hydrogen to form methane in the gas phase. The specific identity of the hydride which is important in such a dynamic equilibrium cannot be determined. However, it seems probable that the methylidyne species is not as important as the methylene and methyl radicals.

As noted from Fig. 2, acetylene assumes importance along with ethylene above 2400°K. Ethylene is most likely formed by direct hydrogenation of acetylene and by a direct free radical recombination mechanism in the gas phase. The decrease in methane concentration above 2200°C may well result from a decrease in the lower hydride concentration and direct losses of methane through side reactions.

More recent high temperature thermodynamic investigations of the carbon-hydrogen system have utilized quench techniques, which were first employed quantitatively by Pring and Hutton^{16,18}. The hot carbon specimen is immersed in an atmosphere of reactant gas, and the gaseous mixture is sampled with a probe. This hot gas sample is rapidly quenched in an effort to "freeze" the reaction products. It is imperative that secondary reactions within the sampling probe be kept to a minimum i.e., quenching must take place immediately. The general philosophy behind this technique involves 1) prediction of the equilibrium reaction network, 2) hypothesis of the quenching mechanism whereby all unstable species present in the hot, equilibrium mixture are reduced to stable species found eventually in the quenched mixture, 3) determination of the concentrations of radicals and other unstable species in the hot equilibrium mixture from observed pressure and temperature dependence of the composition of the quenched sample. The quench technique has the advantage of ease of operation, but the

experimental results are uncertain because of the back-extrapolation procedure. The latter uncertainty is reduced by judicious choice of the quenching mechanism based on existing spectroscopic and thermodynamic information. The choice of sampling probe design is usually based on empirical evidence since the quench composition is found to be sensitive to probe dimensions and flow rates. Generally the probe which yields the highest concentration of stable species is assumed to be the optimum design; the quenched gas cannot yield more than equilibrium concentrations and the probe which yields the highest concentration of the stable species in question (always less than equilibrium concentration) must be quenching the hot gas at the optimum rate.

Plooster and Reed²⁶ used the quench technique in conjunction with a carbon tube reactor at temperatures up to 3100°K. The quenched gas was analyzed only for acetylene, which was assumed to have been formed from the unstable C_2H radical. All calculations were based on the hypothesis that only acetylene, hydrogen, and their decomposition products were present in the equilibrium gas. Because of the large dissociation energy required to rupture the carbon triple bond, it was further assumed that only the C_2H radical was present along with H_2 and H in the hot equilibrium mixture. Methane and its dissociation products were not considered because of the high operating temperature ($> 2000^\circ C$). The results of this work are compared to those of Szabo in Fig. 2.

A more recent quench experiment and theoretical analysis has been carried out by Baddour and Blanchet²⁷ based on earlier work by Baddour and Iwasyk.²⁸ A carbon arc reactor provided reaction

temperatures in the range 2000°K-6000°K. The species, C_1 , C_2 , C_3 , H_1 , H_2 , CH_4 , CH , CH_2 , and CH_3 were considered. Probe and quench techniques were employed. Baddour and Iwasyk discussed possible errors made by Plooster and Reed in neglecting gas phase C_1 , C_2 , C_3 atoms and other hydrocarbon radicals. For both the heterogeneous reaction (below the sublimation point of carbon) and the homogeneous reaction region, elaborate reaction networks were constructed and solved. In addition a more elaborate quenching mechanism which accounted for minute amounts of C_4H_2 , (diacetylene) was proposed. Total pressure ranged from 0.5 to 15 atm. and various carbon/hydrogen ratios were investigated. Experimental results showed 26% acetylene at an equilibrium temperature of 4630°K. Such concentrations are considerably higher than previously reported values although 26% is still below the 40-50% theoretically possible. The carbon-methane reaction was also investigated; calculated and experimental results showed good agreement.

Ievleva²⁹ has studied the graphite-hydrogen equilibrium at 1500°C-2300°C and at pressures up to 45 atm. using a resistively heated graphite tube. Both kinetic and equilibrium experiments were performed. Sample gases were analyzed by gas chromatography and an anemometer device. Although gas samples contained mostly methane (content of unsaturates did not exceed 0.5%), Ievleva shows that most of the observed methane was formed from acetylene and free-radicals during gas sampling. In agreement with Plooster and Reed²⁶ methane was not found at 1.0 atm. and high temperature, although the amount of unsaturates decreased with increasing pressure. Hence, the conversion of acetylene and free radicals to methane

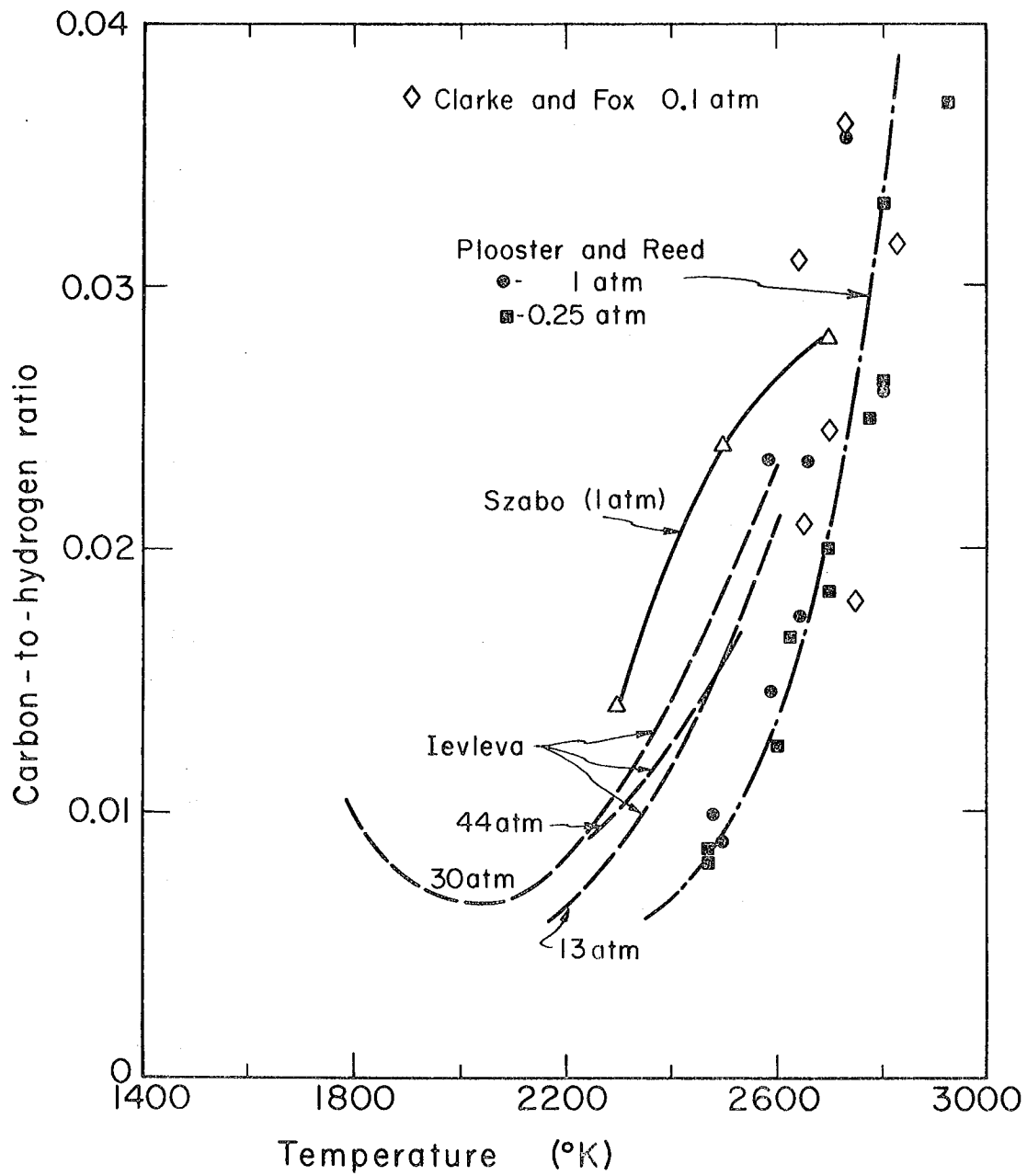
increases with pressure. Thermodynamic calculations of an equilibrium gas-phase concentration containing H_2 , H , CH_4 , CH_3 , CH_2 , CH , C_2H_2 , C_2H , and C_2H_4 agreed with the experimental results, although some systematic differences were observed at elevated pressures. Ievleva's results are given on Fig. 2.

Clarke and Fox^{30,31} report both equilibrium and kinetic results of the reaction of hydrogen and graphite filaments above 1700°C. The hydrocarbons formed in the reaction cell were analyzed directly by a hydrogen flame ionization detector. The sublimation temperature of graphite was determined as a function of C/H ratio in the gas phase. Both methane and acetylene were found in the reaction gas, the acetylene component increasing with temperature. Clarke and Fox present their results in terms of the carbon-hydrogen ratio and the fraction of methane in the methane-acetylene reaction product mixture. These data have been converted to mole fractions of methane and acetylene. The acetylene results have been plotted on Fig. 2 and show reasonable agreement with the measurements of Plooster and Reed.²⁶

Duff and Bauer³² have computed the equilibrium composition of the C/H system over the temperature range 500-5000°K. A total of 57 chemical species and total pressures of 0.1, 1.0 and 10.0 atm. were considered, and computations were made for carbon-to-hydrogen ratios of 0.1, 0.25, 0.5, 1, 2, and 3. Blanchet³³ has made similar calculations at one atmosphere total pressure. The single phase results of Duff and Bauer³² indicate two distinct temperature regions: below 1500°K there is a concentration increase in most stable, hydrogen-rich hydrocarbons. Above 1500°K, the stability of these species diminishes rapidly and above 2000°K, C_2H_2 , CH_2 ,

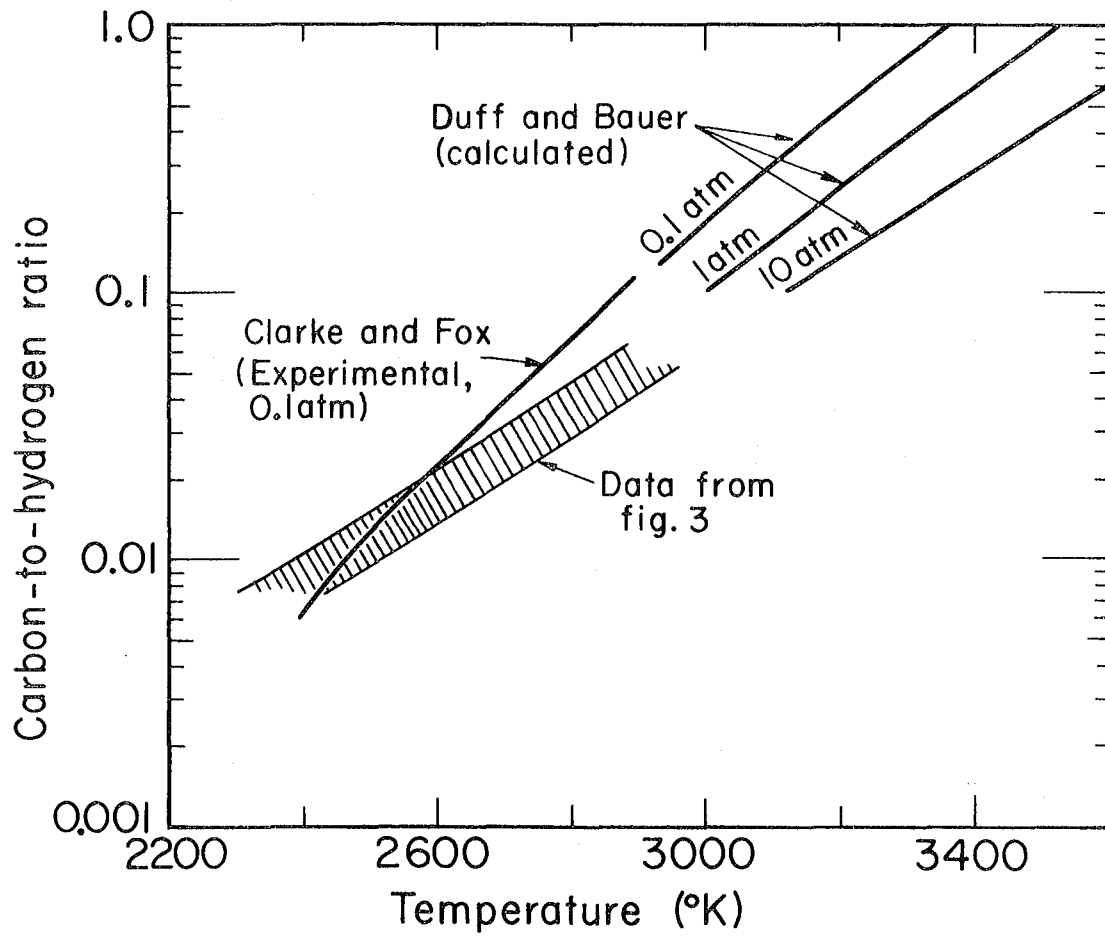
CH , C_n , H and H_2 dominate the equilibrium. The two phase calculations yield a value for the "sublimation temperature" of carbon as a function of (C/H) ratio and total pressure. Upon cooling a given gaseous mixture [(C/H) fixed] at a constant pressure, a temperature is reached where the vapor becomes "saturated" with carbon. Below this sublimation temperature, solid carbon will be deposited until the required (C/H) ratio is established. The variation of the sublimation temperature with the (C/H) ratio defines a unique phase boundary, dependent only on the total pressure. Duff and Bauer³² conclude that from 1000°K to 3000°K, the vapor in equilibrium with solid carbon contains substantial amounts of H_2 , H , CH_4 , C_2H_2 and C_2H_4 ; molecular hydrogen represents a significant portion of the vapor. At temperatures below the sublimation temperature, C_n species exist with vapor compositions dependent only on the temperature, and the concentration of atomic hydrogen is roughly that given by its equilibrium dissociation constant.

The data presented on Fig. 2 represent varying degrees of approach to true equilibrium. The quench products observed in any particular investigation are a sensitive function of sampling probes and other experimental variables. A correlation based on the temperature dependence of (C/H) should be more meaningful, and is presented on Fig. 3. Although scatter exists, agreement between investigations is indicated. Duff and Bauer³² give the calculated dependence of (C/H) on temperature, which has been reproduced on Fig. 4. The data from Fig. 3 are also reproduced in Fig. 4, where the experimental curve reported by Clarke and Fox³⁰ has been shown separately. Agreement between the latter authors and theory



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Fig. 3 Carbon-Hydrogen Ratio in the Gas Phase



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Fig. 4 Comparison of Experimental and Theoretical Carbon-Hydrogen Ratios

is excellent, whereas the correlation of other experimental results with theory is considered good. No attempt was made to resolve the pressure dependence of the experimental (C/H) vs temperature although the pressure trends seem reasonable. The results of Ievleva²⁹ appear to be high, i.e., (C/H) is too large at any given temperature, indicating equilibrium was not fully established.

Blanchet, Parent, and Countois³⁴ have performed a theoretical study of the carbon hydrogen system under high temperature equilibrium conditions. These calculations reveal that many polymeric species must be taken into account. Pressures from 0.1 to 10.0 atm., carbon-to-hydrogen ratios from 0.5 to 20, and temperatures from 2000 to 6000°K were considered. At equilibrium, only C₂H, C₃H, and C₄H species appear to be of importance near the sublimation temperature of carbon. Above the sublimation temperature C₁ and H are predominant. Acetylene was found to be present only in small amounts at equilibrium, implying that C₂H is the precursor to C₂H₂ upon quenching.

The pyrolysis of ethane and propane at 2000 to 5000°K was studied by Blanchet and Parent³⁵ in an electric arc struck between two graphite electrodes. The quench gas was analyzed by gas chromatography; C₂H₂ and H₂ were the major reaction products. The acetylene yield was a function of C/H ratio, power input, reaction temperature, and total pressure. Good agreement between experimental data and theoretical calculations³³ was obtained.

The mass spectrometer has been employed by Chupka, Berkowitz, and Meschi³⁶ to study the carbon-hydrogen equilibrium in a Knudsen cell. This method is characterized by the advantage of direct free radical determination without the ambiguity injected into the

results by quench techniques. C_2H , CH , CH_2 and CH_3 were observed, though at low concentrations. The same species were observed when a variety of hydrocarbons were pyrolyzed, though their relative concentrations varied considerably. In all cases, C_1 , H_2 , H , and C_2H_2 were present in high concentration. The intensity of species from the Knudsen cell were compared to that of the C^+ ion and the partial pressure of these species were computed from existing carbon vapor pressure data. The heats of formation of CH and CH_3 were computed and agreed well with literature values, indicating that equilibrium conditions existed within the Knudsen cell. The heat of formation of CH_3 was computed and various equilibrium constants determined. Although this work was preliminary, the power of mass spectrometric techniques in study of high temperature equilibria was clearly demonstrated.

III. KINETICS OF THE CARBON-HYDROGEN REACTION

The reaction between hydrogen and carbon can be divided into two categories, (1) the reaction of hydrogen with amorphous carbons, (2) the reaction of hydrogen with graphitic carbons. The first definitive kinetic work on the carbon-hydrogen system was carried out by Barrer in 1935 on both amorphous carbon^{37,38} and graphite.³⁹ There has since been a variety of kinetic data published on the system, which we have attempted to correlate.

Because of the great variety of experimental conditions under which specific reactions are studied, correlation of kinetic data is a difficult task. In general, discrepancies between kinetic data from different studies can be attributed to the sensitivity of any particular reaction network to the physico-chemical environment. The many works on the carbon-hydrogen system show widely varying results, a situation which results from the great diversity of reactor systems, analytical techniques, and environmental conditions that characterize these investigations. In addition, the many forms in which the reactant, carbon, can assume adds a further complication to interpretation. The raw material and formation temperature of the graphite has a great influence on its reactivity, chemical structure, and physical properties. In addition to governing the equilibration time and the magnitude of observed formation rates for various products, the past history of the carbon greatly influences outgassing characteristics, i.e., the amounts and the kinds of gases evolved from the carbon when heated in vacuo. These gases contribute to the reaction products and therefore affect results of any kinetic analysis.

For a survey of the early literature on the carbon-hydrogen reaction, one should consult a general review by Burns.⁴⁰ The following discussions will be limited to more recent works.

The temperature dependence of the reaction rate for kinetic studies over the past 15 years are shown in Fig. 5. The experimental conditions and some results are given in Table I.

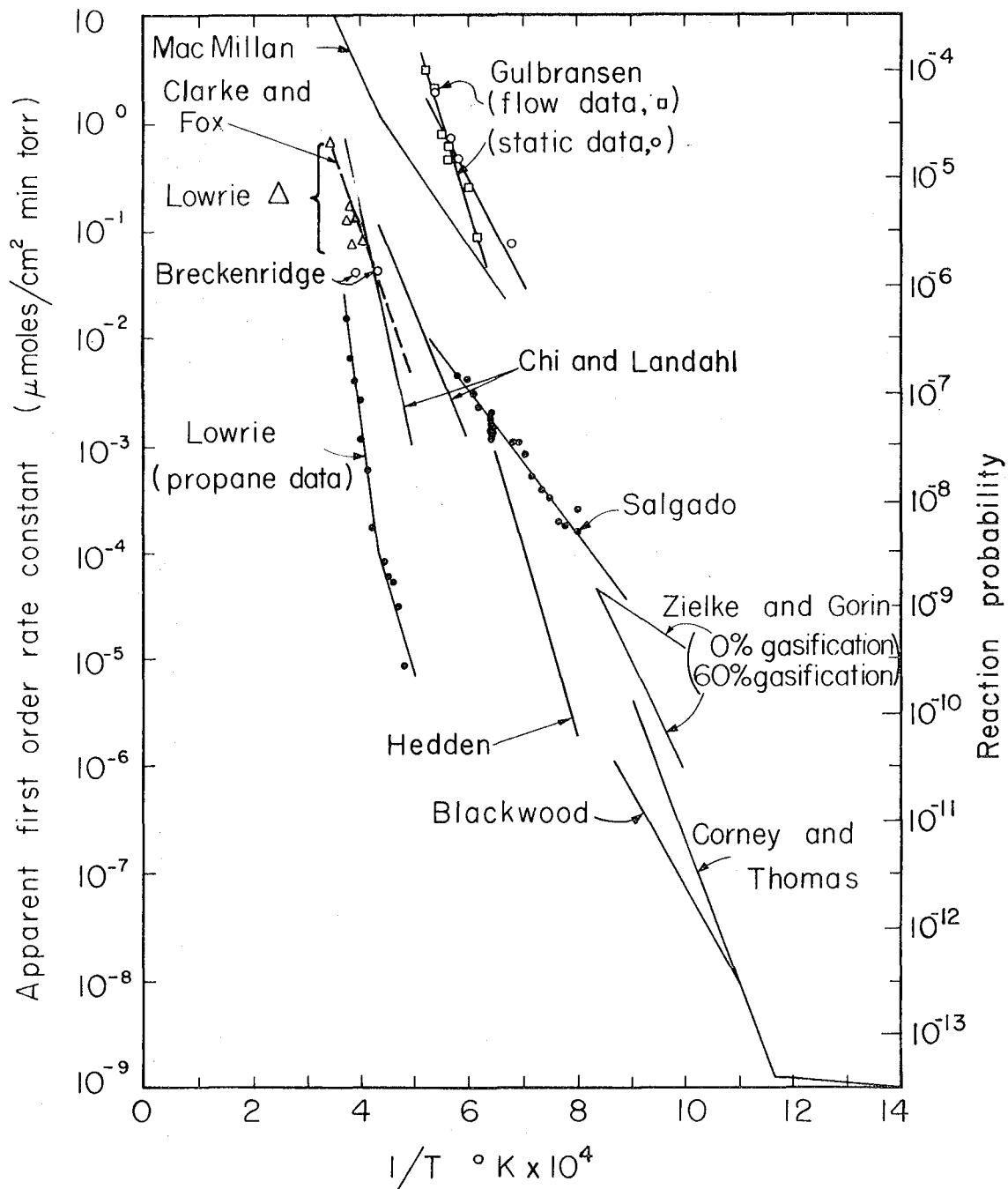
The basic parameter used to compare these works is the apparent first order rate constant, which is defined as follows:

$$k_{app} = \frac{\mu \text{ moles carbon gasified}}{\text{min.} \cdot \text{cm}^2 \cdot \text{torr}}$$

The area refers to sample area (either geometric or BET area, depending on which data were available) and the pressure refers to hydrogen partial pressure. For the case of methane production, k_{app} is the true first order rate constant. However, most works reviewed herein presented data in terms of carbon sample weight loss with no indication of gas analysis. Therefore it is assumed the gasified carbon left the surface as methane. At temperatures above 2000°C, this assumption is poor, as carbon may also evaporate directly into the gas phase and acetylene production becomes important.

The data are also expressed as the hydrogen reaction probability, defined as the rate of gasification of the sample divided by the maximum rate if all hydrogen striking the sample were converted to methane. The rate of gasification is:

$$R = 10^{16} k_{app} P_{H_2} \cdot \frac{\text{molecules CH}_4 \text{ produced}}{\text{cm}^2 \cdot \text{sec}}$$



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Fig. 5 Kinetic Data on the Carbon-Hydrogen Reaction

TABLE I. SUMMARY OF KINETIC STUDIES ON THE HYDROGEN-CARBON SYSTEM.

Investigator	Temperature range (°C)	Hydrogen pressure range	Flow rate	Form of carbon	Experimental geometry	Observed pressure dependence $\frac{p}{p_{H_2}^n}$	Observed flow dependence	Activation energy (kcal/mole)	Mode of Analysis
Zielke and Gorin	820-930	10-30 atm	0.95 l/sec	65-100 mesh "disco" charred at low temp.	Packed bed; used geometrical area of all char pellets in the 3/4 in. x 1.22 in. ² bed (10 g)	1-1.5	none	23.4 at 30 atm and 0% gasification; 10-50 after 0-60% gasification	Weight loss
Blackwood	650-870	1-40 atm	Space velocity 0.01-0.04 sec ⁻¹	-7, + 14 B.S. sieve, coconut-shell char	Packed bed; used geometrical area of all char pellets in the 10-cm-high bed (8.8 g)	≈ 1.0	none	40.7 at 30 atm	Analyzed CH ₄
Salgado	1000-1400	1 atm	0.072 l/sec	Nuclear-grade graphite	Parallel-piped; used geometrical area	≈ 1.0		30	Weight loss
Corney and Thomas	560-800	400-800 torr	0.027-0.015 l/sec	Pile-grade graphite	Tube 8 in. long x 3/4 in. o.d. x 3/8 in. i.d. geometrical area	≈ 1.0		65 at 600-800°C ≈ 10 kcal/mole at lower temp. (<600°C)	Analyzed CH ₄ , gas chromatography
Breckenridge and Bowman	1895-2370	5 torr for data used in this paper	0.045-0.01 l/sec	Nuclear-grade graphite	Carbon filament		Flow is a variable; inc. in H ₂ flow decreased yield per mole H ₂ as well as amount C ₂ H ₂ and C ₂ H ₄ produced	210 at 2136-3270°C 74 at 1895-2000°C for C ₂ H ₂	Analyzed L.N. condensables (C ₂ H ₄ , C ₂ H ₂) CH ₄ not liquified
Lowrie	2200-2370	3.5-12.2 torr for pressure-dependence expt.; ≈ 1 atm for corrosion-rate expt.		Various grades of graphite	Cylinder	≈ 1.0 for carbon loss ≈ 1.0 for C ₂ H ₄	none		Weight loss at one temperature and analyzed for propane
MacMillan	Up to 2600		5x10 ⁴ lb/ft ² .hr	Commercial graphite				31, T ₁ 2200°C 10, T ₂ 2200°C	
Gulbransen	1200-1650	9.5-38 torr	0.0061 l/sec	AGKSP	Cylinder 0.55 cm ² area x 0.05 g		none	72	Weight loss and mass spectrometric analysis of gases
Hedden	1000-1250	10-100 atm	1-120 cm ³ /sec (STP)	Spectroscopically pure electrode carbon	Packed bed; 10 g, 1.8x5 cm.	1.0		85.5	gas analysis
Clark and Fox	1700-3100	0.01-1.0 atm		Carbon filament	Filament 0.20 and 0.50 mm dia.	1.0		43.4 ± 1 atm 64.0 ± 0.01, .50 & 6.92 atm	
Chi and Landahl	1500-2500	11-56.1 atm	.31 to 1.12 #/min	Pyrographite, ATJ, H41M	Coupon, multichannel and annulus	1.0		47	Weight loss

XBL 701-248

where k_{app} has the units of μ moles/cm²-min-torr and P_{H_2} is the hydrogen pressure in torr.

The rate of hydrogen impingement on the sample is:

$$\mu_{H_2} = \frac{P_{H_2}}{(2\pi MkT)^{1/2}} \cdot \frac{\text{molecules } H_2}{\text{cm}^2\text{-sec}}$$

where k is the Boltzmann constant, M is the mass of a molecule of hydrogen and T the absolute temperature (which for convenience is fixed at the typical value of 1600°K).

The reaction probability is

$$\epsilon = \frac{R}{\frac{1}{2}\mu_{H_2}} = 3.5 \times 10^{-5} k_{app}$$

The reaction probability is plotted on the right hand ordinate of Fig. 5. Differences as large as three orders of magnitude can be seen on Fig. 5 at a particular temperature.

A. Amorphous Carbons

Zielke and Gorin⁴¹ passed hydrogen through a packed bed of 65-100 mesh Disco that was charred at low temperature and carried out their investigation over a pressure range of 10 to 30 atm and a temperature range of 1500 to 1700°F. The reaction rate was based on carbon disappearance and was found to be a function of the percent carbon gasified, gas velocity, and other conditions peculiar to the apparatus. For the purposes of this review, only data for zero percent gasification will be discussed to correlate these data with other works. The reaction was found to exhibit first and second order reaction rate kinetics with respect to hydrogen, and over the pressure range studied no pressure effects on the reaction order were observed. All gasified carbon was

assumed converted to methane, which might explain the higher reaction rates of this work. The mechanism proposed by Zielke and Gorin and shown in Fig. 6 is based on hydrogenation of edge atoms of the carbon structure. It is seen from this mechanism that an ethylenic edge group, $\text{HC}=\text{CH}$, is destroyed and a group, $\text{CH}-\text{CH}$, is generated. The ethylenic group is assumed to be regenerated through a resonance mechanism, and on the average an equal number of these groups or active sites are regenerated as are destroyed.

Based on this proposed reaction network, the following rate expression results.

$$R = \frac{k_1 k_2 A P_{\text{H}_2}^2}{k_2 + k_3 P_{\text{H}_2}}$$

This expression is typical of other proposed mechanisms, where the reaction is second order at low pressures and decreases to first order at high pressures. The parameter A is a measure of the number of active sites per carbon atom. Zielke and Gorin also studied the effect of methane addition to determine if methane has an effect on the reaction rate other than the theoretical rate decrease brought about by placing the system closer to equilibrium. A plot of rate vs methane partial pressure followed closely the equation,

$$R = R_0 \left[1 - \frac{1}{K_{\text{eq}}} \frac{P_{\text{CH}_4}}{P_{\text{H}_2}^2} \right]$$

where K_{eq} is equilibrium constant for $\text{C} + 2\text{H}_2 = \text{CH}_4$, i.e., $\left(P_{\text{H}_2}^2 / P_{\text{CH}_4} \right)_{\text{eq}}^{-1}$ and R_0 is the rate of gasification in pure H_2 . This result suggests that methane-inhibiting effects on the overall reaction are not significant.

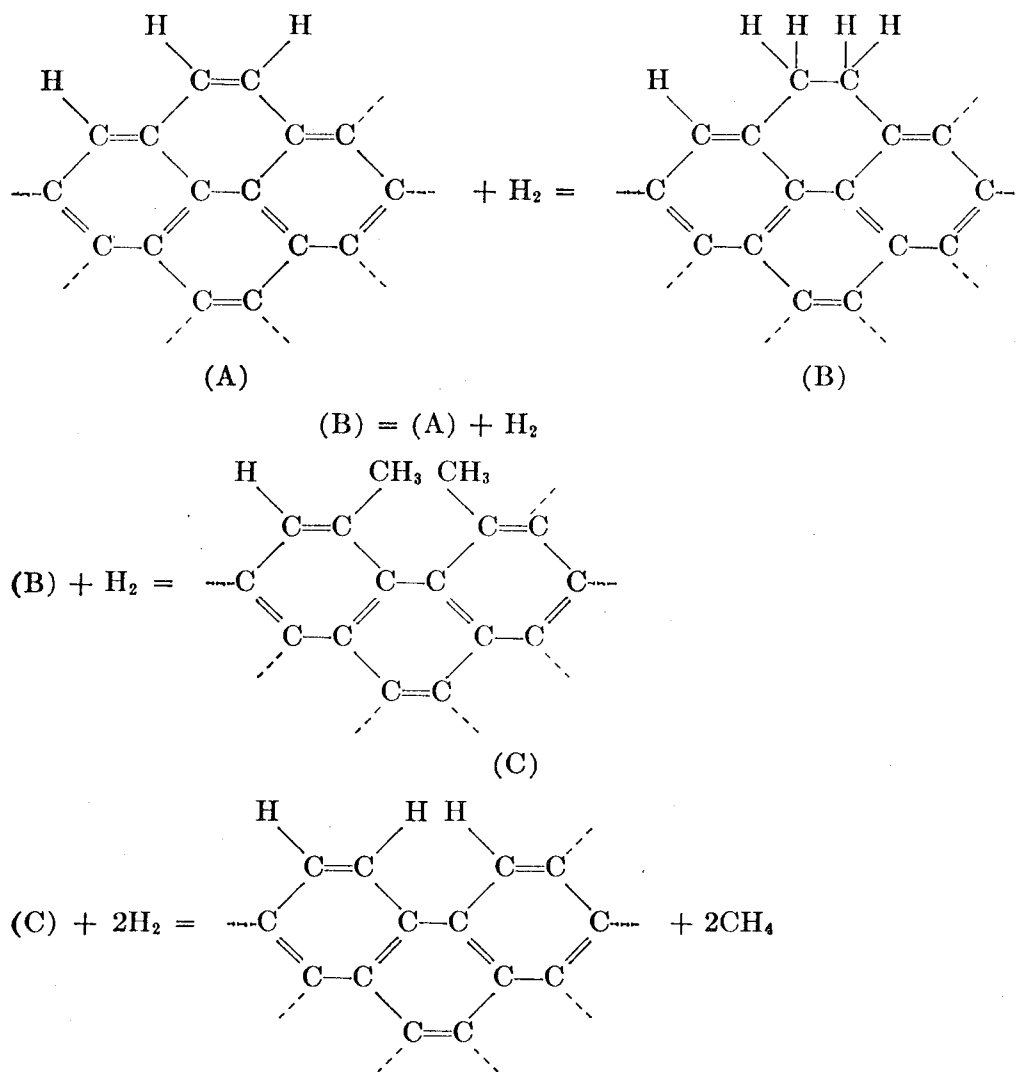


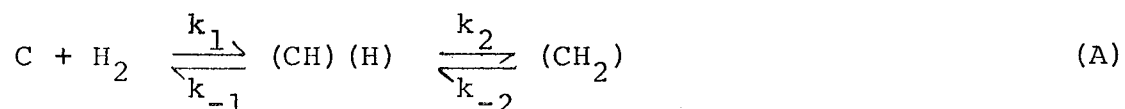
Fig. 6 Zielke-Gorin Mechanism

Blackwood⁴² expressed previous kinetic data on the carbon-hydrogen system within the framework of a consistent theory and also investigated further the methane decomposition rate on carbons. Blackwood used a flow system consisting of a fixed bed of heated carbon. The carbon was obtained from charring coconut shell. At low methane concentrations the reaction rate did not depend on the reactor space velocity. The rate was a linear function of the hydrogen partial pressure in the temperature range 650 to 750°C, but a slight departure from linearity was observed at higher temperature. Below 700°C and 5 atmospheres the rates were so small that chromatographic analysis became inaccurate.

Methane was added to the system in concentrations up to 20 atm of methane to investigate the methane decomposition reaction. The rate of decomposition of methane increased with pressure and gradually reached a constant value which was peculiar to the temperature of the decomposition. Mixtures of methane and hydrogen were passed over the bed, and the concentrations at which the reaction rate went to zero corresponded closely to that predicted by thermodynamics. Data from this work pertaining to the hydrogen-carbon reaction are incorporated into Fig. 5.

Work by Blackwood⁴³ and Blackwood and McTaggart,⁴⁴ in which atomic hydrogen was adsorbed onto carbons, showed no preferential attack on the surface carbons, and methane was readily formed. This observation implies that the function of the activated sites is to dissociate the hydrogen molecule, as adsorption is generally accepted as being atomic. Following dissociative adsorption, one atom is chemisorbed, and the other atom is free to migrate to other adsorption positions, or be adsorbed at the original active

site, since atomic adsorption was shown to be non-preferential. Adsorption on dual sites seems unlikely,³⁷ as desorption would be second order and therefore contrary to experiment. However, adsorption of hydrogen on dual sites is possible if adsorption completely de-activates the active site and re-activation of the site is possible only if the hydrogen molecule breaks apart into atoms. Hence, the above discussion indicates that the most plausible mechanism for the adsorption process is



The subsequent steps whereby methane is formed is somewhat uncertain. In the reverse reaction, (methane decomposition) Boudart⁴⁵ suggests that the methylene radical is actually the first stage of the decomposition. Other workers^{37,46} have also suggested this role of the methyl radical. The hydrogenation of $-\text{CH}_2-\text{CH}_2-$ and the subsequent bond rupture has been considered as the rate determining step of the methane formation reaction (see Fig. 6). However, Blackwood and co-workers consider it unlikely that the CH_3 group is formed in any large amounts. Instead, the final methane formation step is taken to be:



The rate expression derived from the sequence of reactions A and C takes the form,

$$R_{AC} = \frac{a_1 P_{H_2}^2 - a_2 P_{CH_4}}{1 + a_3 P_{H_2} + a_4 P_{H_2}^2 + a_5 P_{CH_4}}$$

where the various constants are groups of the basic rate constants. If the reaction sequence B and C is used, the rate expression becomes,

$$R_{BC} = \frac{a_1' P_{H_2}^2 - a_2' P_{CH_4}}{1 + a_3' P_{H_2} + a_4' P_{CH_4}}$$

where once more the various a' 's are groupings of the basic rate constants. For low concentrations of methane, these rate equations become

$$R_{AC} = \frac{a_1 P_{H_2}^2}{1 + a_3 P_{H_2} + a_4 P_{H_2}^2}$$

$$R_{BC} = \frac{a_1' P_{H_2}^2}{1 + a_3' P_{H_2}}$$

The second expression is equivalent to that derived by Zielke and Gorin.⁴¹ Both of the above expressions satisfy equilibrium requirements, and both adequately represent Blackwood's experimental data. Based on arguments of observed deviations of rate vs pressure plots from linearity at high pressures (as discussed previously), Blackwood concludes that the R_{AC} expression is the correct one. As the deviation is slight and since both curves represent the data over the pressure range studied, a definite distinction between the two expressions cannot be conclusive.

The apparent activation energy determined by Zielke and Gorin at 30 atm was 23.4 kcal/mole, whereas that from the Blackwood

investigation was 40.7 kcal/mole at 30 atm. The agreement between these two works is improved if one uses the higher carbon burn-up data of Gorin. At 50% burn-up the activation energy from the Zielke and Gorin work is in the range of 50-60 kcal/mole.

The specific reactivity of a given char is a sensitive function of the fabrication history. Blackwood, Cullis, and McCarthy⁴⁷ have gasified carefully prepared chars in a static carbon bed reactor. For a given gasification temperature, T_g , the magnitude of the apparent, first-order rate constant ($k_{app} = R/P_{H_2}$) was found to be a sensitive function of the temperature at which the char was formed (T_p), and could be accurately fitted to an expression of the form: $k_{app} = k_0 \exp(E_p/RT_p) \exp(-E_g/RT_g)$. Hence, for a given reaction temperature, T_g , the reactivity of a given char increased with decreasing temperature of preparation, T_p . The activation energies E_p and E_g were determined to be 20.0 and 50.1 kcal/mole, respectively. Furthermore, chars which were reacted at a lower temperature and then reacted further at higher temperatures did not recover their initial reactivity when returned to the lower gasification temperatures. Blackwood et.al.⁴⁷ suggested that the decreased reactivity was associated with structural condensation at the higher temperatures, resulting in a more stable, condensed ring system. When the reaction was returned to lower temperatures, the loss of free electrons previously associated with unsatisfied bonds resulted in a loss in reactivity. This explanation for anomalous reactivity effects differs from the more common interpretation based on thermally induced changes in effective surface area or pore structure.

Hedden⁴⁸ has presented data on the hydrogenation of

spectroscopically pure electrode carbon in the range of temperatures from 1000 to 1250°C and at pressures from 10 to 100 atm of hydrogen. Hydrogen gas was passed through a 1.8 cm dia. x 5 cm high pack bed of carbon particles which had a size range from 0.4 to 1.0 mm. The rate of methane formation, as determined from analysis of the product gas, was proportional to the hydrogen pressure and the mass of the packed bed. Assuming an average particle in the carbon bed corresponded to a sphere of diameter 0.70 mm, Hedden's data has been converted to the rate constant used in this review and plotted on Figure 5. Hedden also investigated the hydrogenation of charcoal and soot and found that the reaction order was a function of temperature, decreasing from second to first order with increased temperature. In addition, the activation energy for methane formation from soot or charcoal was reported to be appreciably different from that measured for electrode carbon.

Gilliland and Harriott⁴⁹ used a batch fluidized bed reactor (2.5 inch dia. x 12 inch ht.) to gasify carbon which was deposited on nickel catalysts. The reaction was investigated over the temperature range from 700°K to 1050°K and gas flow rates from 0.2 to 0.5 ft/sec. Carbon was deposited from methane, carbon monoxide and butane, and an Orsat apparatus was used to analyze the reaction products. Methane was the primary reaction product, higher hydrocarbons being less than 1%. No flow effect was observed and the CH₄ concentration in the exit gas was less than 10%. Most runs showed a dramatic decrease in reactivity as gasification proceeded, the reactivity (given on a per unit carbon basis) dropping to 1/2 the initial value at 50% gasification. The

apparent activation energy for the reaction $C + 2H_2 \rightarrow CH_4$ was given as 36 kcal/mole. The reactivity increased with decrease in the temperature of deposition; 865°K carbon showing 1/10 the reactivity observed for 645°K carbon. Some of the decrease in reactivity can be attributed to a decrease in specific surface area with the formation of thicker deposits. All results showed a wide range of reactivities resulting from the variation in deposition temperatures and degree of gasification, and it is not possible to calculate a meaningful k_{app} from these data. Gilliland and Harriott report no significant difference in reactivity in the pressure range from 1 to 15 atm., using a fixed bed reactor and carbon deposited at 700°K. At lower pressures the reaction rate was reported possibly to be proportional $P_{H_2}^{1/2}$.

B. Graphite

The reaction between hydrogen and non-graphitized carbons has been discussed and a few theoretical and experimental characteristics of the reaction system have been presented. Many of these considerations can be applied directly to the graphite reaction. Data that have been previously discussed will be compared where possible with the few data that have been obtained on the kinetics of the graphite-hydrogen reaction.

Corney and Thomas⁵⁰ have studied the effects of pile radiation on the graphite-hydrogen reaction, and have also carried out an investigation of the thermal reaction. It was concluded that pile radiation causes an increase in the rate of reaction of a factor of ten. Methane is the primary product and the reaction rate depends directly on the hydrogen partial pressure. The reaction was noted to be far from equilibrium. Corney and Thomas attribute the

increased reaction rate when the system was irradiated to an increase in the number of active sites induced on the graphite surface by the radiation. However, an increase in the concentration of atomic hydrogen caused by radiolytic decomposition of the hydrogen molecule could also explain the increase in reaction rate.

The thermal investigation employed a low pressure flow system in which hydrogen gas was passed over a sample of spectrographically pure graphite under controlled conditions of temperature and pressure. The major reaction product was methane. Propane and ethane constituted only 2% of the reaction products. The temperature was varied from 450 to 800°C and the hydrogen pressure was held constant at 800 torr. At 800°C, equilibrium conditions were reported.

An Arrhenius plot exhibited a break at approximately 600°C, indicating a change in the reaction mechanism which produced methane. The activation energy below 600°C was 10 kcal/mole and abruptly increased to a value of 65 kcal/mole above this temperature. Changes in activation energy have been reported previously by Barrer³⁷ who considered that chemisorption was rate determining at low temperature and that gas phase diffusion controlled at the higher temperatures. However, some change in sorption mechanisms seems equally plausible. The idea of boundary layer diffusion being a controlling step seems unlikely, although with increased temperature opening of inaccessible pores may occur and a great amount of "fresh" area may be uncovered. In this case, pore diffusion could become controlling, the importance of which would depend on the relative amount of new reaction area uncovered.

The data of Corney and Thomas⁵⁰ are plotted on Fig. 5.

Lowrie⁵¹ has carried out preliminary studies of the hydrogen-graphite reaction. Methane, acetylene, ethylene, ethane, and propane were observed as reaction products. Lowrie finds the formation of methane and acetylene at zero reaction time to be first order in the hydrogen pressure range 3.5 to 12.2 torr and temperature range of 1800 to 2500°C. Propane was not formed under 2000°C. These data are compared with other works on Fig. 5. An Arrhenius plot for the propane formation reaction(s) is given, and once more the Arrhenius "break" is observed at approximately 2050°C. It was postulated that the new mechanism which assumes importance at this temperature could be the sublimation of C_n becoming the rate determining step. An activation energy of 187 kcal/mole was computed by linear extrapolation of the lower temperature data and subtraction of this curve from the high temperature portion. The enthalpy of sublimation of C_2 is ~190 kcal/mole, which is close agreement with the value of 187 kcal/mole determined by Lowrie.

Lowrie attempted to elucidate the formation mechanism of acetylene by experiments utilizing mixtures of deuterium and hydrogen. If acetylene is formed through a process that involves a single molecule of hydrogen, only C_2H_2 and C_2D_2 would be formed. Equal amounts of hydrogen and deuterium were used, and analysis of the products showed the ratio C_2H_2/C_2HD to be 1/2, indicating the reaction mechanism involves atomic hydrogen. The isotope effect and the influence of the hot graphite surface on the hydrogen-deuterium exchange reaction were not taken into account.

A variety of graphites were used in Lowrie's investigation. The reaction rate showed a dependence on the kind of graphite used. More information on the physical and chemical properties of these

different graphites must be available before an explanation of these differences can be made. Lowrie's work has been extended by McDowell⁵².

Breckenridge and Bowman⁵³ have reported a kinetic study on the graphite-hydrogen system in which both the flow and static modes were investigated. The major products were methane and acetylene, although small amounts of ethylene, ethane, and various other hydrocarbons up to C_6 were observed in the flow experiments. Slightly higher rates were observed using hydrogen feed that contained 5% atomic hydrogen. The increased rates indicate that the hydrogen dissociation equilibrium was not established, since at the experimental temperatures thermodynamic considerations show the hydrogen atom content to be in excess of 5%.

A major effort was devoted to techniques of swift product removal to insure that pyrolysis did not alter the original reaction product concentrations. In the static experiments a Pyrex reaction vessel that contained a carbon filament was partially submerged in a liquid nitrogen bath, which froze out all reaction products with the exception of methane. Hence, methane could react with the hot specimen to form secondary products. Also, diffusion of other products requires a finite amount of time, and further reaction in the gas phase may have occurred. Data obtained under static conditions are indicative of a steady state system which is peculiar to the reactor used. Unwanted secondary reaction is a major problem of this kind of kinetic study. The major products of the flow experiment were methane and acetylene. There were also small quantities of ethylene, ethane, butanes, butydiene, butynes, and diacetylene. No analytical technique for methane was found, since methane will not condense at liquid nitrogen temperatures. The

presence of higher hydrocarbons is indicative of a non-equilibrium system, since thermodynamically these compounds are not stable at the filament temperature associated with this investigation.

A series of short, static runs were made to reduce effects of secondary reactions. The rate of methane production decreased with time, as would be expected if methane underwent secondary decomposition reactions. The rate of production of ethane was also reported to decrease with time, although the acetylene reaction rate remain independent of time. The reaction rates reported by Breckenridge and Bowman were plotted as a function of time and extrapolated to zero time to obtain rate constants for product formation which could be compared with other works. It is of interest to note that methane production extrapolated to a zero time rate of $0.238 \text{ micromoles/cm}^2 \text{ min.}$, irrespective of the temperature. This behavior indicates that at these temperatures the rate constant for methane is not temperature dependent. An average temperature of 2053°C was assumed and the rate constant calculated to be $0.0476 \text{ micromoles/mm min. cm}^2$. This value fits in well with the other data presented on Fig. 5. An extrapolation of the ethane rate vs time data indicates that ethane is initially formed at the same rate as methane is formed. The rapid drop in the apparent rate of formation of ethane with time relative to that for acetylene is to be expected, as ethane is less stable at these temperatures than is acetylene.

The flow experiments reported by Breckenridge and Bowman⁵³ used a graphite sample that was placed at the focal point of a carbon arc image furnace. The reactor was an integral part of a vacuum system, which contained the wire-suspended sample, and

hydrogen was passed over the sample at high velocity to sweep out the products before they underwent secondary reactions. A decrease of reaction rate/mole H_2 with the flow rate was observed, suggesting that much of the feed hydrogen never contacted with the sample because of the high space velocity. Increase in the hydrogen flow rate increased the methane formation and decreased the ethane formation. An increase in temperature increased the formation rate of products condensable at liquid nitrogen temperatures. Acetylene was always 80 to 95% of the condensible products.

The kinetics of the graphite-hydrogen reaction were treated by Salgado⁵⁴, who measured the weight loss of a heated graphite sample suspended in a hydrogen atmosphere. These data are incorporated in Fig. 5. Although there was considerable scatter in these results, an activation energy for carbon removal (or methane production) was calculated to be ~ 30 kcal/mole. Salgado indicated that the reaction rate increased with increased surface area of equal weight samples, and the conclusion was made that the rate determining step involved adsorption of hydrogen on the graphite sample. However, it was pointed out that the experimental evidence does not eliminate the possibility that internal diffusion of reactant and gases in the pure graphitic structure is rate controlling.

In a paper concerned with high temperature materials used in nuclear rockets, MacMillan⁵⁵ includes data pertinent to graphite corrosion in a hydrogen atmosphere at elevated temperatures. These flow data have been converted to the rate constant used in this review and included in Fig. 5.

Gulbransen, Andrews, and Brassart⁵⁶ have investigated the hydrogen-graphite reaction in the temperature range 1200°C to 1650°C in both the static and flow modes. A cylinder of AGKSP graphite was exposed to a hydrogen pressure of 19 torr. An alumina reactor tube was used, the weight loss of the graphite specimen was monitored, and a mass spectrometer was employed to identify the reaction products. The geometric surface was used in computing the reaction rate, and the reaction rate constant showed a slight dependence on whether data were obtained statically or dynamically. No methane could be detected in the reaction products within the sensitivity of the mass spectrometer (0.01%). Carbon monoxide was found to be a major reaction product and its presence was attributed to secondary reactions between hydrocarbon products and the walls of the alumina reaction tube. Blackwood's⁴² interpretation of the graphite-hydrogen reaction was used to explain experimental results. These data are presented on Fig. 5.

Gulbransen and Hickam⁵⁷ have recently re-examined their earlier work⁵⁶ and conclude that: i) a flow system is not adequate for making accurate gas analyses, ii) under static conditions the reaction between the alumina reactor tube and hydrocarbon reaction products (CH_4) lend uncertainty to the results, and iii) hydrocarbon products can decompose on leaving the graphite surface. A new approach was employed whereby a graphite sphere (.22 and .19 gm) was inductively heated in a quartz tube containing hydrogen gas. Although each run was limited to 2 minutes to prevent overheating of the quartz reaction tube, mass spectrometric analysis of reaction gases revealed that N_2 , CO , CO_2 , CH_4 , C_2H_4 , C_2H_2 , C_6H_6 (benzene) and C_7H_8 (toluene) were present as reaction products. The role of

surface oxides was clearly elucidated, in that specimens which were aged for three years in air showed CO and CO₂ contents in the product gas which was an order of magnitude greater than that observed for freshly machined spheres. Furthermore, the hydrocarbon yield was greater when CO and CO₂ was present, indicating the oxide may be important in the mechanism for hydrocarbon formation. Because the contact time of two minutes may be too short to establish either equilibrium or a steady state, these results have not been incorporated quantitatively into the present survey.

In addition to equilibrium studies, Clarke and Fox³⁰ have investigated the kinetics of the gasification of carbon by hydrogen gas. A graphite filament (0.2 and 0.5 mm dia.) was heated to temperatures in the range 2000°K to 3500°K in hydrogen at pressures from 0.01 to 1 atm. The reaction rate appeared to be proportional to hydrogen pressure at any given pressure. Using the geometric area of the carbon filaments used by Clarke and Fox, k_{app} was computed as a function of temperature. With the exception of the 0.1 atm data, which deviated by a factor of ~ 2.5 at the higher temperature, the rate constant was independent of hydrogen pressure. The agreement for the 0.1 atm data becomes better at the lower temperatures. The composite curve is presented on Fig. 5 and indicates good agreement with other results, an exception being those presented by MacMillan⁵⁵ and Gulbransen, et.al.⁵⁶. Below 3000°K only methane and ethane were found, whereas acetylene (and propane in some cases) was found above 3000°K. Surface area determination using a technique⁵⁸ which employed Kr⁸⁵ revealed that a significant pore structure existed in the filaments studied; the measured area was 10 to 20 times the geometric area used for

computation of k_{app} . Therefore, the data plotted on Fig. 5 may represent an upper limit if significant gasification took place at the inner surfaces of pores.

Clarke and Fox³⁰ assumed the rate of hydrocarbon formation was given by

$$R = k_{SR} K_D^{1/2} P_{H_2}$$

where k_{SR} is the rate constant for the surface reaction leading to a gaseous hydrocarbon product and K_D represents the equilibrium dissociation constant for hydrogen gas. The constant k_{SR} was calculated to be 80 ± 20 (μ mole/sec torr^{3/2}) for the pressure range 0.01 to 1.0 atm, and was independent of temperature over the range 2000°K to 2800°K. Hence, the conclusion was made that most of the activation energy associated with carbon gasification is associated with hydrogen dissociation. This hypothesis was further substantiated by the value of 51 kcal/mole computed from Arrhenius plots for hydrogen pressures of 0.01, 0.50, and 0.92 atm. A mechanism for this observation was presented, whereby an atom of hydrogen incident on the surface (rate of impingement proportional to $P_{H_2}^{1/2} K_D^{1/2}$) interacts with a hydrogen adatom (surface concentration proportional to $P_{H_2}^{1/2}$) and reacts to yield a gaseous hydrocarbon species. The product, $(P_{H_2} K_D)^{1/2} (P_{H_2})^{1/2}$ yields the assumed rate expression, predicting both the observed linear pressure dependence and the 51 kcal/mole activation energy (half dissociation energy of H_2). The increased reaction rate with (thermally produced) atomic hydrogen partial pressure confirms the findings of Corney and Thomas⁵⁰, who attribute higher gasification rates in a radiation field to radiolytic dissociation of gas-phase

hydrogen.

Chi and Landahl⁵⁹ used a water-cooled pressure vessel to contain a graphite test specimen over which a high velocity hydrogen stream was passed. In addition to employing a flat plate geometry, in which a recessed graphite coupon served as a test specimen with surface oriented parallel to the high pressure stream of hydrogen, multichannel graphite blocks and long concentric cylinders of graphite were used. A temperature range from 1500°C to 2500°C was studied, with pressures ranging from 11 to 56 atm. The reaction was monitored via weight-loss measurements as well as dimensional changes. Pyrographite (AUC), ATJ, and H4LM graphites were used. Data obtained from tests with the coupon (flat plate) geometry are presented in terms of the rate of weight-loss per geometric area and have been used to compute k_{app} as a function of temperature. Although no dependence on form of graphite is indicated, some scatter exists between runs made at the various pressures. Two best fit curves to k_{app} vs temperature are given on Fig. 5, yielding activation energies of 47 and 85 kcal/mole respectively.

In their analysis Chi and Landahl added Hedden's^{48,60} rate expressions for CH_4 and C_2H_2 formation to obtain an expression for the rate of carbon gasification. Under the assumption that the gas velocity was of sufficient magnitude to maintain negligible concentrations of CH_4 and C_2H_2 , the rate expression becomes

$$R = R_{CH_4} + 2 R_{C_2H_2}$$

$$= \left(k_{CH_4} + 2 k_{C_2H_2} \right) P_{H_2}$$

Chi and Landahl used a curve fitting routine to obtain the activation energies associated with the rate constants for methane and acetylene formation for which values of 44 and 86 kcal/mole respectively, were determined.

C. Transient Kinetic Studies

A number of non-steady state experiments have been conducted on the hydrogen/carbon system. Although flash filament and exploding wire experiments cannot be viewed from either an equilibrium or steady-state viewpoint, information obtained from these studies can be used to infer the energy required to form a particular hydrocarbon product.

Clarke and Fox⁶¹ have investigated the production of C_2H_2 from elemental carbon and hydrogen under extremely transient conditions. Energy was delivered to a carbon filament at a constant rate for very short times and the yield of acetylene was monitored as a function of hydrogen pressure and heating time. Sample heating was accomplished by either applying a constant voltage to the specimen for a short time or by discharging a condenser across the specimen. For a given power and hydrogen pressure, the energy to the filament is used to i) increase the enthalpy of the filament, ii) supply conduction and radiation losses, iii) vaporize carbon, iv) dissociate hydrogen, and v) provide energy for any other surface reactions. Keeping the power constant, a decrease in hydrogen will decrease the energy requirements for hydrogen dissociation and surface reactions. This portion of the energy is available to increase the enthalpy of the filament and to increase the vaporization rate. Hence, for a given power to

filament, the temperature rise of the filament and its evaporation rate increases as the hydrogen pressure is reduced. Although increased temperature results in increased conduction and radiative heat loss, these quantities do not increase with temperature as rapidly as the vaporization rate. For a fixed hydrogen pressure a temperature is reached where the energy going to vaporization equals that attributed to radiation and conduction losses. Increased vaporization of carbon leads to an increased C_2H_2 yield via the gas phase reaction $C_2(g) + 2H(g) \rightarrow C_2H_2$. Clarke and Fox⁶¹ employ an apparatus which was essentially identical to that used in a previous work⁵⁸. Sample weight change and a gas chromatograph were used to analyze the products evolved from both types of heating experiments. Hydrogen pressures of 700, 380, 76, and 38 torr were used. Methane, acetylene, and propane were the major reaction products in the constant voltage heated experiments, although ethylene and ethane were also formed in measurable quantities. The capacitor discharge experiments yielded primarily C_2H_2 and C_3H_8 . Final results of the capacitor discharge experiments were expressed as the energy required to form one mole of carbon as $C_2H_2 + C_3H_8$ (mostly C_2H_2) which decreased by a factor of two when P_{H_2} was reduced from 380 torr to 76 torr. The yields at the lower pressures corresponds to a thermal efficiency of 30% (i.e., 30% of total energy input went to form C_2H_2) as compared to 10% calculated from the results reported by Baddour and Blanchet²⁷ via the arc process.

Spangler and Lott⁶² report results of an exploding wire experiment in which a 31 μ f capacitor charged to 10 kv deposited 13,800 joules of energy into graphite filaments and yarns in less

than a microsecond. Hydrogen pressures of 1500 torr were used and a mass spectrometer analyzed the reaction products. Under conditions where secondary arcing to the reactor walls did not obscure results, methane (35.7%), ethane (14.8%), ethylene (19.3%), acetylene (28.2%), propane (0.7%), propylene (0.8%) and butene (.3%) were observed. The high hydrogen pressures used in this investigation indicates that a significant portion of the energy deposited into the graphite was used to dissociate hydrogen and initiate surface reactions. The significant proportion of CH_4 , C_2H_4 , and C_2H_6 in the reactant gas indicates appreciable heterogeneity.

Palmer⁶³ has reported reaction between hydrogen and carbon in the extremely non-equilibrium environment of a graphite ball mill. When graphite was pulverized with steel shot in a hydrogen atmosphere, hydrogen was taken up by the graphite in quantities which were far in excess of the amount expected if only surface adsorption on freshly exposed crystal planes took place. Palmer contends the high, instantaneous temperatures ($\sim 1500^\circ\text{C}$) generated at frictional contacts between the steel balls and graphite are sufficient to initiate the reaction. Since these high temperatures are extremely localized, the reaction proceeds under conditions which are not unlike those of other deliberately transient experiments. The reaction proceeds under thermodynamically unfavorable conditions if the products are rapidly quenched and removed. Palmer, however, does not report the identity of these reaction products.

Other studies of the graphite-hydrogen kinetics have been reported by Gulbransen⁶⁴ Rogers and Sesonske^{65,66}, and Sanders⁶⁷.

IV. ADSORPTION OF HYDROGEN ON GRAPHITE

Dissociative adsorption is necessarily the precursor to surface reaction. Unfortunately, the adsorption and reaction steps have never been studied as steps of a single process. Reaction of hydrogen and graphite generally occur at temperatures at which the surface concentration is low ($> \sim 1500^\circ\text{C}$), and adsorption studies are difficult. At temperatures where easily measurable adsorption occurs, the reaction rates are too slow to be conveniently measured.

We summarize here two studies of hydrogen adsorption on graphite (without reaction) which span temperatures from 600 to 1500°C . Adsorption isotherms are based upon the Tempkin model which assumes a linear dependence of activation energy on coverage⁶⁸:

$$E = E_0 + \sigma\theta$$

where E is the activation energy for adsorption, σ is a constant and θ is the coverage:

$$\theta = V/V_m$$

where V is the volume of gas adsorbed and V_m is the maximum adsorption at a particular temperature. The Tempkin isotherm is:

$$\theta = \eta \ln P_{\text{H}_2} + \beta$$

where β is a constant and

$$\eta = \frac{RT}{\sigma}$$

Thomas⁶⁹ observed appreciable hydrogen adsorption in the

temperature range 600 to 750°C. Five gram samples of reactor grade graphite were degassed under vacuum at 900°C for 24 hours and gave a BET surface area of 3.0 m²/gm. The adsorption rate was sufficiently large to insure equilibrium conditions at the end of 2 to 3 hours. Experiments at 450°C indicated very slow adsorption. The amount of hydrogen adsorbed at equilibrium showed a progressive decrease with increase in temperature, although equilibrium was reached at shorter times at these higher temperatures. The rate of hydrogen adsorption was shown to follow the Elovich or Roginsky-Zeldovich equation⁶⁹ which is also based on a linear increase of activation energy with surface coverage.

Redmond and Walker⁷⁰ studied sorption phenomena on TSP and AGKSP graphites in the temperature range 900 to 1500°C. BET surface areas were determined to be 0.3 and 0.4 m²/gm. respectively, which are considerably lower than the specific area of the pile graphite used in Thomas' investigation. This difference is most likely a result of different gases being used in the BET determinations, as the graphites used in both investigations should be relatively similar.

The data at 920°C for TSP graphite followed the Tempkin isotherm over the pressure range of 1 to 760 torr. At the higher temperatures (1085, 1335, 1495°C) the isotherms consisted of two linear portions, each of a different slope. The break in the adsorption isotherm occurred at a critical pressure. Both the slope of the isotherm and the critical pressure increased with temperature. Each segment individually conformed to a Tempkin isotherm. These breaks were attributed to surface heterogeneity or the onset of a new adsorption mechanism.

Values of η/T from Thomas' low temperature data and Redmond's high temperature data in the low pressure range (below 100 torr) agree within a factor of two, but the η/T values from Redmond's high pressure data (100 to 1000 torr) are an order of magnitude larger than Thomas' results. Whatever the mechanism for adsorption which becomes significant in the higher pressure, high temperature range, the results of this comparison imply that the new process proceeds with an activation energy which is a weaker function of the coverage than the processes in the lower temperature range and at lower pressures.

The Tempkin isotherm is based on a linear increase in activation energy with coverage, which implies a linear decrease in the heat of adsorption, Q , with coverage. Both studies obtained expressions for the variation of the heat of adsorption in the middle range of coverage (the region of validity of the Tempkin isotherm):

$$Q = 58 - 56\theta \text{ kcal/mole} \quad (\text{Redmond and Walker})$$

$$Q = 46.7 - 54\theta \text{ kcal/mole} \quad (\text{Thomas})$$

For low surface coverages an activation energy for adsorption equal to ~ 50 kcal/mole agrees well with earlier experimental work by Barrer³⁹ on carbon (50 kcal/mole) and calculations by Sherman and Eyring⁷¹ (42 kcal/mole). It is generally assumed that hydrogen chemisorbs as atomic hydrogen at edge atoms of the graphite crystal lattice, and no adsorption takes place on the basal plane surfaces. Redmond and Walker⁷⁰ calculated the maximum surface area for adsorption based on chemisorption only at lattice edges, using an average crystal size of 400 \AA long x 1000 \AA in diameter for TSP graphite. These calculations indicated that 44% of the area associated with a typical specimen is edge area and the remaining

area is basal area. Based on this model, it was shown that the surface area covered by the equilibrium volume of adsorbed hydrogen was much greater than that available. Two explanations for the difference are (i) hydrogen penetrates between the basal planes, (ii) there is more area available for chemisorption at the higher temperatures than that measured at the temperature of the BET surface area determinations. Since electrical conductivity and basal plane spacings remained the same before and after experiments, the first explanation is eliminated. Much of the surface area of graphite is closed off in isolated pores, which are formed during the graphitization process. The size and population of these pores depends greatly on the manufacturing process and the raw materials used. Since the hydrogen atom is smaller than nitrogen or helium, which are used in BET determinations, diffusion would be greater at elevated temperatures, and pore openings would be larger at higher temperatures; increased area for chemisorption of hydrogen at elevated temperatures seems plausible.

Only 2% of the total crystallite edge area was calculated to be necessary for accommodation of the hydrogen adsorbed in the temperature range of Thomas' investigation. Thomas reports 2.8% of the surface carbon atoms are occupied at 700°C; interaction of hydrogen atoms with carbons in the basal planes was insignificant.

Coulson⁷² distinguishes three types of boundary atoms in a graphite lattice, each of which has a different affinity for hydrogen atoms. The situation is quite complex as the boundary atoms can acquire a partially triple bond character, a double bond character, or show unpaired electrons. First, there are edge atoms

with unused sp^2_π orbitals having only one electron. Second, there are atoms which exist as pairs with a partially triple bond character and are stabilized by contributing to the resonance energy of the carbon ring. Third, there are isolated atoms which can revert to a s^2p^2 state. The first type of atom would be expected to be very reactive and chemisorb hydrogen atoms quite readily; at high temperatures ($> 450^\circ\text{C}$), all edge sites may be active.

V. EVAPORATION OF GRAPHITE

An important aspect of the chemical characteristics of the carbon-hydrogen system involves direct evaporation of the graphite surface. Sublimation of graphite is particularly important at elevated temperatures, as the vapor pressure of carbon at 2400°K is approximately 2.4×10^{-4} torr. In view of the possibility of gas phase reactions involving vaporized carbon, the thermo-chemistry of direct carbon gasification will be reviewed briefly.

Studies concerned with evaporation of carbon date back to the 1930's, when experiments were directed towards determining the heat of sublimation. The determination of the heat of sublimation of carbon has historically followed four routes; 1) vapor pressure vs temperature data, 2) dissociation energy of carbon monoxide and oxygen, in conjunction with the heat of formation of CO, 3) a stoichiometric approach similar to that of (2) using CN, 4) calculation of bond energies from spectroscopic data.

Measurement of the vapor pressure of carbon is the most direct method to determine the thermochemical properties of graphite. Although considerable error was inherent in early vapor pressure experiments because of crude weight loss techniques employed, the advent of the mass spectrometer as a research tool rendered direct vapor pressure measurement much more accurate. This review is limited to the direct vapor pressure measurement technique. Mass spectrometer studies also provide information on the species which leave the hot graphite surface under vacuum conditions and on the rate at which these species vaporize.

The rate at which molecules of the gas impinge upon a unit area of surface is given by

$$\mu = \frac{P}{(2\pi MkT)^{1/2}} \quad (1)$$

where P is the gas pressure, M is the mass of the atoms and k is Boltzmann's constant. Of the μ molecules/cm²-sec striking the surface, a fraction α condense upon it while the fraction $1-\alpha$ are reflected back to the gas phase without having undergone significant interaction with the solid. The magnitude of the quantity α , which is called the condensation coefficient, depends upon the mechanism of the condensation and evaporation processes.⁷³

Condensation and evaporation rates characteristic of thermodynamic equilibrium are attained only in a completely enclosed, thermally insulated cavity of the material of interest. Under conditions of equilibrium between the gas and solid, the rates of condensation and evaporation are given by $A\alpha\mu_e$, where A represents the inner area of the cavity. In order to measure this impingement rate, and hence the equilibrium vapor pressure, P_e , it is necessary to perturb the ideal cavity. The perturbation acts as an external sink for gaseous molecules. The vapor pressure experiment which attempts to minimize this loss historically has been designated as a Knudsen experiment. Knudsen evaporation takes place when the ideal cavity is punctured with a small hole, and gases effuse from the cavity. The rate of effusion is measured. In this new, steady state it is assumed equilibrium still exists in the gas phase and that the rate of evaporation from the surface is not influenced by the condition of the gas phase.

Under conditions of Knudsen evaporation, the rate of effusion is given by $a\mu$, where a represents the area of the effusion orifice. A particle balance is taken across an area placed just above the

solid surface:

$$\left[\begin{array}{l} \text{rate of} \\ \text{effusion} \end{array} \right] + \left[\begin{array}{l} \text{rate at which molecules} \\ \text{impinge upon the surface} \end{array} \right] = \left[\begin{array}{l} \text{rate of} \\ \text{evaporation} \end{array} \right] + \left[\begin{array}{l} \text{rate of surface} \\ \text{reflection} \end{array} \right]$$

The rate at which particles impinge upon the surface is simply $A\mu$, and the rate at which they are reflected is given by, $(1 - \alpha)\mu$.

Thus at steady state,

$$a\mu + A\mu = \alpha\mu_e A + (1 - \alpha)\mu A \quad (2)$$

or

$$\mu_K = \frac{\mu_e}{1 + \frac{a}{\alpha A}} \quad (3)$$

Equation (3) gives the rate at which molecules effuse from a Knudsen cell under conditions of thermal equilibrium in the gas phase and steady state conditions on the surface. A subscript K has been added to the effusion rate of Equation (3) to denote Knudsen conditions. If $a/A \ll \alpha$, the measured pressure within the Knudsen cell is identical to the equilibrium vapor pressure.

Evaporation from a free surface into vacuum is called a Langmuir experiment. Rates of evaporation obtained by the Langmuir technique measure directly the surface evaporation rate, $\alpha\mu_e$, where μ_e is referred to equilibrium conditions at temperature T and pressure P_e :

$$\mu_L = \alpha\mu_e \quad (4)$$

To obtain the vapor pressure P_e from effusion rates under Knudsen conditions by Equation (3) or evaporation rates by a Langmuir experiment and Equation (4), the condensation coefficient, α ,

must be known. This factor may be a function of temperature and depends upon the nature of the surface.

Experimental results on the carbon system have generally been presented in terms of the heat of sublimation, which is related to the temperature derivative of the vapor pressure. Brewer, Giles, and Jenkins⁷⁴ have criticized previous works which were obtained from rate of evaporation data on the premise that the evaporating species may not have been in the ground electronic state and that the relative amounts of the dimer, trimer and higher carbon polymers were unknown. In addition, the uncertainty in the values of the condensation coefficients further cloud the interpretation of vaporization rate data. The effects of multiple species and non-unity condensation coefficients on experimental results are illustrated below.

Under conditions of equilibrium, the Gibbs-Helmholz equation assumes the form

$$\frac{d \ln P_{xe}}{d(1/T)} = \frac{-\Delta H_x}{R} \quad (5)$$

where P_{xe} is the equilibrium vapor pressure of gaseous carbon species containing x carbon atoms, ΔH_x is the heat of sublimation of that species and R is the gas constant. For the Langmuir case where the pressure measured is not the equilibrium pressure, but is given by $P_{xL} = \alpha_x P_{xe}$ where α_x is the condensation coefficient of the C_x species, Equation (5) becomes:

$$\frac{d \ln P_{xL}}{d(1/T)} = \frac{-\Delta H_x}{R} + \frac{d \ln \alpha_x}{d(1/T)} \quad (6)$$

or the measured heat of sublimation is $\Delta H_x - R \frac{d \ln \alpha_x}{d(1/T)}$. Furthermore,

the effect of the accommodation coefficient is even more significant in experiments which rely on deposition techniques to determine evaporation rates. These effects will not be discussed, since they are highly specific to the particular investigation.

When no effort is made to account for the various gaseous species of carbon leaving the surface, the measured heat of sublimation diverges even more from the true equilibrium quantity, ΔH_x . Consider, for example, the case where only the monomer and dimer are present in the gaseous phase and that the degree of dissociation of the dimer is given by δ . This quantity is not the equilibrium fraction of the monomer, but that which actually exists in the non-equilibrium, steady state experiment. Assuming ideal gas behavior, the measured total pressure P_L is,

$$P_L = P_{1L} + P_{2L} \quad (7)$$

By differentiating Equation (7) with respect to $1/T$ and substituting into Equation (6) it is seen that the measured heat of sublimation is of the form,

$$-\delta \Delta H_1 - (1-\delta) \Delta H_2 + \delta \frac{d \ln \alpha_1}{d(1/T)} + (1-\delta) \frac{d \ln \alpha_2}{d(1/T)}$$

When δ is close to the true equilibrium dissociation factor the first two terms together give the true equilibrium heat of sublimation for a monomer-dimer mixture. The measured heat deviates from the true equilibrium heat by the factor

$$\delta \frac{d \ln \alpha_1}{d(1/T)} + (1-\delta) \frac{d \ln \alpha_2}{d(1/T)}$$

Early carbon sublimation and vapor pressure data are in error due to these unknown factors.

It has been pointed out that from the heat of formation of CO and the dissociation energies of CO and O₂, it is possible to obtain a value for the heat of sublimation of monomer carbon. However, a series of possible dissociation energies for CO exist, because of various predissociation states which exist in CO.⁷⁵ Using these data, the heat of sublimation has been estimated to be either 170, 141 or 125 kcal/mole at 0°K. A few of the more important experiments concerned with elucidation of this situation will now be reviewed briefly.

Brewer, Gilles and Jenkins⁷⁴ evaporated graphite from a narrow slitted Knudsen cell under equilibrium conditions ($a/A \rightarrow 0$). The concentration of C₂ was monitored spectroscopically, assuming that spectroscopic peak intensities of the molecular bands of C₂ was proportional to the partial pressure of that molecule. It was assumed only C and C₂ species were present in the gas. From the variation of the C₂ molecular band intensities with temperature, the heat of sublimation of C₂ was found to be 233 kcal/mole at 0°K. The vapor pressure curve for C₂ was computed from this value. The rate of evaporation of the monomer was determined by the amount of carbon collected over a period of hours on a platinum plate placed in front of a Knudsen cell. Using Equation (1) and assuming the prime constituent in the gas phase to be monomer, a value of 170 kcal/mole for the heat of sublimation of graphite was computed. The assumption of pure monomer evaporation was shown to be valid since the spectroscopically determined vapor pressure of C₂ is very small compared to that of the monomer. The heat of dissociation of C₂ was calculated as 4.7 ± 0.3 kcal/mole.

Brewer et. al.⁷⁴ varied the size of the effusion furnace hole

to observe changes in vaporization rates and thus to observe effects of the condensation coefficient by Equation (3). The hole-to-surface area ratio (i.e., a/A) was varied from 4.03×10^{-3} to 1.43×10^{-3} without affecting the evaporation rate. Therefore it was concluded that the accommodation coefficient for carbon is greater than 4×10^{-3} and that equilibrium conditions prevailed.

Thorn and Winslow⁷⁶ have obtained evaporation data on the carbon system in the 2300-2500°K temperature range by heating cylinders of graphite in vacuo and observing the change in optical transmissivity of a quartz target placed in front of the specimen. Data were obtained under two surface conditions: 1) evaporation from a plane surface, 2) evaporation from a surface in which many small holes were drilled, thereby approximating equilibrium conditions. Total film weight data based on pure monomer evaporation for both the plane surface and perforated surface yielded $\Delta H_0 = 174$ kcal/mole. The experiments which employed time vs transmissivity data required knowledge of the form of carbon which strikes the quartz surface. Based on calculations which indicated that dissociation of the dimer at equilibrium was very close to completion it, was again assumed that only monomer was present in the gas phase. The transmissivity method yielded values of 198 kcal/mole for the plane surface and 185 kcal/mole for the perforated surface. The deviations between these values of the heat of sublimation and those obtained by weight loss measurements were examined in terms of a vaporization coefficient, deviations of the drilled surface from ideal Knudsen conditions, and a non-unit value of condensation coefficient at the target film. The inability to specify exactly the results of these effects on the experimental data left the problem essentially

unresolved, although based on Brewer's work⁷⁴, it was concluded that the 170 kcal/mole value for ΔH is most likely correct.

Doehaerd, Goldfinger and Waelbroeck⁷⁷ performed an experiment which was similar to that of Thorn and Winslow⁷⁶. The rate of evaporation and the rate of (equilibrium) effusion were simultaneously observed by measurement of the thickness of the deposited film on a glass microscope slides. The results of this experiment gave condensation coefficients between 2×10^{-3} to 2×10^{-4} , and a value of 146 kcal/mole for the heat of sublimation of carbon (comparable to the 141 spectroscopic value). These data were obtained with a hole-to-surface area ratio of 4×10^{-5} in the Knudsen cell. The discrepancy of these results with the earlier data of Brewer⁷⁴ was attributed to the small value of the condensation coefficient (if the above quoted range of values are assumed correct) and thus a variation of measured Knudsen cell vapor pressure with the hole-to-surface area ratio. Doehaerd et. al.⁷⁷ claimed that hole-to-surface area ratios used by previous authors were too large to indicate any dependence of effusion rates on this area ratio, and in fact if smaller area ratio were used, results of such experiments would indicate small condensation coefficients. This apparent dependence of the condensation coefficient on the hole-to-surface area ratio was explained by the possibility of an evaporation mechanism whereby the high α value C_2 molecules constitute most of the effusion beam when there is a relatively large area ratio, and the low α monomer carbon make up the primary species when the area ratio is very small. Brewer⁷⁸ defended his work on the basis of observed constancy of the rate of evaporation with changes on the area ratio and the fact that his results are

supported by other investigators.⁷⁶

Chupka and Inghram^{79,80} realized the potential of the mass spectrometer to resolve the problems encountered in the vapor deposition techniques. By employing a heated carbon filament, they evaporated carbon into the ionizer of a magnetic sector mass spectrometer. They found heats of sublimation of C_1 and C_2 to be 179 and ~ 200 kcal/mole, respectively.

These results verify the findings of Brewer.⁷⁴ In later work with the same system,⁸¹ Chupka and Inghram showed the existence of the C_3 molecule, which constituted the major species at 2500°K. The large C_3 component of the vapor invalidated many of the earlier works based on the assumption of pure monomer evaporation.

A mass spectrometric analysis of evaporated species from a carbon filament has been carried out by Honig⁸² and essentially parallels the work of Chupka and Inghram.⁸¹ The important role of the polyatomic species was verified, though effects of fragmentation in the ionizer were not fully elucidated. The heats of sublimation C_1 , C_2 , C_3 were computed to be 179 ± 10 , 210 ± 20 , 190 ± 10 , respectively. Negatively charged carbon species up to the octomer were emitted from the graphite at 2400°K.

Chupka and Inghram⁸³ used a mass spectrometer in conjunction with a Knudsen cell source of carbon species to measure vapor pressure-temperature dependence. The C_1 , C_2 , C_3 species were observed and from temperature variations of their respective mass peaks the heats of sublimation were calculated to be 170, 190 and 200 kcal/mole, respectively. Carbon vapor pressures were reported as:

<u>T, °K</u>	<u>Vapor Pressure of C₁, torr</u>	
2380	1.4 x 10 ⁻⁵	
2400	3.0 x 10 ⁻⁵	P _{C₂} /P _{C₁} ~ 0.5
2430	6.8 x 10 ⁻⁵	P _{C₃} /P _{C₁} ~ 6.5
2440	1.0 x 10 ⁻⁴	

It was also observed that the C_3^+/C_1^+ ratio from the Knudsen cell was about four times that for evaporation from a free surface. This precludes any extremely small value of the accommodation coefficient, as reported by Doehaerd, et al.⁷⁷

Using the mass spectrometer, Burns, Jason and Inghram⁸⁴ measured the condensation (evaporation) coefficients of monomer, dimer and trimer carbon. Langmuir and Knudsen evaporation were simultaneously measured. The ratio of observed rates for a given species gave the following condensation coefficients at 2500°K for the case where the surface normal coincided with the c-direction of the graphite lattice:

<u>Species</u>	<u>α</u>
C ₁	0.14±.04
C ₂	0.26±.04
C ₃	0.03±.005

Condensation coefficients on the plane perpendicular to the a-axis were ~ 50% greater than those listed above. No temperature dependence of the condensation coefficients was measured.

The mass spectrometer has resolved the composition of evaporating species from graphite surface at elevated temperatures and in doing so has brought forth the serious limitations of earlier equilibrium

effusion data and vaporization results. The latter works were based on the assumption that the monomer was the sole subliming species. Honig⁸² has attempted to make use of these early works, whose great value lies in their results since they are based on absolute rates of mass evaporation. Using these absolute rates (which are in reality a sum of the individual rates of evaporation) and assuming the corresponding pressure is given by $P_F = 1/M_F^{1/2} (P_1 M_1^{1/2} + P_2 M_2^{1/2} + P_3 M_3^{1/2})$, where M_F , P_F are fictitious molecular weights and pressure, and P_i is the relative partial pressure as computed from mass spectrometer ions intensities, Honig computed effective heats of evaporation. The results were compatible with results of similar calculations based on Honig's data. It was pointed out that effects such as uncertainty of re-evaporation from collecting targets and evaporation of particles from other parts of the apparatus serve to further obscure the conclusions drawn by the early works.

In addition to these factors, the outgassing problem or "tar effect" has affected the early investigations. Knowledge of the outgassing problem is of great importance if results of surface studies are to be truly useful. Though outgassing characteristics are highly specific to the history of the particular graphite, sufficiently long periods of time at elevated temperatures will give the sample under investigation more uniform properties and to a great extent serves to remove this "tar effect" from experimental results.

Redmond and Walker⁸⁵ observed gases released from nuclear graphite and electrode graphite when heated in vacuo to temperatures in the range 1,500-2000°C. Results of this investigation were:

- 1) Significant amounts of hydrocarbons (C_2H_4 , C_2H_2 , C_2H_6 , CH_4 , iso- C_4H_8) were evolved from nuclear graphite up to $1200^\circ C$. Electrode graphite evolved hydrocarbons up to $800^\circ C$.
- 2) For both graphites, hydrogen was the major component of the evolved gas.
- 3) More water came off electrode graphite at low temperature than for nuclear graphite. Above $1000^\circ C$, no water was observed for either types of graphite.
- 4) Carbon monoxide was a major high temperature outgassing product for electrode graphite, where H_2 was the major component for nuclear-graphite.

Supplementary Bibliography

A number of papers and reports which either were missed by us or appeared after the preparation of this manuscript are simply listed as refs 86-108. We are grateful to Dr. J. C. Bowman of the Union Carbide Corp. for providing us with his bibliography on the carbon-hydrogen system from which we have taken the last 23 references.

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