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RATE CONSTANTS FOR THE REACTION
OF CARBON DIOXIDE AND WATER VAPOR WITH KC GRAPHITE

R. C. Giberson

INTRODUCTION

A considerable volume of literature exists concerning the oxidation reactions of graphite or carbon. The articles by Walker, et. al.⁽¹⁾ and Clark, et. al.⁽²⁾ may be consulted for a review. Although disagreements still exist concerning the mechanism of the reaction of CO_2 with graphite, the rate expression appears well established. Giberson and Walker⁽³⁾ have derived the rate expression and appropriate mechanism for the $\text{C} + \text{H}_2\text{O}$ reaction.

Nuclear graphites vary in the amounts and types of impurities present. These variations cause differences in the oxidation rate for various graphites. It is, therefore, necessary to determine reaction rates for specific reactor graphites.

KC graphite was chosen for this study as being typical of the core graphite of B Reactor. Since carbon dioxide is used as a component of the reactor gas system and water vapor is often present as an impurity, the reaction of these two gases with KC graphite was studied. The inhibiting effect of CO (on the $\text{C} + \text{CO}_2$ reaction) and H_2 (on the $\text{C} + \text{H}_2\text{O}$ reaction) was determined also.

SUMMARY

Rate constants for the $\text{C} + \text{CO}_2$ reaction and the $\text{C} + \text{H}_2\text{O}$ reaction are presented for KC graphite. The inhibiting effect of CO and H_2 on the CO_2

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and H_2O reactions, respectively, is also shown. KC graphite is found to oxidize about three times as fast as TSX graphite for the CO_2 reaction and about equal to TSX graphite for the H_2O reaction.

EXPERIMENTAL DETAILS

KC graphite was made from Kendall coke and Chicago pitch by the National Carbon Company. It is a thermally purified, anisotropic graphite with a density of 1.70 g/cm^3 .⁽⁴⁾ The BET surface area is typically about $0.55 \text{ m}^2/\text{g}$. The graphite samples studied were in the form of small cylinders 5 cm. long by 1.10 cm. in diameter.

Gas mixtures were made from Coleman grade carbon dioxide (99.99% min. purity) and Matheson Company carbon monoxide (99.9% min. purity). Bureau of Mines grade A helium as used as an inert diluent as required.

Figure 1 is a schematic drawing of the experimental apparatus for the $C + CO_2$ reaction study. The gas is passed through a copper furnace at 350°C and then through a Drierite column to remove oxygen and water vapor, respectively. The flow rate of the gas is controlled at about $8.0 \text{ cm}^3/\text{second}$. The purified gas is passed down a quartz tube over a graphite sample which is suspended from one end of a semimicro recording balance. A resistance furnace surrounds the sample tube. Two thermocouples are used in the system, one to record the graphite sample temperature and the second as a sensor to the temperature control for the furnace. The temperature during the course of the rate measurements is held constant to $\pm 3^\circ\text{C}$.

The apparatus used for the water-graphite reaction study was similar to that shown in Figure 1 with the addition of a controlled temperature humidifier just upstream from the sample.

The samples were pre-oxidized in air at 550°C to about 5% oxidation prior to the rate determinations. The rate measurements were made by taking

hourly readings from the recorder and applying the method of least squares to calculate the rate per unit time. These values are normalized by the weight of the graphite present and so the results are given in units of grams of graphite lost per gram of the graphite sample per hour.

RESULTS

C + CO₂ Reaction - The experimental results are presented in Table I and are illustrated in Figures 2 and 3. Figure 2 is an Arrhenius plot comparing the reaction of carbon dioxide with KC graphite and TSX graphite. Figure 3 is an Arrhenius plot for the reaction of a mixture containing 95% carbon dioxide per 5% carbon monoxide with KC graphite.

C + H₂O Reaction - The reaction of water vapor with KC graphite was studied in the temperature range from 800 to 1000°C. Water levels of 500, 1000, 5000, and 10,000 ppm and hydrogen levels of 0, 100, 1000, and 5000 ppm were used. In all cases the rates were similar to those calculated for TSX graphite. Figure 4 shows an Arrhenius plot for the reaction of water vapor with KC graphite in the presence of 5000 ppm of hydrogen.

DISCUSSION

C + CO₂ Reaction - There are two mechanism proposed for the carbon dioxide graphite reaction. They are commonly called the Gadsby⁽⁵⁾ mechanism and the Ergun⁽⁶⁾ mechanism and differ primarily in their assumptions regarding the inhibition step.

Gadsby mechanism:

TABLE I

Reaction Rate Date for KC Graphite

Reacting Gas, Percents	Temp. °C	Rates (g/g/hr) for Sample Nos.		
		714A	1144A	1144B
100% CO ₂	950		5.42 x 10 ⁻³	1.60 x 10 ⁻²
	926	4.95 x 10 ⁻³		
	900		2.24 x 10 ⁻³	2.88 x 10 ⁻³
	864	8.28 x 10 ⁻⁴		
	850		4.58 x 10 ⁻⁴	6.66 x 10 ⁻⁴
	800		9.91 x 10 ⁻⁵	1.13 x 10 ⁻⁴
	775	5.09 x 10 ⁻⁵		
	750		2.23 x 10 ⁻⁵	2.99 x 10 ⁻⁵
	730	1.45 x 10 ⁻⁵		
	700	6.31 x 10 ⁻⁶		
75% CO ₂	950			9.98 x 10 ⁻³
	945		5.70 x 10 ⁻³	
	900		1.64 x 10 ⁻³	3.03 x 10 ⁻³
	850		3.98 x 10 ⁻⁴	7.81 x 10 ⁻⁴
	800		8.19 x 10 ⁻⁵	1.49 x 10 ⁻⁴
	750		1.72 x 10 ⁻⁵	5.49 x 10 ⁻⁵
50% CO ₂	966		7.48 x 10 ⁻³	
	950			8.72 x 10 ⁻³
	900	1.88 x 10 ⁻³	1.70 x 10 ⁻³	1.95 x 10 ⁻³
	893	4.89 x 10 ⁻⁴		
	850		3.56 x 10 ⁻⁴	4.58 x 10 ⁻⁴
	800	9.53 x 10 ⁻⁵	8.19 x 10 ⁻⁵	1.10 x 10 ⁻⁴
	750		1.63 x 10 ⁻⁵	3.17 x 10 ⁻⁵
	741	1.62 x 10 ⁻⁵		
95% CO ₂ /5% CO	950			8.76 x 10 ⁻³
	948		4.57 x 10 ⁻³	
	940	4.17 x 10 ⁻³		
	900	1.30 x 10 ⁻³	9.76 x 10 ⁻⁴	1.98 x 10 ⁻³
	850	1.86 x 10 ⁻⁴	1.68 x 10 ⁻⁴	3.33 x 10 ⁻⁴
	800	1.73 x 10 ⁻⁵	1.70 x 10 ⁻⁵	3.42 x 10 ⁻⁵
	770	4.85 x 10 ⁻⁶		
	750		3.32 x 10 ⁻⁶	5.36 x 10 ⁻⁶
90% CO ₂ /5% CO	958			1.03 x 10 ⁻²
	950		4.78 x 10 ⁻⁴	
	913		1.48 x 10 ⁻³	
	900			1.90 x 10 ⁻³
	850			2.87 x 10 ⁻⁴
	843		1.15 x 10 ⁻⁴	
	800		1.72 x 10 ⁻⁵	2.23 x 10 ⁻⁵
	753		3.19 x 10 ⁻⁶	
	750			5.27 x 10 ⁻⁶

TABLE I (Cont.)

75% CO ₂ /5% CO	950		3.26×10^{-3}	5.24×10^{-3}
	900		6.67×10^{-4}	1.20×10^{-3}
	850		8.60×10^{-5}	1.59×10^{-4}
	800		8.50×10^{-6}	1.20×10^{-5}
95% CO ₂ /2-1/2% CO	976		1.14×10^{-2}	
	974			1.53×10^{-2}
	950			7.86×10^{-3}
	900	1.31×10^{-3}		2.27×10^{-3}
	894		1.28×10^{-3}	
	850	2.07×10^{-4}		4.55×10^{-4}
	800	2.51×10^{-5}		3.99×10^{-5}
	797		2.66×10^{-5}	
	750	3.01×10^{-6}		
95% CO ₂ /1-1/4% CO	965		9.23×10^{-3}	
	960		8.99×10^{-3}	
	950			1.07×10^{-2}
	900		1.52×10^{-3}	3.16×10^{-3}
	850		3.16×10^{-4}	6.26×10^{-4}
	800		4.17×10^{-5}	6.63×10^{-5}
			4.62×10^{-6}	1.54×10^{-5}
	750			

Ergun mechanism:

Neither the present experimental work nor previous studies distinguishes between the two mechanisms since both yield the following rate expression:

$$R = \frac{k_1^P CO_2}{1 + k_2^P CO + k_3^P CO_2} \quad (5)$$

The data of Table I have been fitted to equation (5) with the results shown in Table II. Each k_i is an exponential function of temperature:

$$k_i = A_i e^{-E_i/RT} \quad (6)$$

Table II gives the rate constants for the reaction of carbon dioxide with TSX graphite. Also listed in Table II are the standard deviations for each of the constants.

In the experimental range of this study KC graphite consistently oxidized at a rate 3-5 times that of the TSX graphite. The rate constants provided in Table II are empirically useful for reactor applications. It should be noted, however, that these constants apply only to the homogeneous reaction. In a massive graphite system diffusion effects must also be considered.

TABLE II

Rate Constants for the C + CO₂ Reaction

<u>Constant</u>	<u>KC*</u>	<u>TSX</u>	<u>Units</u>
E ₁	-63.6 ± 2.6	-66.8	kcal/mole
E ₂	38.5 ± 10.1	29.5	kcal/mole
E ₃	11.7 ± 7.0	~ 0.0	kcal/mole
A ₁	(7.19 ± 0.45) × 10 ⁺⁶	8.01 × 10 ⁺⁶	g/g-hr/mm
A ₂	(5.61 ± 1.50) × 10 ⁻⁹	4.15 × 10 ⁻⁷	mm ⁻¹
A ₃	(2.11 ± 0.37) × 10 ⁻⁵	3.50 × 10 ⁻³	mm ⁻¹

* ± values represent standard deviation. Estimates of the standard deviation for the TSX data are not available but they are certainly no better than KC data.

C + H₂O Reaction - The rate expression derived by Giberson and Walker⁽³⁾ for the C + H₂O reaction is:

$$R = \frac{k_1 P_{H_2O}}{1 + k_2 P_{H_2}^{1/2} + k_3 P_{H_2O}} \quad (7)$$

The mechanism yielding this expression is:

The rate expression, equation (7), was derived from data obtained on TSX graphite. In the case of the KC graphite not only is the rate expression shown to be valid but also within the experimental accuracy of the measurements, the rate constants are the same as found for TSX graphite. Table III lists the activation energies and frequency factors observed.

TABLE III

Rate Constants for the C + H₂O Reaction

<u>Constant</u>	<u>Value</u>	<u>Units</u>
E ₁	32.7	kcal/mole
E ₂	60.8	kcal/mole
E ₃	79.3	kcal/mole
A ₁	1.27 x 10 ⁺²	g/g-hr/mm
A ₂	1.24 x 10 ⁻¹¹	mm ^{-1/2}
A ₃	6.51 x 10 ⁻¹⁹	mm ⁻¹

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FIGURE 1
Gas Graphite Reaction Apparatus

FIGURE 2
Log Rate Versus $1/T$ $^{\circ}\text{K}$

FIGURE 3
 Log Rate Versus $1/T$ $^{\circ}\text{K}$

FIGURE 4
Log Rate Versus 1/T °K