CONCLUSIONS

This study primarily concerned the derivation of reaction sequences when coke (or carbons in general) is gasified with steam or carbon dioxide. Based on the reaction sequences, rate equations were developed so that the postulated sequences could be more critically examined under a wide range of experimental conditions. In deriving rate equations two important simplifying assumptions were made, largely because of the lack of information regarding the phenomena involved. First, oxygen exchange reactions are extremely fast compared to the gasification step. Second, composition of the gas phase inside a particle is uniform and identical to that surrounding the particle. Whenever divergences were found between the observed and calculated results, it was necessary to consider carefully if the divergences were due to the inadequacy of the postulated mechanism or to the invalidity of the assumptions.

For the reaction sequence postulated here to be valid, the following requirements should be fulfilled.

1. The rate of gasification with CO_2 or H_2O should be independent of the inert gas concentration when the flow rate of inert gas is the only variable in a series of experiments.

2. The fraction of CO_2 or H_2O reacting should be independent of the space velocity when the ratio of the weight of the coke to the inlet rate of reactant gas (CO_2 or H_2O) is kept constant in a series of experiments.

3. Gasification rate of coke with steam-carbon dioxide mixture should be predictable from the gasification rates of coke using steam and carbon dioxide separately.

4. Equilibrium constants of the oxygen exchange reactions between CO_2 and CO obtained separately from the CO_2-coke and H_2O-coke reactions should agree within the precision of the attainment of the water-gas shift equilibrium.

The fulfillment of all of these requirements experimentally indicates that the postulated reaction sequence is valid.

The assumption made in rate equations did not complicate significantly the verification of the above criteria. However, these assumptions involve the ancillary phenomena important to the development of rigorous rate equations; therefore, they in turn were examined very closely.

Water-gas shift equilibrium was not always obtained as required by the first assumption. The deviations from the equilibrium were not excessive for a flow system. The devia-tions proved to be inconsequential in the analyses made because the overall rate equations are very insensitive to the values of the equilibrium constant. A separate study of the oxygen exchange reactions is very desirable not because such a study would enable the derivation of more rigorous rate equations, for the complications they introduce may well offset any refinement they will permit, but because such a study should elucidate the nature of reaction sites.

The second assumption involved largely the solid state. Experiments employing particles of various sizes and different space velocities showed that boundary-film diffusion (outside the particle) is extremely fast and does not influence gasification rates.

Experiments with H_2O+H_2 and H_2O+CO mixtures showed that both H_2 and CO retarded the reaction. However, the effect of H_2 was less than predicted and that of CO slightly more than predicted. The high escaping tendency of H_2 in an upward flow system could explain the behavior of hydrogen. However, the behavior of CO implies some diffusional hindering.

The relative number of reaction sites per unit weight of coke obtained from H_2O-coke reactions was about 60-pct. higher than that obtained from CO_2-coke reactions. The difference could be explained by a concentration gradient in the gas phase inside the particles (hence a concentration gradient for the occupied and unoccupied sites) and/or by a polymodal distribution of reaction sites; that is, steam is capable of reacting with more types than carbon dioxide is.

Reactions of coke with H_2O-CO_2, H_2O-H_2, and H_2O-CO mixtures suggest that penetration of the reactant gases into the interiors of the solid particles may not be very important; that is, the chemisorbed oxygen is mobile, and the retarding diffusional hindrance involves the outward flow of CO, the product of the gasification step.

Experiments involving particles of various sizes and differing space velocity showed that film boundary diffusion (outside the particle) is extremely fast and does not influence the gasification rates. If diffusion rate within particles (pore diffusion) influenced the reaction rate, this was not manifested by change in particle size because macropores could have

diminished any effect that particle size may have had.

The reaction sequence outlined here accounts well for the reactions of coke with carbon dioxide and steam under diverse experimental conditions. More rigorous rate equations require a knowledge of the solid state of carbons, that is, their microporosity, crystallinity, and electronic state of free and oxygen-containing reaction sites. The importance of the solid state to kinetic behavior of carbons has been stressed throughout the text.

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