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THE SUSPENDED SPECIMEN METHOD FOR DETERMINING THE RATE OF STEAM-CARBON REACTION

By W. T. Abel and J. H. Holden

UNITED STATES DEPARTMENT OF THE INTERIOR

BUREAU OF MINES

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UNITED STATES DEPARTMENT OF THE INTERIOR
Stewart L. Udall, Secretary

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by

W. T. Abel[2] and J. H. Holden[3]

SUMMARY

The rate of the steam-carbon reaction, which is of fundamental importance to coal gasification, was determined by passing steam over graphite specimens suspended in an electrically heated tube. The measurements were made at 1,900° to 2,400° F. and at steam-feed rates of 0.1 to 2.0 moles of steam per mole of carbon per minute.

At the maximum steam-feed rate, the reaction rate of carbon ranged from 0.4 percent per minute at 1,900° F. to 7 percent per minute at 2,400° F. Up to about 2,200° F., the steam-feed rate had only a slight effect; above this temperature, it limited the reaction velocity when the final mole fraction of steam in the reaction products was much less than 1.

Diluting the steam with an inert gas retarded the reaction rate but not to the same extent as the reaction products did. The order of the overall reaction of graphite with respect to steam ranged from about 0 at 2,000° F. to 0.45 at 2,300° F.

Apparent activation energy at 1,900° to 2,100° F. and 2.0 moles of steam per mole of graphite ranged from 50 kilocalories per gram-mole for 7.9 by 7.9 by 31.7 millimeter specimens to 70 kilocalories for 0.7 by 19 by 28.5 millimeter specimens, comparing with 83 kilocalories previously obtained by another technique for 200- to 230-mesh particles (68-micron diameter) of the same graphite. The activation energy neared a constant maximum as the size of the graphite decreased to 200 to 230-mesh.

INTRODUCTION

The Bureau of Mines is interested in the rate of the steam-carbon reaction because of its fundamental importance in developing processes for gasifying coal with steam to produce synthesis gas. Synthesis gas, mainly carbon

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monoxide and hydrogen, is used as a substitute for natural gas and also for making liquid fuels and chemicals.

The oxidation of carbon by steam, apparently the slowest of the several reactions believed to occur in the gasifier, governs the rate of the overall gasification reaction. Thus, the velocity of the steam-carbon reaction largely determines how long the reactants must be in the gasifier and how large the vessel should be. A review of the voluminous literature on the kinetics of the reaction reveals much contradiction.[4] The reaction has been variously reported as negative, zero, fractional, first or higher order, or indeterminate with respect to steam.[5] [6] Likewise, many different values for the activation energy of the reaction have been reported. Many investigators report a change in slope of the Arrhenius plot at 2,100° to 2,300° F., but opinions differ as to the magnitude and cause.[7] [8] Furthermore, there is disagreement regarding the effect of particle size. Some investigators report little effect, particularly at temperatures below 2,100° F.; others indicate that the effect is pronounced at higher temperatures.

To aid in the design of a gasifier and to improve the economy of gasification and combustion processes, the Bureau has done considerable basic research on the reaction. This report presents the results of an experimental study of the steam-carbon reaction by a suspended-specimen technique.

ACKNOWLEDGMENTS

This investigation was conducted by the Bureau of Mines, Morgantown, W. Va., in cooperation with West Virginia University. Most of the experimental data was obtained by V. E. James in partial fulfillment of requirements for a Ph. D. in chemical engineering. The assistance of his faculty advisor, Prof. W. A. Koehler, West Virginia University, is gratefully acknowledged.

APPARATUS

Figure 1 shows the apparatus used in this study. Figure 2 is a flow diagram of the system. A graphite specimen of predetermined size is suspended in the reactor tube from one arm of an analytical balance. Distilled water is fed through a calibrated flowmeter and vaporized in an electrically heated evaporator (steam generator). The steam is passed through an alloy-steel-tube preheater and into the bottom of the reactor. Helium from a standard cylinder is fed at 10 p.s.i.g. through one of the two flowmeters and into the electrically heated section of the steam line. The flowmeters are arranged in parallel to give a wider range of flow.

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[4] Batchelder, H. R., Busche, R. M., and Armstrong, W. P., Kinetics of Coal Gasification, II, Development of Reaction-Rate Equations: Ind. Eng. Chem., vol. 45, 1953, pp. 1856-1878.

[5] Binford, J. S., Jr., and Eyring, H., Kinetics of the Steam-Carbon Reaction: Jour. Phys. Chem., vol. 60, 1956, p. 486.

[6] Pilcher, J. M., Walker, P. L., Jr., and Wright, C. C., Kinetics of Steam-Carbon Reaction: Ind. Eng. Chem., vol. 47, 1955, p. 1742.

[7] Hunt, B. E., Mori, S., and Katz, S., Reaction of Carbon With Steam at Elevated Temperatures: Ind. Eng. Chem., vol. 45, 1953, pp. 677-680.

[8] Work cited in footnote 6.

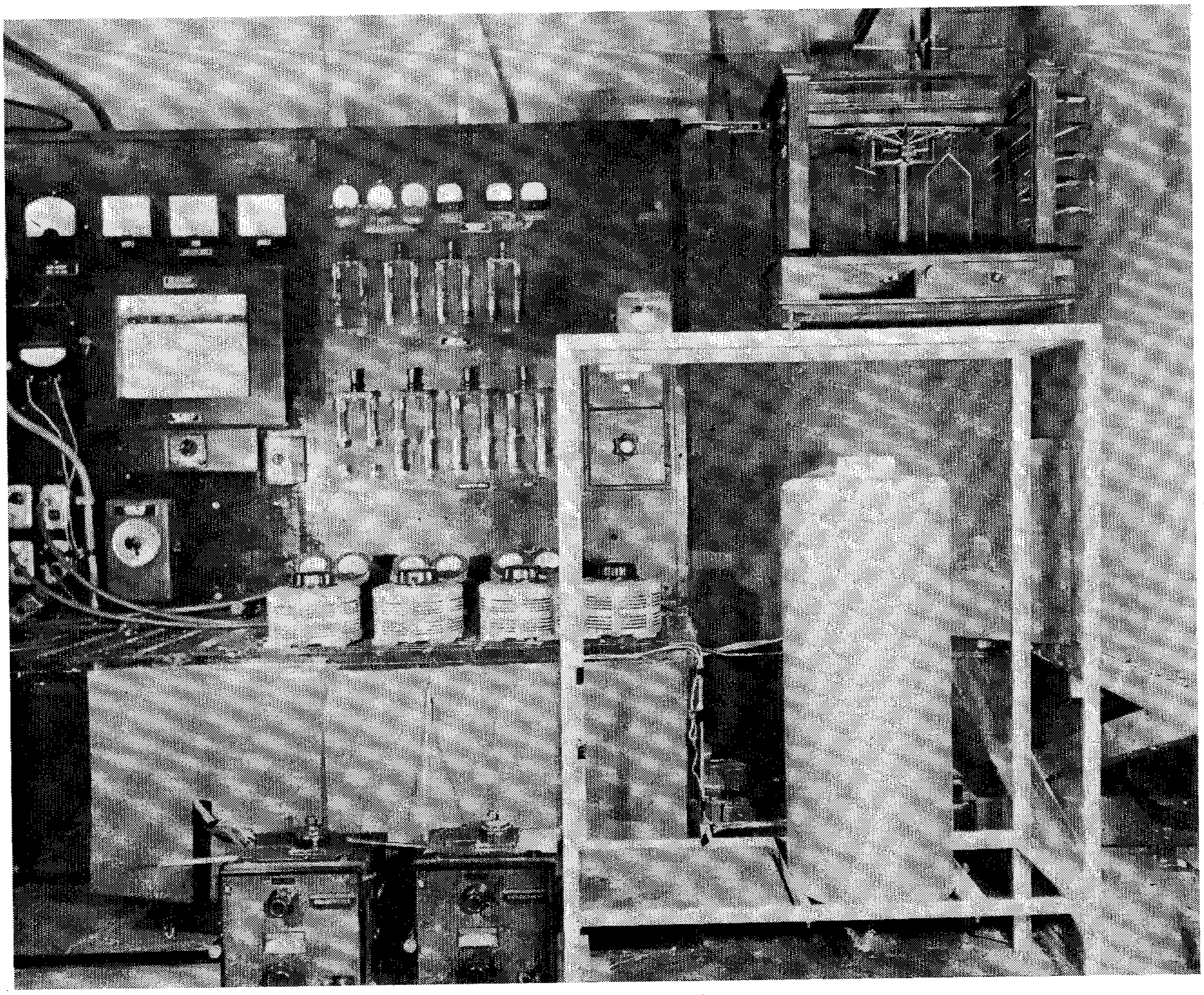

FIGURE 1. - Suspended Specimen Reactor for Investigating the Steam-Graphite Reaction.

Figure 3 shows a cross section of the reactor. The reaction chamber is a 3.3-centimeter-inside-diameter, 61 centimeters long, mullite tube, heated electrically by two separate coils of platinum wire. The tube, insulated throughout its length with 1 centimeter of alumina bubbles and 11.4 centimeters of insulating brick, is encased in a steel shell 3 millimeters thick. There are two platinum, platinum-10-percent rhodium thermocouples in the reaction zone. One thermocouple extends 23 centimeters from the top of the tube; the other extends 30 centimeters to approximately the center of the tube. The bottom 20 centimeters of the chamber is packed with 6- by 25-millimeter fragments of mullite that preheat the steam to the reaction temperature. Reactant steam is introduced through a 3-millimeter-inside-diameter mullite tube that extends through the bottom of the reactor.

Figure 4 is a diagram of the wiring and temperature-control system for the reactor. The heating sections are controlled with powerstats and relay

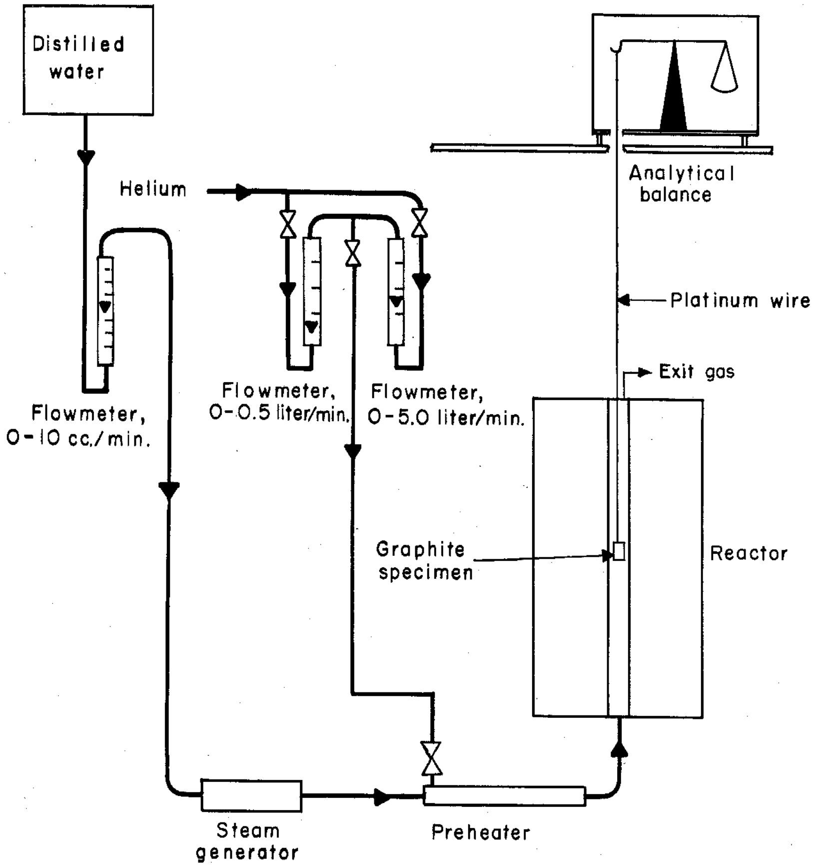

FIGURE 2. - Diagram of Equipment Used to Study the Kinetics of the Steam-Graphite Reaction by the Suspended Specimen Method.

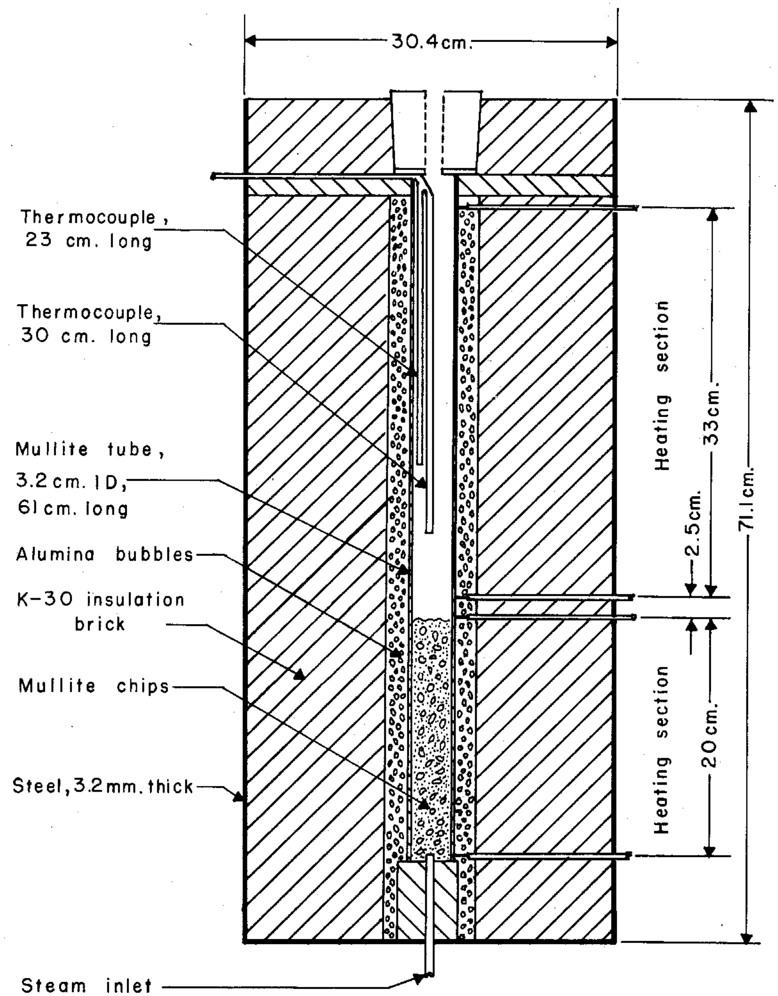

FIGURE 3. - Cross Section of Reactor.

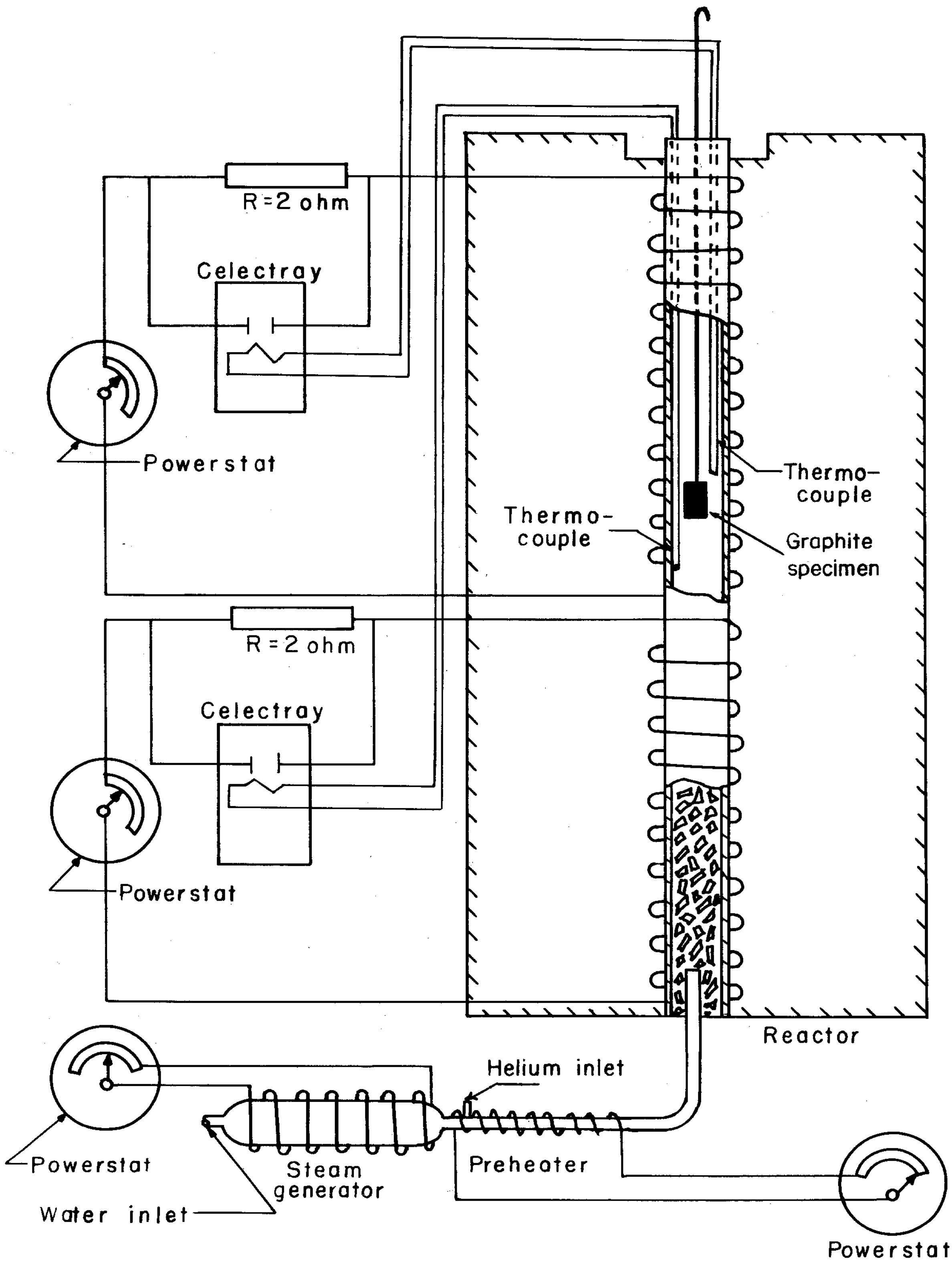

FIGURE 4. - Wiring Diagram and Temperature-Control System for Reactor.

devices. The powerstats are manually adjusted until the thermocouples indicate that the temperature is within the desired range. Final control of temperature is maintained by means of Celectray[9] controllers that relay resistance in or out of the circuit, as required.

REACTANTS

Graphite for these experiments was cut from a 25-centimeter-diameter rod of a thermic type electrode. The graphite is manufactured as follows: Petroleum coke is calcined at 2,460° F. in the absence of air, ground to flour size, and blended with a refined coal-tar pitch binder. The electrodes formed from this material are baked at 1,380° F. and graphitized in an electric-arc furnace at 5,160° F. The petroleum coke matrix forms broad, flat, hexagonal rhombohedral crystals; the graphite crystallites from the pitch binder are smaller and shorter.

Two different types of samples were used; the size and shape depended upon the relationships under investigation. Some of the samples were 3.000-gram rectangular prisms 7.9 by 7.9 by 31.7 millimeters long. Others were thin sections, 0.7 by 19.1 by 28.5 millimeters long, weighing 0.620 grams. Each sample was cut parallel to the extrusion axis of the graphite electrode.

Steam or a steam-helium mixture was the reactant gas. Steam was generated from doubly distilled water. The helium was high-purity grade A and contained 0.0028 volume-percent oxygen.

EXPERIMENTAL METHODS

A graphite sample is suspended in the reaction zone of the reactor from one arm of an analytical balance, and the time required to react a given amount is measured. The sample is first balanced in air, and when the gas flow and temperature are established at the desired levels, the sample is lowered into the reaction zone and an electric timer is started. A predetermined weight, for example 100 milligrams, is removed from the balance pan, and the time is recorded when the system balances again. The procedure is repeated until enough readings are obtained to graph burnoff (cumulative weight loss) as a function of time. Figure 5 is a typical curve. The slope of the curve is the reaction rate.

Steam flow is measured as cubic centimeters of water per minute fed to the vaporizer, and helium is measured in liters per minute. When the steam-helium mixture was used, the flow rates of each were controlled to provide a constant flow of 0.556 gram-mole of mixture per minute.

The influence of steam-flow rate on the rate of the reaction at 1,900° to 2,400° F. was determined with 3.000-g. samples and steam rates corresponding to 0.5 to 10.0 cubic centimeters of water per minute. In the typical curve (fig. 5), the reaction rate is virtually constant within 10 to 25 percent

[9]Reference to specific makes or models of equipment is made to facilitate understanding and does not imply endorsement of such brands by the Bureau of Mines.

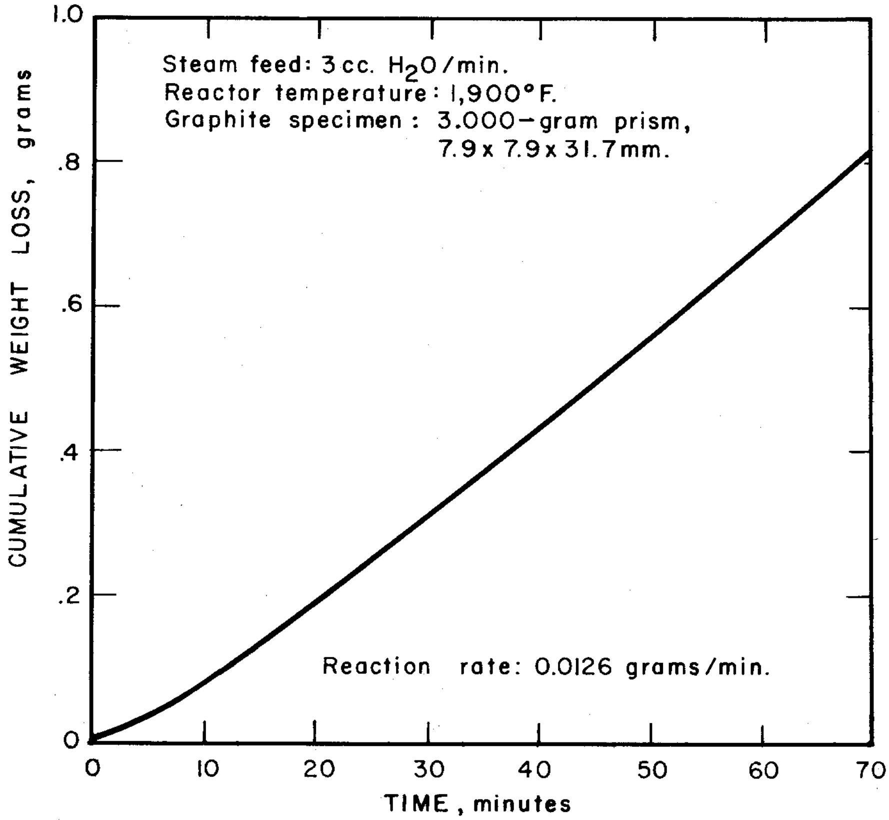

FIGURE 5. - Typical Curve of Graphite Conversion as a Function of Reaction Time.

of the carbon reacted; therefore, the experimentally measured rates were determined within this range.

Results and Discussion--Theoretical Considerations

The overall steam-graphite reaction can be expressed by two stoichiometric equations:

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

(gasification reaction);

$$CO + H_2O \rightleftarrows CO_2 + H_2$$

(shift reaction).

The shift reaction represents the interaction between CO, H_2O, CO_2, and H_2. The interactions are known to be heterogeneous in the presence of carbon, and the overall rate of the shift reaction is known to be faster than the rate of reaction of CO_2 or steam with carbon. In relating the rate of consumption of steam to the rate of consumption of carbon, thermodynamic equilibrium may reasonably be assumed to exist between the gases. When this existence is assumed, the moles of water reacted can be calculated from the experimental values of the graphite reacted and from the equilibrium constant for the shift reaction. The equations for this calculation are given in appendix B. The rate at which the steam flows past the sample and the concentration of steam in the gas can then be related to the reaction rate.

Effect of Steam-Flow Rate on the Reaction Rate

In figure 6, the reaction velocity is shown as a function of the inlet steam-flow rate. Figure 7 shows the reciprocal of the reaction rate as a function of the reciprocal of the inlet steam rate. Because the reciprocal plot is linear, the reaction rate may be expressed as a function of steam rate according to the equation:

$$r = as/(1 + bs),$$

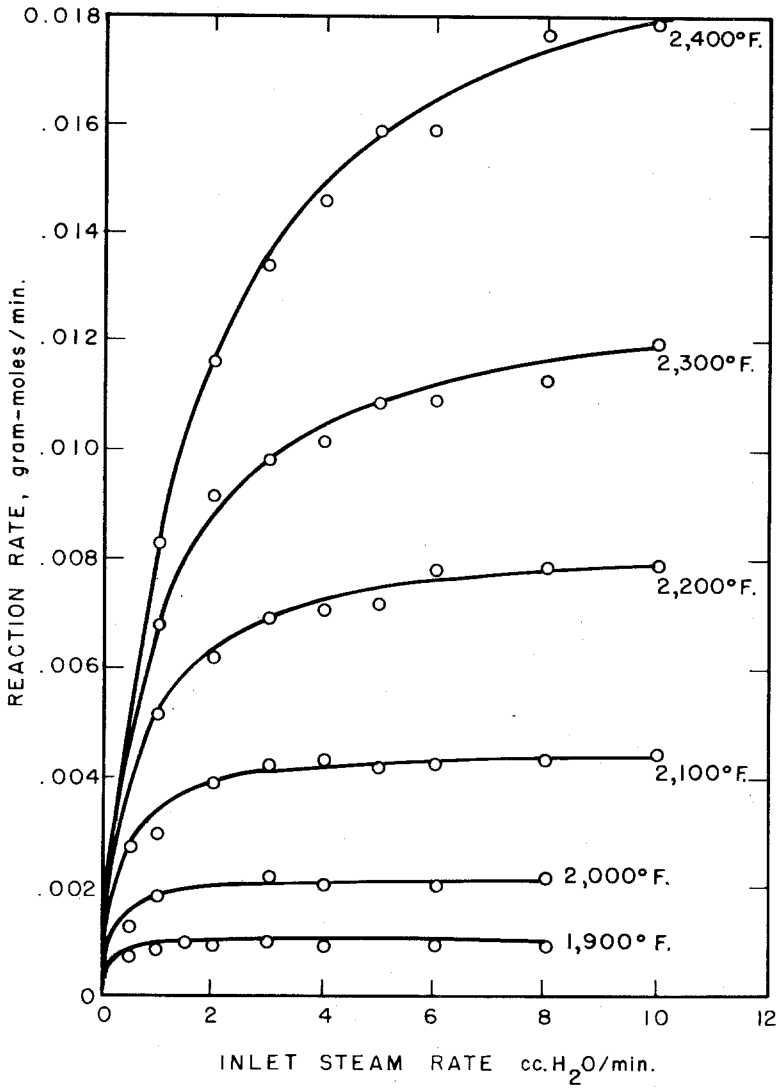

FIGURE 6. - Effect of Steam-Feed Rate on the Velocity of the Steam-Graphite Reaction at 1,900° to 2,400° F.

where r is the reaction rate, s is the steam rate, and a and b are constants determined from the data by a least squares procedure.[10] The slope of the curve plotted from this function is $\frac{a}{(1 + bs)^2}$. At zero steam rate, s equals zero, and the slope equals a and is independent of the temperature. Consequently, a is the same at any temperature in the range considered. The asymptote of the reaction rate curve is a/b, which is the reaction rate at which the steam rate has no further influence or the true chemical reaction rate at the temperature under consideration. The curves (figs. 6 and 7) were determined from the constants thus found. As reaction temperature increases (fig. 6), higher steam rates are required before the reaction rate curve approaches its asymptote.

Further treatment of these data, with the reaction products taken into consideration, helps to explain the behavior of the reaction at different temperatures. Summarized results, including calculated values of the percent of reaction products shifted and the final mole fraction of steam, are given in table A-1. Up to 2,100° F. the final steam concentration remains high for all steam-feed rates (fig. 8, table A-1), approaching a mole fraction of 1. The net reaction under these conditions is essentially the sum of the gasification and shift reactions (100 percent shift). In contrast, above 2,100° F. the final steam concentrations at the feed rates of this experiment are appreciably lower because the steam is diluted by reaction products, and the net reaction yields an appreciable amount of CO. Thus, at the higher temperatures

[10]Turner, M. E., Monroe, R. J., and Lucas, H. L., Jr., Generalized Asymptotic Regression and Non-Linear Path Analysis: Biometrics, vol. 17, No. 1, 1961, pp. 120-143.

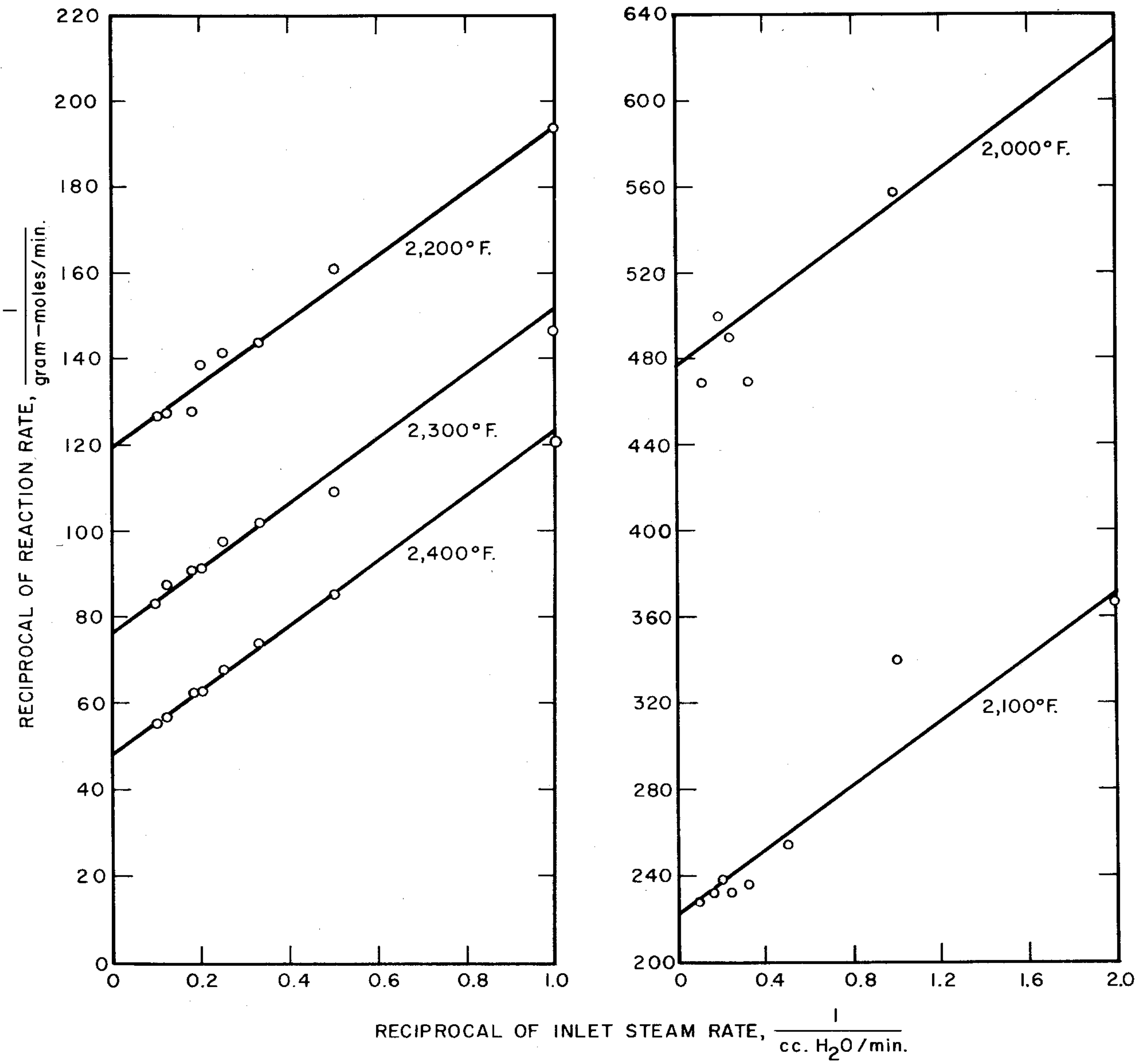

FIGURE 7. - Reciprocal of Reaction Rate Plotted Against Reciprocal of Inlet Steam Rate.

the rate curves cover a much wider range in final steam concentration, permitting a continued response to increase in steam feed. When reaction rate is plotted against final steam concentration (fig. 8), a straight line results. When the rate curves are extrapolated to a final steam mole fraction of 1, the reaction rate corresponding to infinite steam flow is obtained. The reaction rates obtained in this way compare quite well with the corresponding values from the curves of figure 7, as is shown in table 1.

Steam concentration and steam velocity varied simultaneously in these runs; hence, the separate effects of each cannot be evaluated. The dashed curves of figure 8 are lines of constant steam flow. The apparent change in slope of these lines at approximately 2,100° F. demonstrates the same trend shown in figure 6. Because the separate effects of steam concentration and steam velocity were not determined, calculating the order of the reaction with respect to steam or calculating other values that depend individually on steam concentration or velocity would be misleading.

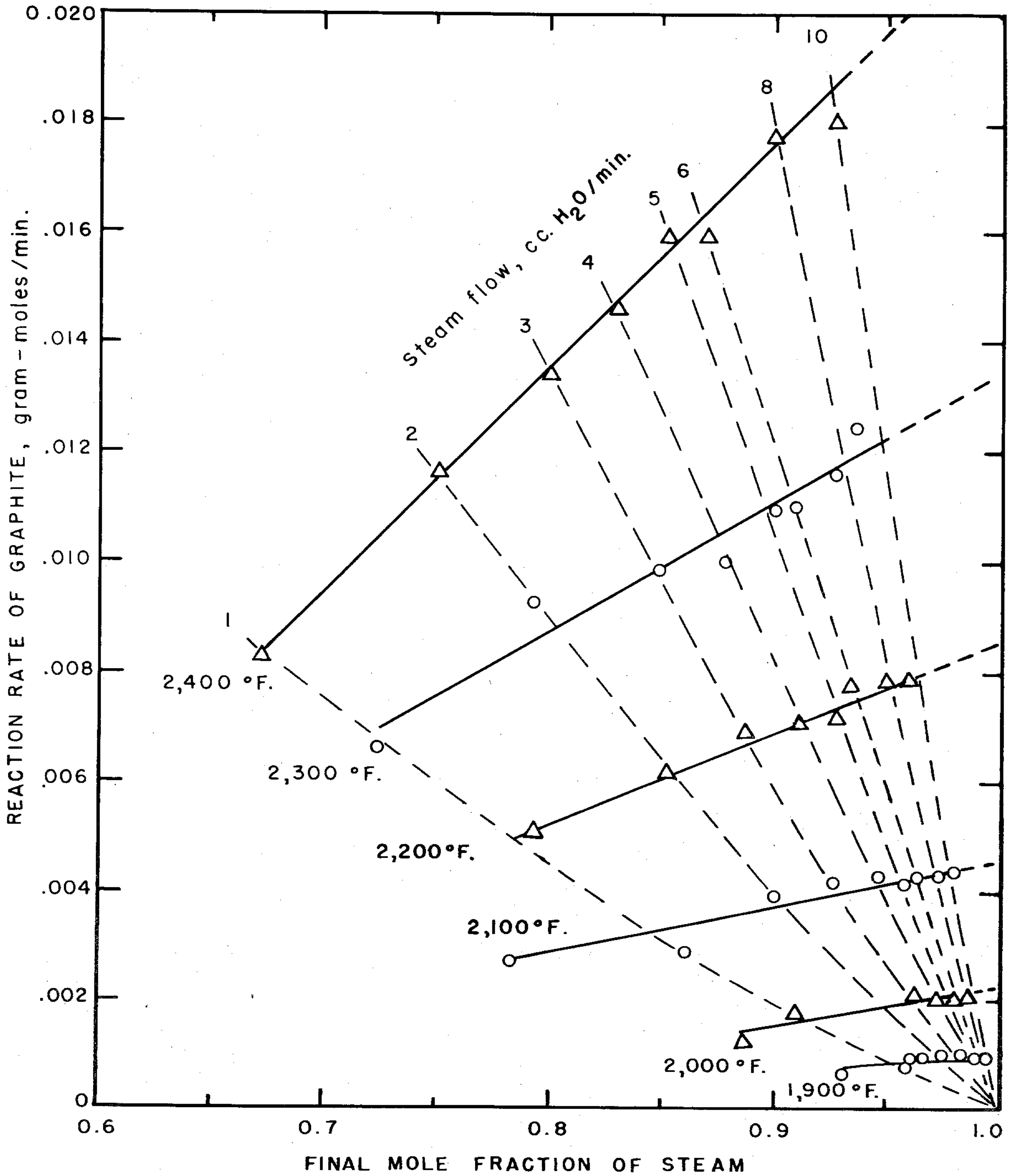

FIGURE 8. - Effect of Concentration of Steam on the Rate of the Steam-Graphite Reaction at Various Temperatures and Steam Flows.

TABLE 1. - Reaction rates at infinite steam-feed rate

Temperature, ° F.	Reaction rate--	
	From reciprocal plot[1]	From extrapolation to final steam mole fraction of 1[2]
1,900[3]	0.00095	0.0010
2,000	.0021	.0023
2,100	.0045	.0046
2,200	.0084	.0086
2,300	.0131	.0130
2,400[4]	.0207	.0217

[1]Figure 7.
[2]Figure 8.
[3]Data for 1,900° F. is off scale in figure 7.
[4]Data for 2,400° F. is off scale in figure 8.

Figures 9 and 10 show Arrhenius plots of the data of table A-2. The curve with the triangle data points (fig. 9) is based on reaction rates at the maximum steam feed of 0.556 gram-mole per minute. The upper curve, marked by circles, is based on rates obtained by extrapolation of the rate curves in figure 8 to final steam mole fractions of 1. The upper curve more closely approaches a straight line. The curve without data points shows the data of Mayers,[11] and demonstrates that the experimental procedure used in this investigation gives results that are in close agreement with those obtained by other methods. The same data are replotted (fig. 10) with reaction temperatures corrected for the heat required by the endothermic steam-graphite reaction. The upper curve, based on extrapolated rates, is nearly a straight line over the entire temperature range.

The fact that the apparent change in slope of the Arrhenius plot between 2,100° and 2,200° F. was nearly removed by (1) correcting the reaction temperatures for the heat required by the endothermic reaction and (2) using extrapolated rates suggests that product gas films do not retard the reaction when enough steam is supplied at a high enough velocity. When the concentration or velocity of the steam is not high enough, however, the product gases retard the reaction.

Effect of Concentration of Steam at Constant Velocity on the Reaction Rate

In the foregoing experiments, any change in steam-feed rate was necessarily accompanied by a corresponding change in steam velocity, and the separate effect of steam concentration could not be evaluated. Accordingly, experiments were conducted in which the rate of reaction of identical graphite specimens was determined in constant velocity steam-helium mixtures containing different concentrations of steam. The flow rate was fixed at 0.556 gram-moles per minute. A summary of these data, including calculated values of the final mole

[11]Mayers, M. A., The Rate of Oxidation of Graphite by Steam: Jour. Am. Chem. Soc., vol. 56, No. 9, Sept. 8, 1934, pp. 1879-1881.

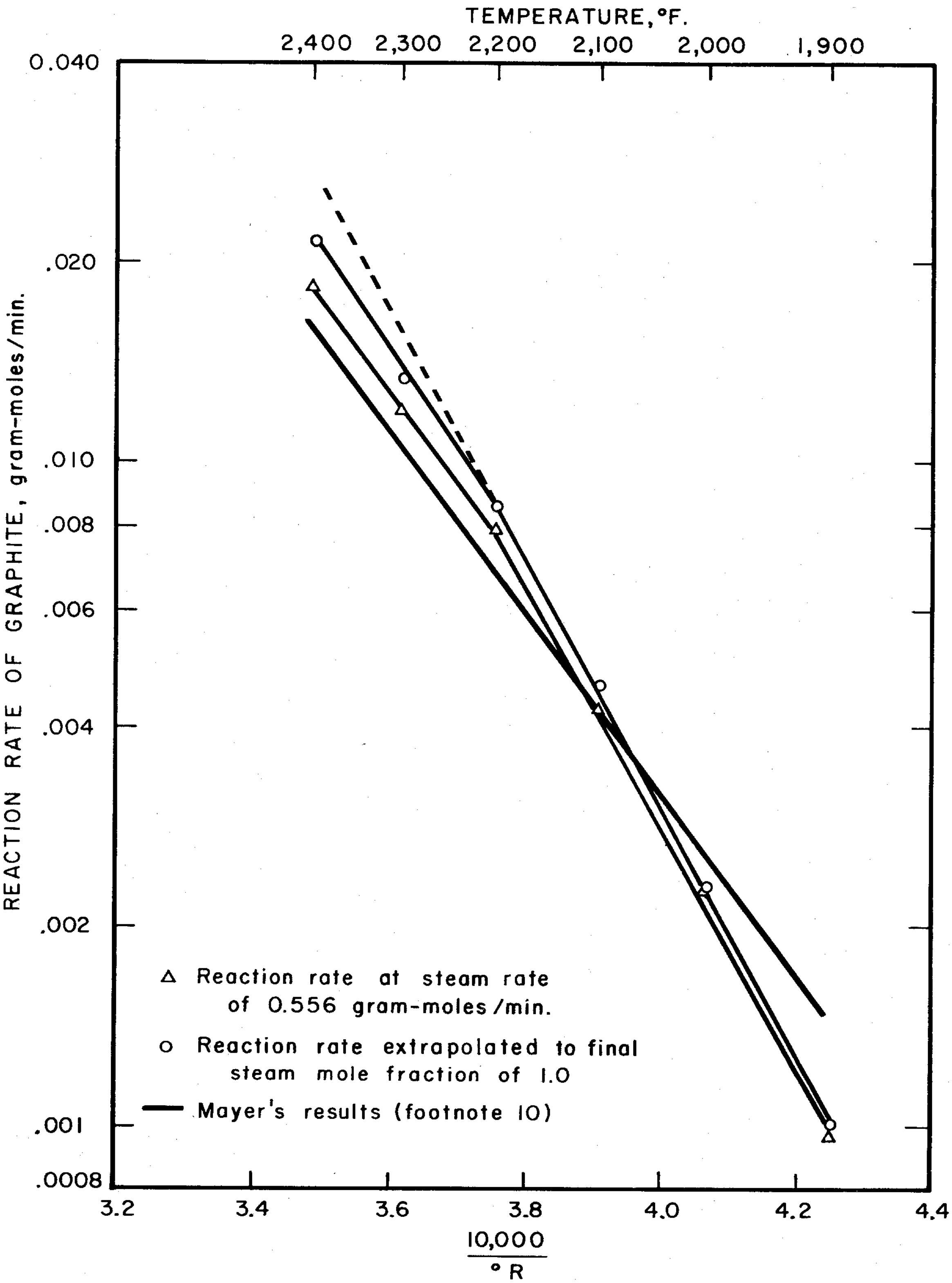

FIGURE 9. - Arrhenius Plot Over Entire Temperature Range, Temperature Not Corrected for Heat Required by Reaction.

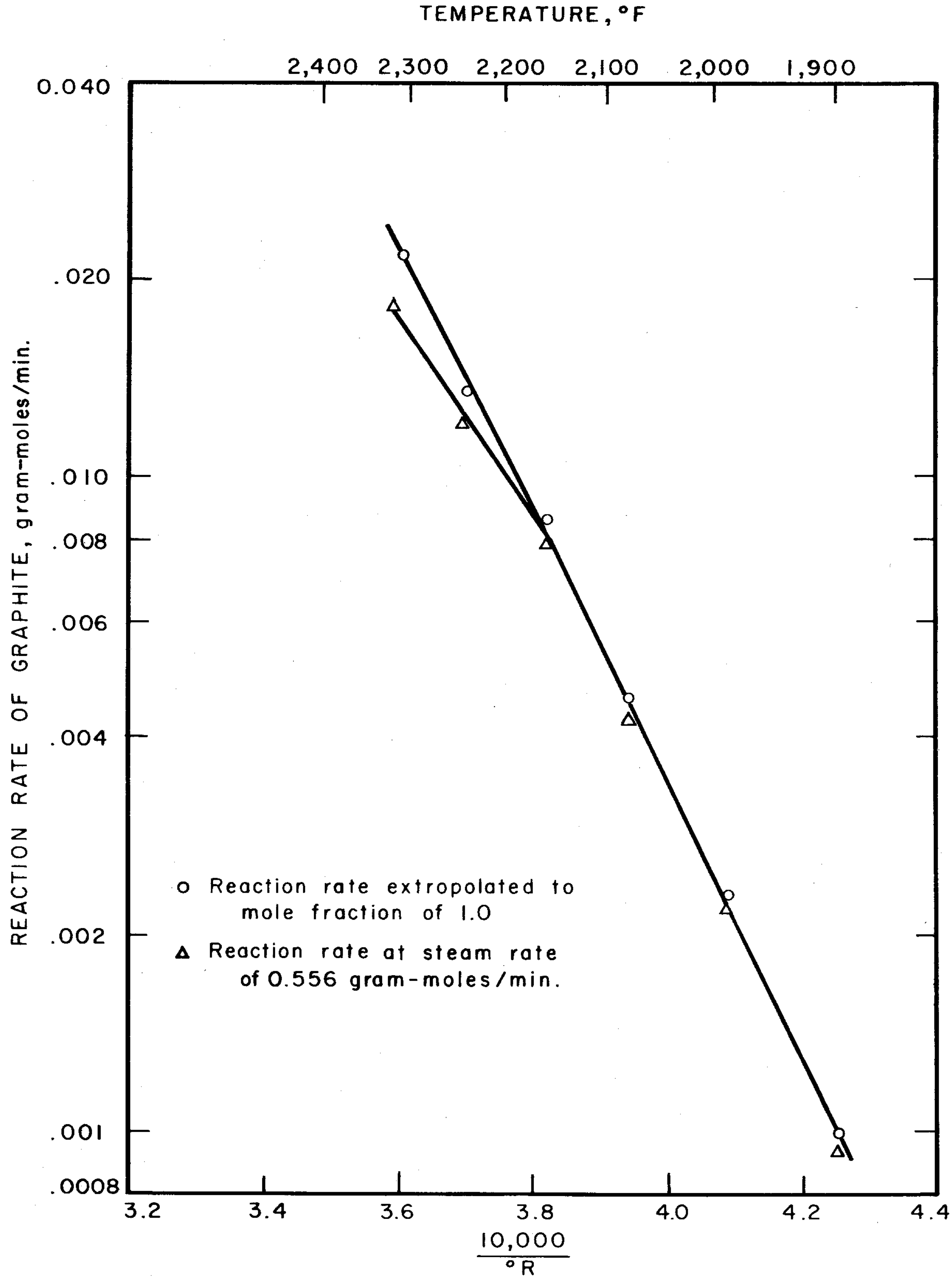

FIGURE 10. - Arrhenius Plot Over Entire Temperature Range, Temperature Corrected for Heat Required by Reaction.

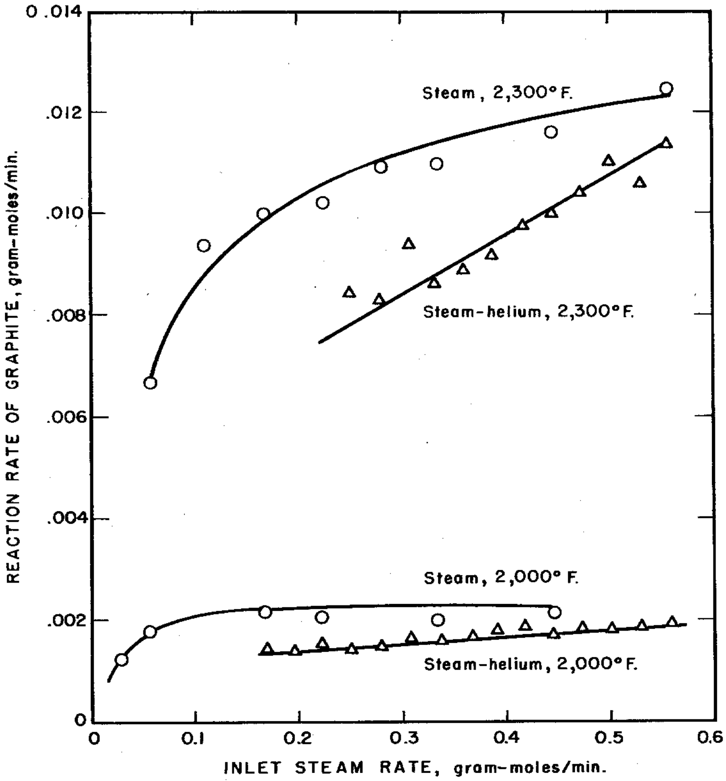

FIGURE 11. - Reaction Rate as a Function of Steam-Feed Rate at Different Inlet Steam Concentrations.

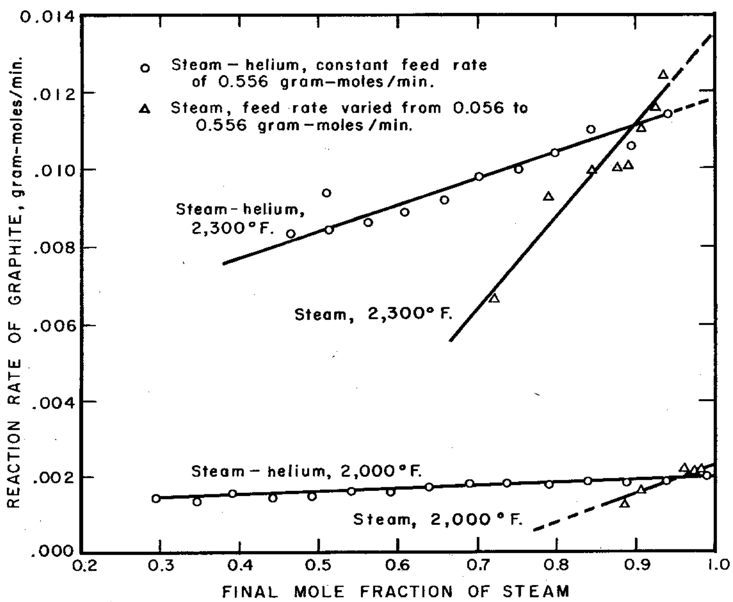

FIGURE 12. - Reaction Rate as a Function of Final Steam Concentration at Constant and Varying Feed Velocities.

fraction of steam and the percentage of carbon gasified that is shifted to CO_2, are given in table A-3 and shown graphically in figures 11 and 12. The corresponding rate curves for undiluted steam (from table A-1) are also shown to facilitate comparison.

Figure 11 shows that helium in the steam feed decreased the reaction rate. Because the thermal conductivity of helium is greater than that of steam, the lower reaction rate might be attributed to the transfer of heat between the helium and the sample. However, radiation rather than convection supplied most of the heat transferred. Consequently, the difference in temperature of the sample in the helium-steam runs and in the undiluted steam runs is not large enough to explain the observed effect.

Figure 12 shows the effect of the helium on the relation between final steam concentration and the reaction rate. In this instance the position of the curves is reversed, with the steam-helium curve lying above the steam curve. Thus, helium dilution decreased the reaction rate; however, dilution by helium did not decrease the reaction rate as much as did the products of the reaction. As shown from the steam-helium curves of figure 12, the order of the reaction with respect to steam increased from essentially zero at 2,000° F. to about 0.45 at 2,300° F.

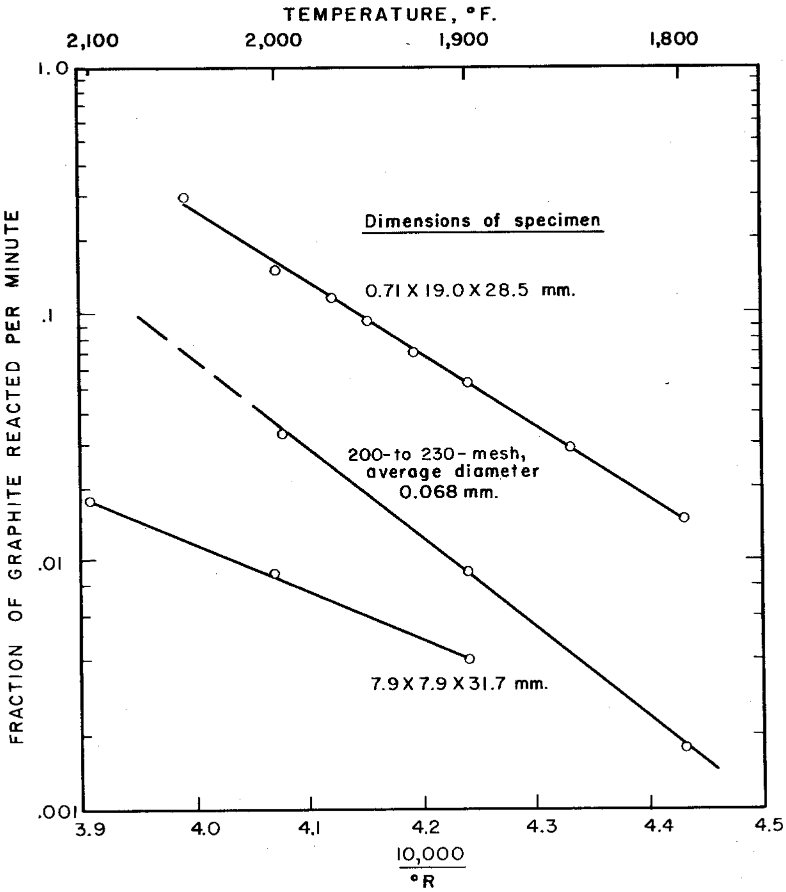

FIGURE 13. - Rate of the Steam-Graphite Reaction as a Function of Specimen Thickness.

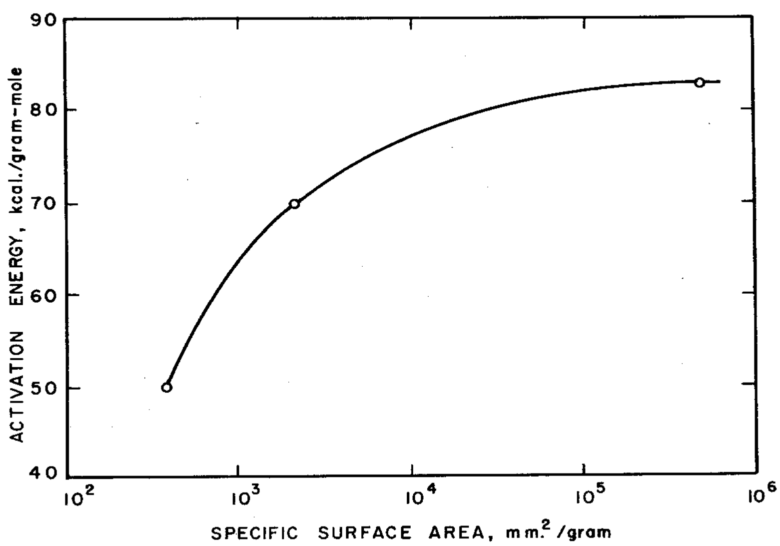

FIGURE 14. - Effect of Surface Area on Activation Energy of the Steam-Graphite Reaction.

Effect of Particle Size on the Reaction Rate

Because change in particle size is known to influence gasification rates, the rate of reaction of steam with graphite was determined with specimens of different thicknesses but of nearly the same geometric surface area.

The tests were made in the temperature range in which the effects of steam velocity, steam concentration, and heat of reaction were negligible at the higher flow rates. The data are presented graphically in Arrhenius plot (fig. 13). The lower curve represents the rates for 7.9- by 7.9- by 31.7 millimeter specimens and was taken from figure 8. The upper curve shows the rates determined with thinner specimens. Both curves were determined at steam-feed rates corresponding to 10 cubic centimeters of water per minute. The center curve shows data obtained by Dotson, Holden, and Koehler[12] for the reaction of steam with 200- to 230-mesh particles of the same graphite. The apparent activation energy ranged from about 50 kilocalories per gram-mole for the thicker graphite prisms to 80 kilocalories for the 200- to 230-mesh particles. Because

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[12] Dotson, J. M., Holden, J. H., and Koehler, W. A., Rate of the Steam-Carbon Reaction by a Falling-Particle Method: Ind. Eng. Chem., vol. 49, No. 1, January 1957, pp. 149-154.

Dotson, Holden, and Koehler used different velocities and concentration of steam, their rates cannot be directly compared with those in this report. However, velocity and concentration variation would not change the energy of activation provided the overall reaction was chemically controlled; hence, a comparison of these values is meaningful.

Figure 14 shows the apparent activation energies as a function of specific area. Because the experimental conditions for this phase of the study were such that further increase in steam velocity and concentration had little effect on the reaction rate for a given specimen, the increase in apparent activation energy with increase in specific surface area indicates that the reaction rate is not entirely chemically controlled. When particle thickness is greater than 0.5 millimeter (corresponding to a specific surface area of 10^4 square millimeters), the diffusional resistance inside the particle influences the rate appreciably.

APPENDIX A. - TABLES OF DATA

TABLE A-1. - Effect of steam flow rate on the rate of the steam-graphite reaction, 3,000-gram, 7.9- by 7.9- by 31.7-millimeter specimen

Run	Temperature, ° F.	Steam flow rate		Shift equilibrium constant	Gasification rate, gram-mole per minute	Gasified graphite shifted to CO_2, percent	Calculated steam consumption, gram-mole per minute	Total gas (CO, CO_2, H_2, H_2O, H_e), gram-mole	Final mole fraction of steam
		Cubic centimeter per minute	Gram-mole per minute						
4..........	1,900	0.5	0.028	0.529	0.00070	91.5	0.00134	0.0287	0.930
1A.........	1,900	1.0	.056	.529	.000815	94.8	.00159	.0568	.958
1B.........	1,900	1.5	.083	.529	.000985	95.2	.00193	.0839	.965
2A, 2B.....	1,900	2.0	.111	.529	.000990	96.7	.00195	.1120	.973
3A, 3B.....	1,900	3.0	.167	.529	.00102	97.7	.00201	.1680	.982
6..........	1,900	4.0	.222	.529	.00091	96.1	.00181	.2229	.961
7..........	1,900	6.0	.333	.529	.00091	98.9	.00181	.3339	.991
8..........	1,900	8.0	.444	.529	.000935	98.3	.00186	.4449	.993
18.........	2,000	.5	.028	.469	.00125	83.8	.00230	.0293	.887
15, 16.....	2,000	1.0	.056	.469	.00179	87.0	.00347	.0578	.910
17.........	2,000	3.0	.167	.469	.00213	94.8	.00415	.1691	.963
12.........	2,000	4.0	.222	.469	.00204	95.8	.00400	.2240	.973
11B........	2,000	6.0	.333	.469	.00200	97.5	.00395	.3350	.982
10.........	2,000	8.0	.444	.469	.00213	97.9	.00422	.4461	.986
25.........	2,100	.5	.028	.422	.00275	67.9	.00462	.0299	.783
24.........	2,100	1.0	.056	.422	.00293	80.0	.00527	.0589	.861
26.........	2,100	2.0	.111	.422	.00393	85.7	.00786	.1149	.897
27.........	2,100	3.0	.167	.422	.00420	88.3	.00795	.1712	.924
21.........	2,100	4.0	.222	.422	.00430	91.6	.00824	.2263	.945
30.........	2,100	5.0	.280	.422	.00418	93.4	.00808	.2842	.957
23.........	2,100	6.0	.333	.422	.00430	94.2	.00835	.3373	.962
28.........	2,100	8.0	.444	.422	.00433	95.6	.00847	.4483	.972
29.........	2,100	10.0	.556	.422	.00440	96.3	.00864	.5604	.977

TABLE A-1. - Effect of steam flow rate on the rate of the steam-graphite reaction, 3,000-gram, 7.9- by 7.9- by 31.7-millimeter specimen (Con.)

Run	Temperature, ° F.	Steam flow rate: Cubic centimeter per minute	Steam flow rate: Gram-mole per minute	Shift equilibrium constant	Gasification rate, gram-mole per minute	Gasified graphite shifted to CO_2, percent	Calculated steam consumption, gram-mole per minute	Total gas (CO, CO_2, H_2, H_2O, H_e), gram-mole	Final mole fraction of steam
49-51.......	2,200	1.0	0.056	0.384	0.00514	69.8	0.00901	0.0607	0.792
46-48.......	2,200	2.0	.111	.384	.00620	77.7	.01100	.1172	.853
43-45.......	2,200	3.0	.167	.384	.00695	82.3	.01267	.1740	.887
36, 40-42...	2,200	4.0	.222	.384	.00705	86.1	.01312	.2291	.911
35, 38, 39..	2,200	5.0	.280	.384	.00720	88.1	.01358	.2872	.928
34, 37.....	2,200	6.0	.333	.384	.00780	89.2	.01476	.3408	.934
33, 78-79...	2,200	8.0	.444	.384	.00785	91.8	.01487	.4517	.950
32, 76-77...	2,200	10.0	.556	.384	.00790	93.1	.01526	.5629	.959
52-54.......	2,300	1.0	.056	.356	.00665	60.0	.01064	.0627	.722
55-57.......	2,300	2.0	.111	.356	.00930	68.4	.01567	.1203	.792
58-60.......	2,300	3.0	.167	.356	.00990	75.4	.01736	.1769	.847
61-63.......	2,300	4.0	.222	.356	.01020	79.8	.01834	.2322	.877
64-66.......	2,300	5.0	.280	.356	.01095	82.4	.02000	.2910	.893
67-69.......	2,300	6.0	.333	.356	.01105	84.5	.02043	.3441	.908
70-72.......	2,300	8.0	.444	.356	.01160	87.3	.02170	.4556	.927
73-75.......	2,300	10.0	.556	.356	.01245	88.9	.02357	.5675	.936
80-82.......	2,400	1.0	.056	.334	.00830	53.0	.01270	.0644	.672
83-85.......	2,400	2.0	.111	.334	.01165	62.1	.01890	.1227	.751
86-88.......	2,400	3.0	.167	.334	.01340	68.1	.02253	.1804	.801
89-91.......	2,400	4.0	.222	.334	.01460	72.3	.02517	.2366	.832
99-101......	2,400	5.0	.280	.334	.01590	75.1	.02775	.2959	.852
96-98.......	2,400	6.0	.333	.334	.01590	78.2	.02835	.3489	.873
102-104.....	2,400	8.0	.444	.334	.01770	81.1	.03205	.4617	.892
107-109.....	2,400	10.0	.556	.334	.01795	84.1	.03308	.5630	.927

TABLE A-2. - Data of Arrhenius plots, temperatures adjusted for heat of reaction

Indicated temperature, ° F.	Reaction rate[1] at steam flow rate of 0.556 gram-mole per minute, gram-mole per minute	Specimen temperature adjusted for reaction in steam flow rate of 0.556 gram-mole per minute, ° F.	Reaction rate obtained by extrapolation to final steam mole fraction of 1, gram-mole per minute	Specimen temperature adjusted for reaction at the extrapolated rate, ° F.
1,900	0.0009	1,895	0.0010	1,895
2,000	.0023	1,985	.0023	1,985
2,100	.0042	2,075	.0046	2,075
2,200	.0079	2,160	.0086	2,160
2,300	.0120	2,245	.0130	2,240
2,400	.0183	2,325	.0217	2,315

[1]Values were obtained from graphs. They differ slightly from the experimental data of table 2.

TABLE A-3. - Effect of final steam concentration on the rate of the steam-graphite reaction in constant velocity steam-helium mixtures

Run	Temperature, ° F.	kw rate: Steam, gram-mole per minute	kw rate: Helium, gram-mole per minute	Gasification rate, gram-mole per minute	Calculated steam consumption, gram-mole per minute	Total gas present (CO, CO_2, H_2, H_2O, H_e), gram-mole	Final mole fraction of steam, moles of steam / total moles of gas
16, 122	2,000	0.556	([1])	0.00195	0.00405	0.5570	0.991
21	2,000	.528	0.028	.00185	.00373	.5579	.939
29	2,000	.500	.056	.00180	.00340	.5578	.890
25	2,000	.473	.083	.00183	.00362	.5578	.841
27	2,000	.445	.111	.00171	.00340	.5577	.791
19	2,000	.417	.139	.00184	.00353	.5578	.741
24	2,000	.389	.167	.00179	.00355	.5578	.690
26	2,000	.361	.195	.00168	.00348	.5578	.641
18	2,000	.334	.222	.00159	.00319	.5576	.593
23	2,000	.306	.250	.00165	.00315	.5577	.543
17	2,000	.278	.278	.00149	.00290	.5575	.493
28	2,000	.250	.306	.00142	.00274	.5574	.443
42	2,000	.222	.334	.00155	.00296	.5576	.392
44	2,000	.195	.361	.00139	.00252	.5574	.345
45	2,000	.167	.389	.00146	.00278	.5575	.294
46,147	2,300	.556	([1])	.0114	.0226	.5674	.942
31, 148, 164-166	2,300	.528	.028	.0106	.0202	.5666	.896
32, 149	2,300	.500	.056	.0110	.0209	.5670	.845
33, 150, 167	2,300	.473	.083	.0104	.0196	.5664	.800
34, 151	2,300	.445	.111	.0100	.0190	.5660	.753
35, 152, 168	2,300	.417	.138	.0098	.0184	.5660	.704
36, 153	2,300	.389	.167	.0092	.0173	.5650	.658
37, 154, 169	2,300	.361	.195	.0089	.0168	.5650	.609
38, 155, 161	2,300	.334	.222	.0086	.0161	.5644	.563
39, 156, 163, 170	2,300	.306	.250	.0094	.0172	.5650	.511
40, 157, 172	2,300	.278	.278	.0083	.0155	.5640	.465
41, 171	2,300	.250	.306	.0084	.0156	.5640	.515

[1] None.

APPENDIX B. - EQUATIONS USED TO CALCULATE WATER CONSUMED AND THE PERCENTAGE OF SHIFT FROM REACTION RATE DATA

The two step reaction assumed to represent the overall steam-carbon reaction is as follows:

$$C + H_2O \rightarrow CO + H_2 \text{ (gasification reaction);} \tag{1}$$

$$CO + H_2O \rightleftarrows CO_2 + H_2 \text{ (shift reaction).} \tag{2}$$

The number of moles of water present at any time equals the number of moles of water fed per minute minus the number of moles of water consumed per minute, or

$$N_{H_2O} \text{ present} = N_{H_2O} \text{ fed} - N_{H_2O} \text{ consumed,} \tag{3}$$

where

N_{H_2O} present = moles of water present at any time;

N_{H_2O} fed = moles of water fed per minute;

N_{H_2O} consumed = moles of water reacted per minute.

This equation may be expressed in terms of reaction products and the equilibrium constant of the shift reaction, as follows:

$$N_{H_2O} \text{ present} = \frac{(N_{CO_2})\ (N_{H_2})}{(N_{CO})\ (K)} \tag{4}$$

where

N_{CO_2} = moles carbon dioxide formed per minute;

N_{H_2} = moles hydrogen formed per minute;

N_{CO} = moles carbon monoxide formed per minute;

K = equilibrium constant for the shift reaction.

For the concurrent reactions (1) and (2),

$$N_{H_2} = N_C + N_{CO_2}, \tag{5}$$

where

N_C = moles of graphite reacted per minute,

and

$$N_{CO} = N_C - N_{CO_2}. \tag{6}$$

Since

$$N_{H_2O} \text{ consumed} = N_C + N_{CO_2},$$

$$N_{H_2O} \text{ present} = H_2O \text{ fed} - (N_C + N_{CO_2}). \qquad (7)$$

Substituting equations (5), (6), and (7) in equation (4), rearranging and transposing terms for solution of the quadratic (second power) formula, and solving for N_{CO_2} gives

$$N_{CO_2} = \frac{-\left(KN_{H_2O} \text{ fed} + N_C\right) + \sqrt{(KN_{H_2O} \text{ fed} + N_C)^2 + 4KN_C\,(K-1)(N_C = N_{H_2O} \text{ fed})}}{2\,(1-K)}. \qquad (8)$$

From equations (3) and (7),

$$N_{H_2O} \text{ consumed} = N_C + N_{CO_2}. \qquad (9)$$

Substituting equation (8) into equation (9), and rearranging N_{H_2O} consumed is expressed in terms of experimentally measured quantities.

$$N_{H_2O} \text{ consumed} = N_C + N_{CO_2} =$$

$$\frac{-KN_{H_2O} \text{ fed} + N_C(1-2K) + \sqrt{(KN_{H_2O} \text{ fed} + N_C)^2 + 4KN_C(K-1)(N_C - N_{H_2O} \text{ fed})}}{2\,(1-K)}. \qquad (10)$$

From the water consumed, the final mole fraction of steam and percent of shift can be calculated.