KINETICS OF THE OXYGEN EXCHANGE BETWEEN CO_2 AND CO ON CARBON

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A study was made of the reversible exchange of oxygen between CO_2 and CO on the surface of carbon (Spheron 6),

$$CO_2 + C_f \underset{k_1'}{\overset{k_1}{\rightleftarrows}} CO + C_O$$

at temperatures from 750° to 850° C and at atmospheric pressure. Direct measurements of the exchange reaction were effected with carbon-14 used as a tracer. Under these conditions the rates of oxygen exchange were always a few orders of magnitude greater than the rates of gasification. The gasification of carbon,

$$C_O \overset{k_3}{\rightarrow} CO + C_f$$

occurring during these experiments, was too slow to be considered an interfering factor.

From measurements of oxygen exchange, composite rate constants were determined for the forward and backward directions of the reaction; $k_1(C_t)$ ranged from 0.02 to 0.22 x 10^{18} sites/g sec and $k_1'(C_t)$ from 0.28 to 1.33 x 10^{18} sites/g sec where (C_t) represents the concentration of reaction sites in the solid. The corresponding range of the equilibrium constant for oxygen exchange, K_1, was 0.07 to 0.16.

Numerical values of the equilibrium constant for oxygen exchange between CO_2 and CO have been reported in several previous, independent studies. In most instances, however, these values were produced indirectly as a result of analysis of kinetic data obtained from the gasification of carbon by CO_2 or CO_2-CO mixtures. The direct determinations of K_1 made in this study agreed well with these earlier results. Thus oxygen exchange appears to be established as a valid and important step in the reaction sequence for the carbon dioxide-carbon reaction.

Activation energies for the forward and backward exchange reactions were 53 and 36 kcal/mole, respectively, and that for the gasification of carbon was 58 kcal/mole. These results indicate that oxygen exchange is not likely to become the rate-controlling step in the reaction of carbon with carbon dioxide at higher temperatures, and further that the retarding effect of CO on gasification rates should diminish with increasing temperature. (15 min.)