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SUMMARY

The rates of reaction of a pitch-free, petroleum coke-base graphite with purified hydrogen were determined in the temperature range 1550° to 2260° C. Experimental weight losses agree very well above 1800° C with calculations based on thermodynamic data for the hydrogen-graphite theoretical equilibrium compositions, where acetylene is calculated to be the major reaction product. Although the experimental curve and the theoretical curve diverge below 1800° C, equilibrium might be achieved at temperatures below 1800° C if slower hydrogen flow rates were employed.

INTRODUCTION

Past experimental investigations of the thermal equilibrium between hydrogen and carbon agree reasonably well with the results obtained by calculation to about 1000° C (ref. 1) and indicate that methane (CH_4) is essentially the sole reaction product, the equilibrium concentration of CH_4 decreasing with increasing temperature. One investigator, however, reports a minimum methane concentration at 1450° C followed by an increase in methane concentration with increase in temperature to 2000° C (ref. 2). Up to 1450° C, the methane concentrations measured were somewhat higher than the calculated equilibrium concentrations. Reference 2 suggested that this disagreement was possibly due to a thermal diffusion effect and that the increase in CH_4 concentration between 1450° and 2000° C resulted from the increasing production (with increasing temperature) of radicals, such as methenyl (CH), methylene (CH_2) or methyl (CH_3), that diffuse away from the hot zone and react with hydrogen to form CH_4 (ref. 2). In this same study acetylene (C_2H_2) and ethylene (C_2H_4) were found to form above 1750° C. Other investigators report that C_2H_2 is the major product at 2050° C (ref. 3).

The work reported herein concerns the determination of the graphite weight loss due to the reaction of a graphite surface with flowing hydrogen in the temperature range 1550° to 2260° C. The goal of the investigation was to approximate equilibrium conditions and compare experimental weight losses with those calculated from thermodynamic data. The work was prompted by disagreements noted between some experimental weight-loss measurements made at this laboratory and losses predicted by assuming CH_4 formation only.

Graphite test shapes were spherical to eliminate sharp edges and to provide a uniform hydrogen flow around the test piece. The low hydrogen flow of 0.1 standard cubic foot per minute (0.031 lb/hr, 0.38 ft/sec) was chosen in an effort to achieve equilibrium.

MATERIALS

The test graphite was a moldable, pitch-free, petroleum coke-base graphite. Molded bodies are graphitized at about 2500° C and exhibit isotropic properties. For this study the graphite test shapes were 1.48-inch-diameter spheres with a density of 1.65 grams per cubic centimeter. The as-received spheres were machined, outgassed, and weighed before testing.

Tank hydrogen was purified with a palladium tube purifier. Water content of the purified hydrogen was less than 1 part per million by volume (analyzer detection limit).

APPARATUS

The induction furnace used to heat the graphite spheres is described in reference 4. Figure 1 shows the furnace and the loaded tungsten susceptor detail. The graphite sphere was supported on a tripod stand constructed of 1/8-inch tantalum rod positioned within a $1\frac{3}{4}$-inch-diameter, 0.050-inch-wall tungsten susceptor $3\frac{1}{2}$ inches long. The susceptor had a 5/8-inch hole both in its base and in its removable lid for hydrogen gas exit and entrance.

Temperature was determined with a disappearing filament optical pyrometer, which, along with the furnace sighting prism, had been calibrated against a National Bureau of Standards certified standard lamp. Curves of induction-coil voltage setting against temperature were plotted for sighting on a tungsten button at the bottom of the susceptor and for sighting on the top of a graphite sphere in the test position, which was 1/2-inch below the susceptor lid. These determinations were made under hydrogen test flow conditions and provided a relation between tungsten button temperature and graphite sphere temperature for the same coil voltage settings. The tungsten button within the susceptor was under approximately blackbody conditions, and the test temperatures reported were determined from the measured ball temperature and the established relation between ball temperature and tungsten button temperature (true temperature). The reported temperatures are believed accurate within ±25° C.

Hydrogen flow into the induction furnace was measured with a flowmeter, which was calibrated for the flow range 0.02 to 0.20 standard cubic foot per minute at 770 millimeters of mercury (1.01 atm) and 22° C. The graphite-sphere - susceptor geometry resulted in a minimum annular cross-sectional area for hydrogen gas flow of 4.37×10^{-3} square foot. For a test flow of 0.1 standard

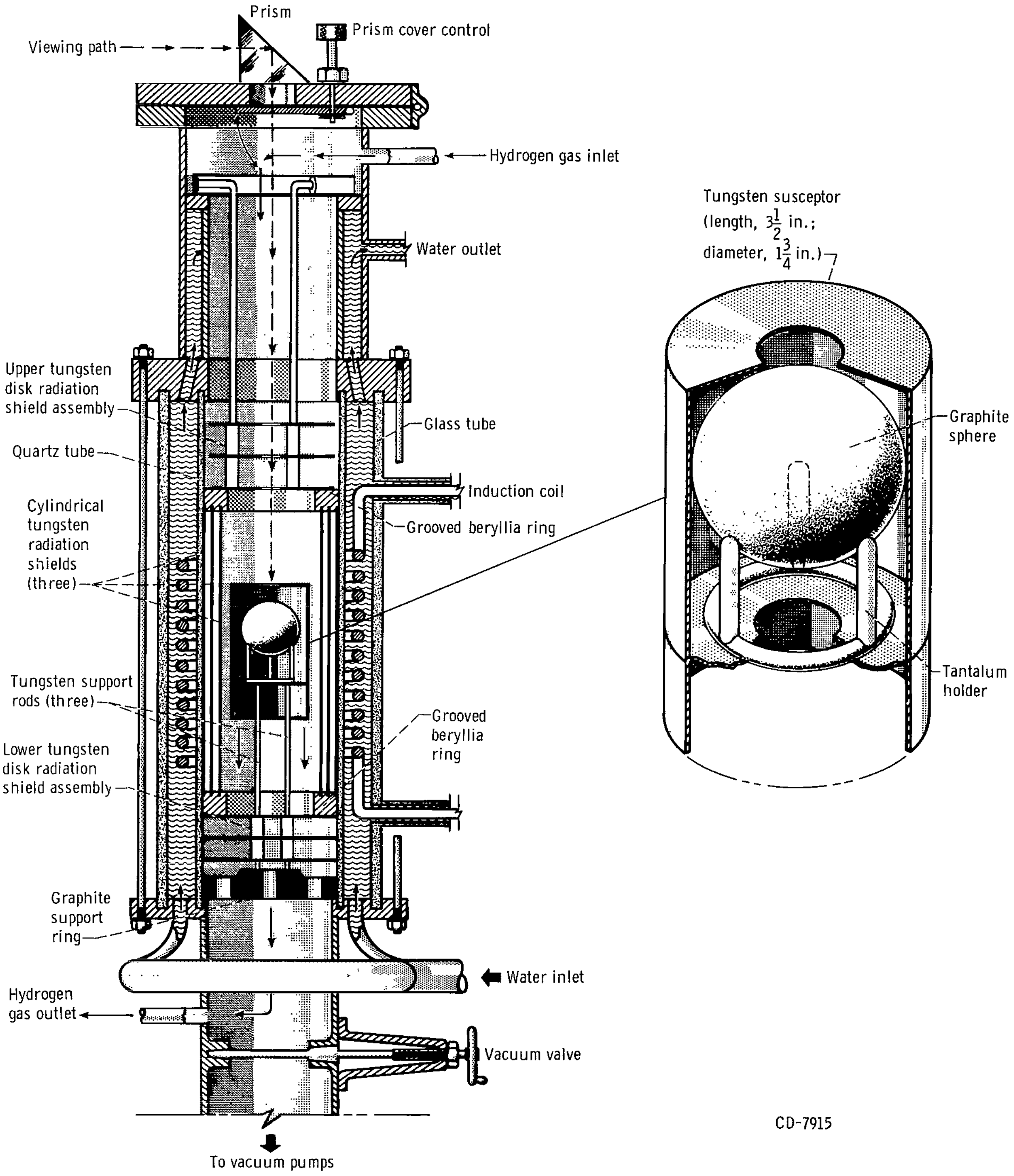

Figure 1. - Schematic view of induction furnace.

cubic foot per minute, the maximum hydrogen flow velocity is then 0.38 foot per second. The hydrogen flow could be read directly to 0.005 standard cubic foot per minute and estimated to 0.001 standard cubic foot per minute.

EXPERIMENTAL PROCEDURE

The graphite spheres were first machined to remove molding bands and then outgassed in vacuum at 2320° C for 1 hour. They were then weighed and stored in a vacuum desiccator. Weighing was done with a direct-reading analytical balance having a precision of ±0.05 milligram. To perform a test, a weighed sphere was loaded into the induction furnace, which was then evacuated to about 5×10^{-6} millimeter of mercury, and blanked off. High-purity helium was bled into the furnace to a static pressure of 550 millimeters of mercury, and heating was begun. An inert gas blanket was used while heating in order to suppress graphite evaporation. Helium, having a heat conductivity close to that of hydrogen, was chosen to minimize the power correction necessary to maintain the desired test temperature once the hydrogen flow was started. The heating time to test temperature varied from 22 to 36 minutes, depending on the temperature. When the test temperature was reached, hydrogen flow was started at the rate of 0.10 standard cubic foot per minute, and power was adjusted so that in 4 minutes the desired constant temperature was attained. The test period of 1 hour began at this point. The furnace pressure remained constant at the slightly positive pressure of 770 millimeters of mercury (1.01 atm).

At the conclusion of the 1-hour test period, the hydrogen flow was stopped, the power was shut off, and the furnace was evacuated and then filled with helium. When the furnace had cooled, the graphite sphere was removed and weighed. Weight loss was determined from the weights before and after the test and compared with the losses predicted by calculations based on thermodynamic data.

DISCUSSION OF RESULTS

The results of the weight-loss study are presented in figure 2. The weight-loss data were plotted on a log scale against the reciprocal of the absolute temperature. A straight line determined by the least-squares method was found to fit the data points well. Thermodynamic property data for 1-atmosphere equilibrium compositions in the hydrogen-graphite system (ref. 5) were used to calculate the theoretical graphite weight losses for CH_4 formation and also for the formation of other hydrocarbons. The equilibrium constants for several hydrocarbons and the computed amounts of graphite consumed as a result of the formation of each hydrocarbon for the temperatures 1527° C (1800° K) and 2327° C (2600° K) are presented in table I. The computations were for the following test conditions: hydrogen flow, 0.1 standard cubic foot per minute; hydrogen pressure, 1 atmosphere; graphite sphere area, 44.6 square centimeters. It can be seen that the contributions to graphite consumption by hydrocarbons other than CH_4 and C_2H_2 are negligible at 1527° C (1800° K), while at 2327° C (2600° K) only C_2H_2 is a significant contributor to graphite loss. A sample calculation is presented in the appendix. The relations between calculated graphite weight loss rate and reciprocal temperature for CH_4 formation, for C_2H_2 formation, and for both CH_4 and C_2H_2 formation combined are also plotted in

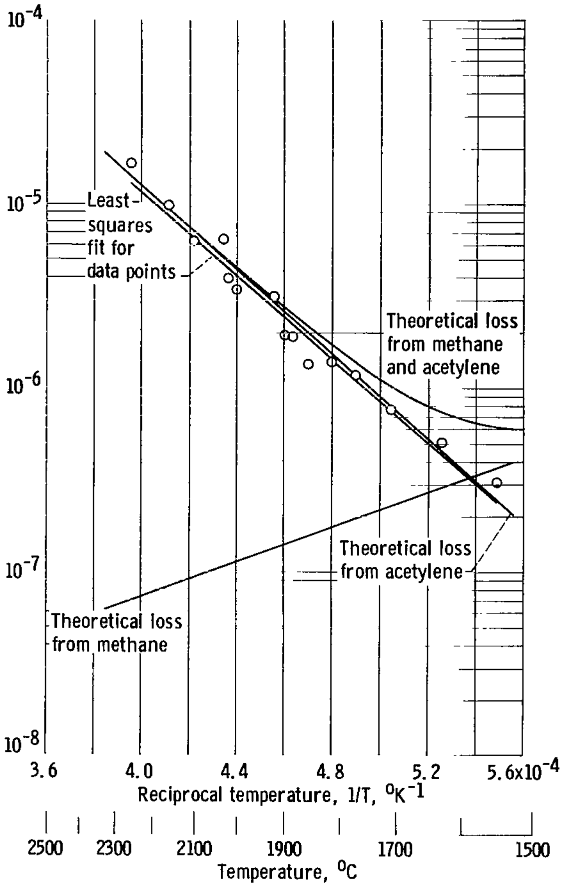

Figure 2. - Graphite weight-loss rate as function of reciprocal temperature. Atmosphere, flowing hydrogen; flow rate, 0.1 standard cubic foot per minute (0.031 lb/hr); flow velocity, 0.38 foot per second.

figure 2 for comparison with the experimental data. No plots for the other hydrocarbons are included since their contributions to graphite loss are not significant.

Comparison of the experimental and theoretical curves of figure 2 indicates that the experimental curve compares very well above 1800° C with the calculated summation curve for CH_4 and C_2H_2 formation. Formation of C_2H_2, the major reaction product above 1800° C, accounts for 10 times as much graphite loss as does CH_4 formation at 1800° C and 200 times as much at 2260° C. Because of the good overall agreement between the experimental curve and the theoretical curve for graphite weight loss due to C_2H_2 formation, it might be concluded that C_2H_2 formation is the principal reaction over the entire range of test temperatures. Such a conclusion would be highly questionable, however, since it precludes the formation of any CH_4 in a temperature region where significant quantities of CH_4 are reported to form. The achievement of equilibrium at temperatures below 1800° C might be possible if a slower flow rate were employed.

TABLE I. - EQUILIBRIUM CONSTANTS FOR VARIOUS HYDROCARBONS AND COMPUTED AMOUNTS OF CARBON CONSUMED BY FORMATION OF EACH

Hydrocarbon	Temperature			
	1527° C (1800° K)		2327° C (2600° K)	
	Equilibrium constant, K	Carbon consumed, (g/sq cm)/sec	Equilibrium constant, K	Carbon consumed, (g/sq cm)/sec
Methane (CH_4)	7.54×10^{-4}	3.98×10^{-7}	1.19×10^{-4}	6.26×10^{-8}
Acetylene (C_2H_2)	1.98×10^{-4}	2.09×10^{-7}	1.81×10^{-2}	1.91×10^{-5}
Ethylene (C_2H_4)	4.78×10^{-6}	5.03×10^{-9}	9.91×10^{-6}	1.04×10^{-8}
Methyl radical (CH_3)	9.47×10^{-6}	5.00×10^{-9}	1.30×10^{-4}	6.85×10^{-8}
Methylene radical (CH_2)	3.50×10^{-7}	1.85×10^{-10}	1.06×10^{-4}	5.59×10^{-8}
Methenyl radical (CH)	3.67×10^{-12}	1.93×10^{-15}	7.08×10^{-7}	3.73×10^{-10}

CONCLUSIONS

An investigation was conducted concerning the reaction of graphite and hydrogen in the temperature range 1550° to 2260° C. In this temperature range the reaction had not been well defined. The experimental data agree very well with theoretical calculations based on thermodynamic data for temperatures above 1800° C, which indicates that acetylene is the major reaction product.

Since equilibrium is apparently achieved above 1800° C at the hydrogen flow rate employed (0.1 standard cu ft/min), any lesser flow would also be expected to yield equilibrium conditions in the apparatus employed and would permit the attainment of equilibrium below 1800° C.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, January 12, 1965.

APPENDIX - SAMPLE CALCULATION OF THEORETICAL GRAPHITE LOSS CALCULATED FROM THERMODYNAMIC PROPERTY DATA FOR 1-ATMOSPHERE EQUILIBRIUM COMPOSITIONS IN HYDROGEN-GRAPHITE SYSTEM

The theoretical equilibrium constants for CH_4 and for C_2H_2 for the temperature range 1527° to 2327° C (1800° to 2600° K) given in reference 5 were used to determine the quantity of CH_4 or C_2H_2 formed.

For methane

$$\left.\begin{aligned} C(s) + 2H_2(g) &\rightarrow CH_4(g) \\ K_{CH_4} &= \frac{p_{CH_4}}{\left(p_{H_2}\right)^2} \end{aligned}\right\} \tag{1}$$

For acetylene

$$\left.\begin{aligned} 2C(s) + H_2(g) &\rightarrow C_2H_2(g) \\ K_{C_2H_2} &= \frac{p_{C_2H_2}}{p_{H_2}} \end{aligned}\right\} \tag{2}$$

where

K equilibrium constant

p partial pressure

H_2 molecular hydrogen

At 1 atmosphere of hydrogen pressure, equations (1) and (2) become

$$p_{CH_4} = K_{CH_4} \tag{3}$$

$$p_{C_2H_2} = K_{C_2H_2} \tag{4}$$

From the equilibrium data of reference 5 for 1827° C (2100° K)

$$K_{CH_4} = 3.17\times10^{-4} = p_{CH_4}$$

$$K_{C_2H_2} = 1.63\times10^{-3} = p_{C_2H_2}$$

For a 1-atmosphere hydrogen pressure at a hydrogen flow rate of 0.00196 gram-mole per second (0.1 standard cu ft/min), the quantity of hydrocarbon formed is

For methane

$$CH_4 = \frac{p_{CH_4}}{p_{H_2}} \times 0.00196 = \frac{3.17\times10^{-4}}{1} \times 0.00196 = 6.21\times10^{-7} \text{ moles/sec}$$

For acetylene

$$C_2H_2 = \frac{p_{C_2H_2}}{p_{H_2}} \times 0.00196 = \frac{1.63\times10^{-3}}{1} \times 0.00196 = 3.19\times10^{-6} \text{ moles/sec}$$

The moles of hydrocarbon formed per second are then converted to grams of carbon lost per square centimeter per second by assuming a graphite surface area of 44.6 square centimeters (the surface area of a graphite test sphere):

$$\text{C loss for } CH_4 = \frac{6.21\times10^{-7}(\text{moles/sec})CH_4}{44.6 \text{ sq cm}} \; \frac{12 \text{ g C}}{\text{mole } CH_4} = 1.67\times10^{-7}(\text{g/sq cm})/\text{sec}$$

$$\text{C loss for } C_2H_2 = \frac{3.10\times10^{-6}(\text{moles/sec})C_2H_2}{44.6 \text{ sq cm}} \; \frac{24 \text{ g C}}{\text{mole } C_2H_2} = 1.72\times10^{-6}(\text{g/sq cm})/\text{sec}$$

$$\text{C loss for } CH_4 + C_2H_2 = 0.17\times10^{-6} + 1.72\times10^{-6} = 1.89\times10^{-6}(\text{g/sq cm})/\text{sec}$$

These computed equilibrium losses are plotted against the reciprocal of 2100° K, 4.76×10^{-4} in figure 2.

REFERENCES

1. Nightingale, R. E., ed.: Nuclear Graphite. Academic Press, Inc., 1962, p. 422.

2. Szabo, Zoltan: Examination of a System Carbon and Hydrogen in the Temperature Range 1100-2600° C. J. Am. Chem. Soc., vol. 72, Aug. 1950, pp. 3497-3502.

3. Lowrie, Robert: Reaction of Hydrogen Gas with Carbon. Research on Physical and Chemical Principles Affecting High Temperature Materials for Rocket Nozzles. Semiannual Prog. Rept., Union Carbide Corp., June 30, 1961, p. 27.

4. Sanders, William A.; and Drell, Isadore L.: Compatibility of Molten Uranium Dioxide with Five Refractory Materials. NASA TN D-1442, 1963.

5. McBride, Bonnie J.; Heimel, Sheldon; Ehlers, Janet G.; and Gordon, Sanford: Thermodynamic Properties to 6000° K for 210 Substances Involving the First 18 Elements. NASA SP-3001, 1963.

NASA-Langley, 1965 E-2770

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