Mechanism of the Carbonization of Chromium(III) Oxide

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Many kinds of carbides are formed by the solid state reaction of metal oxides with carbon at high temperatures. As most solid-solid reactions occur by counter diffusion of the cations of the reactants through the product layer, the kinetics of compound formation are considered to depend on the nature of the reactant and of the product. In the present study, the carbonization of chromium oxide was thermogravimetrically examined, and the mechanism was compared with that of the previously reported reaction of calcium oxide with carbon[1].

Experimental.—Extra pure chromium(III) oxide was obtained from Wako Chemicals Co. The particles were about 1 μ in diameter. Artificial graphite ($d_{002}=3.389$ Å, pulverized below 250 mesh sieve) for an atomic pile was used as carbon. A mixture of 1.00 g. of carbon and 2.92 g. of chromium oxide was compressed at about 1 ton/cm^2 into a cylindrical pellet, 15 mm. in diameter and 8 mm. in height. It was found by X-ray and chemical analysis that only chromium carbide, Cr_3C_2, was formed on the reaction of chromium oxide with carbon in the temperature range between 1060 and 1200°C and at 2×10^{-2} mmHg. The mixing ratio of carbon to chromium oxide was chosen according to the following equation: $3Cr_2O_3+13C=2Cr_3C_2+9CO$.

The apparatus for the kinetic experiments consisted of a spring balance in a vacuum electric furnace[1]. In the hot zone of the furnace a graphite bucket was suspended with fine molybdenum wire from the spring. The shrinkage of the spring upon a loss in weight was observed with a microscope with an eyepiece scale. The elongation of the spring against weight was 1.036 cm./g. The reaction temperature was measured with a platinum-platinum·13% rhodium thermocouple and was maintained at a desired value within ±3°C with the aid of an automatic temperature controller. The electric furnace was evacuated to 2×10^{-2} mmHg during the course of the experiments.

Results and Discussion.—All the curves of the weight decrease against time were parabolic in the temperature range 1060 to 1200°C. Figure 1 shows the course of the reaction at four temperatures.

Generally, the rate of solid state reaction determined by a diffusion process is expressed by the following equation:

$$(1-\sqrt[3]{1-x})^2=2kt \qquad (1)$$

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[1] H. Tagawa, H. Sugawara and H. Nakajima, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **64**, 1751 (1961).

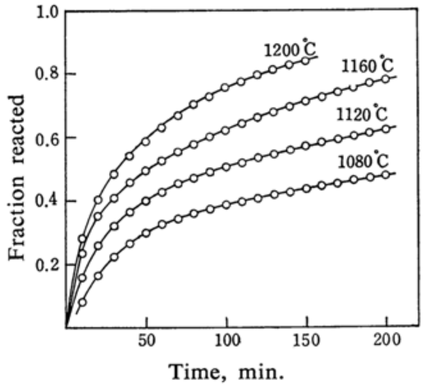

Fig. 1. Relation between fraction reacted and time.

where x is the fraction reacted, t the time, and k the reaction rate constant. To determine whether the reaction followed the parabolic kinetics shown in Eq. 1, the data in Fig. 1 were plotted as the values of $(1-\sqrt[3]{1-x})^2$ vs. time in Fig. 2. The linearity of the curve suggests that the diffusion process is rate-controlling. The constant k in Eq. 1 was found from the slope of each curve. The logarithm of the slope was plotted against the reciprocal of the absolute temperature in Fig. 3. The activation energy was calculated as 89.4±3.4 kcal./mol. from the least-squares slope of this plot.

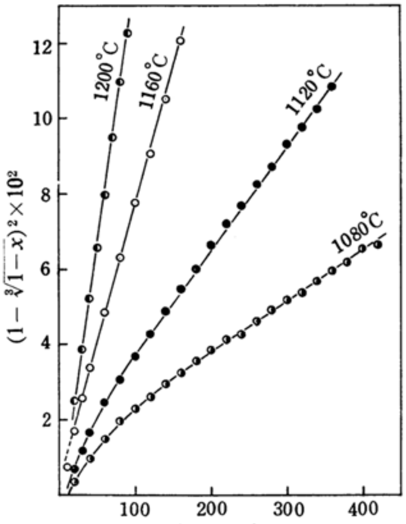

Fig. 2. Relation between $(1-\sqrt[3]{1-x})^2$ and time.

Boericke[2] has concluded that the reduction of chromium oxide with carbon involves four distinct, consecutive and reversible reaction steps:

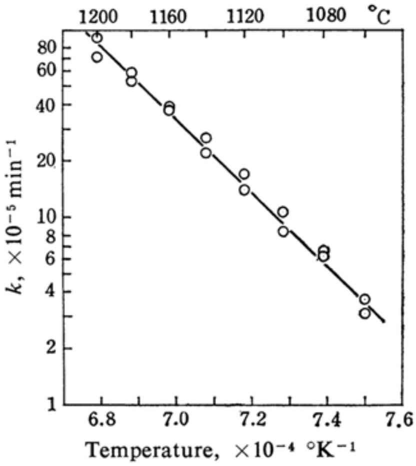

Fig. 3. Relation between the reaction velocity and reciprocal absolute temperature in the reaction of chromium oxide with carbon.

$$3Cr_2O_3 + 13C = 2Cr_3C_2 + 9CO \qquad (2)$$

$$5Cr_2O_3 + 27Cr_3C_2 = 13Cr_7C_3 + 15CO \qquad (3)$$

$$5Cr_2O_3 + 14Cr_7C_3 = 27Cr_4C + 15CO \qquad (4)$$

$$Cr_2O_3 + 3Cr_4C = 14Cr + 3CO \qquad (5)$$

It has been shown in this experiment that Cr_3C_2 is formed as an intermediate compound between chromium oxide and metallic chromium. The predominant formation of Cr_3C_2 is to be expected, as the equilibrium carbon monoxide pressure in Eq. 2 is the largest one in the reaction system of chromium oxide with carbon.

It is recognized that calcium vapor and carbon monoxide are formed in the reaction of calcium oxide with carbon below 1400°C in vacuo according to the following equation: $CaO+C=Ca+CO$[3]. As has previously been reported[1], when the plot of the weight decrease vs. time became linear, the reaction rate constant was obtained from the slopes of these curves. The activation energies from the Arrhenius plots were 92±5, 136±10 and 147±6 kcal./mol. for calcium oxides burned at 900, 1100 and 1300°C respectively for 3 hr. The difference in activation energy may be due to the sintering of calcium oxide during the course of the experiments and to the decrease in the reactivity with carbon.

When chromium carbide and calcium carbide are formed by the diffusion of cations through the oxide and the product layer, the reaction rate may depend on the mobility of the cations and on the reactivity of carbon as a reducing agent at the interface. Oxygen ions may not be considered to play an important role in

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[2] F. S. Boericke, *U. S. Bur. Mines, Tech. Paper,* R. I. 3747 (March, 1944).

[3] N. Kameyama, "Electrochemistry: Theory and Practice", Vol. III-2, Maruzen, Tokyo (1956), p. 131.

carbonization, as their mobility is small in comparison with that of the cations.

The solid state reaction of carbon with chromium oxide and calcium oxide is considered from the standpoint of diffusion phenomenon. The self-diffusion coefficient of chromium ions in the oxide was determined by Lindner⁴⁾, the activation energy being 100 kcal./mol. The activation energy of the self-diffusion of calcium ions in the oxide was 80 kcal./mol.⁵⁾, while that of ^{14}C in graphite was 163 kcal./mol.⁶⁾ In the reaction of carbon with chromium oxide and with calcium oxide, the activation energy was 89 and 147 kcal./mol. respectively, the former value being similar to the activation energy for the self-diffusion of chromium ions in the oxide and the latter being similar to that of the self-diffusion of carbon and the lattice energy of graphite (170.9 kcal./.g.atom)⁷⁾. Consequently, it may be considered that the rate determing factor is closely related to the diffusion of chromium ions in the oxide in the chromium carbide formation and to the structure of the carbons for the reduction of the oxide in the reaction with calcium oxide.

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4) R. Lindner and Å. Åkstrom, *Z. physik. Chem.* (*N. F.*), 6, 162 (1956).

5) J. A. Hedvall, "Einführung in die Festkörperchemie", Friedr. Vieweg & Sohn, Braunschweig (1952), p. 85.

6) M. A. Kanter, *Phys. Rev.*, 107, 655 (1957).

7) D. Smith, A. S. Dworkin and E. R. van Artsdanlen, *J. Am. Chem. Soc.*, 77, 1654 (1955).