# KINETICS OF THE REACTIONS OF CARBON DIOXIDE AND STEAM WITH COKE [1]

By

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Summary

A COMPREHENSIVE kinetic analysis has been made of the reactions of a metallurgical coke with carbon dioxide and with steam in the temperature range 900 to 1,200° C. at atmospheric pressure. Theories on the mechanisms of both reactions have been advanced, and a close analogy has been found to exist between the two reactions. According to the theory, some terminal atoms of the polycrystallites of the solid carbon (C_f, reaction sites) are capable of detaching oxygen atoms from carbon dioxide and water molecules that collide with them. In a reverse manner, carbon monoxide and hydrogen molecules that collide with solid-phase carbon atoms that retain oxygen (C_0, occupied sites) can remove oxygen.

$$CO_2 + C_f \rightleftarrows C_0 + CO$$

$$H_2O + C_f \rightleftarrows C_0 + H_2$$
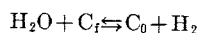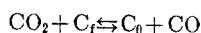
These reactions result in a dynamic oxygen exchange between the solid and gas phases. In both reactions the actual gasification, that is, carbon transfer from solid to gas phase, originates at the occupied sites and constitutes the slowest step of the reaction.

$$C_0 \rightarrow CO + C_f$$

Both carbon monoxide and hydrogen retard the reaction rate by maintaining a low concentration of occupied reaction sites.

The postulated sequence involves the following critical requirements:

1. 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. Fraction of CO_2 or H_2O reacted should be independent of space velocity (or amount of the solid) when the ratio of the weight of the coke to the inlet flow rate of reactant gas (CO_2 or H_2O) is kept constant in a series of experiments.

3. Gasification rate with CO_2-H_2O mixtures should be predictable from gasification rates with CO_2 and H_2O 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.

All of these requirements are fulfilled, indicating that the sequence postulated is valid. To derive rigorous rate equations for flow systems it is neces-

sary to establish the reaction sequence and to consider the influence of the ancillary phenomena, such as flow conditions, thermal and molecular diffusion, and the state of the solid. Flow conditions have been considered carefully, and the experiments have been conducted in fluidized beds to maintain isothermal conditions. 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 rate.

There were indications that diffusional resistance involved inside the micropores of the particles influenced the reaction rates appreciably. For example, the relative number of reaction sites per unit weight of the coke obtained from H_2O-coke reactions was about 60 percent higher than that obtained from CO_2-coke reactions; that is, H_2O was more reactive with coke than CO_2 was. To incorporate the role of diffusional resistance in the rate equations it is essential that the solid state of the carbons be better understood; that is, their microporosity, crystallinity, and electronic state of free and oxygen-containing reaction sites. The importance of the solid state to kinetic behavior has been stressed throughout the text.

SURVEY OF PREVIOUS WORK

Several extensive reviews of carbon dioxide-carbon[3 4] and steam-carbon reactions[5-7] have been made. Even though these reactions may differ in details of their reaction sequences, some aspects of reaction mechanisms are analogous. Therefore, in more recent review articles[8-10] all of the gasification reactions of carbons are considered as a group, that is, the reactions of carbon with oxygen, carbon dioxide, or steam.

Any assessment of previous studies is made difficult by the many and varied types of equipment that have been employed and by the multiplicity of operating variables. The experimental arrangements include gas-flow and static systems in which carbon may exist as a fixed or fluidized bed of granular particles, particles falling through a hot zone, a single massive piece, thin filaments, or evaporated films. Carbons varying in structure from roentgenamorphous to crystalline graphite have been employed. Operating variables encompass a wide spread in temperature (from 200° to 2,300° C.), pressure (from 10^{-4} mm. Hg to 50 atmospheres) and gas velocity (from zero to 100 m./sec.). Whereas some experiments involved the reaction of an appreciable portion of carbon samples (several weight-percent), others were confined to reactions of only parts per million.

The temperature coefficients of the specific gasification rates do not generally conform to the Arrhenius equation over an extended temperature range. At the higher temperatures the apparent activation energies show a decrease with increase in temperature. Many earlier workers and some recent ones sought the explanation in purely physical factors.

Rossberg[11] and Hedden and Wicke[12] have described three distinct ranges of temperature: (1) At low temperatures the reaction is chemically controlled, the reaction rates obtained yielding the true activation energy; (2) at intermediate temperatures pore diffusion influences the reactions and the activation energy obtained is half of the true value; (3) at high temperatures boundary diffusion between the main gas stream and solid becomes important and controls the reaction rate, and the activation energy approaches zero. From a study of the oxidation of graphite, Blyholder and Eyring[13] postulated only the first two of the above temperature ranges. On the other hand, experimental results of Earp and Hill[14] and Day and coworkers[15] on oxidation of carbon and those of Hunt and coworkers[16] and Pilcher and coworkers[17] on steam-carbon reactions have been interpreted as showing a transition from a chemically controlled reaction to a film boundary diffusion controlled reaction. These explanations were based largely on decreases in activation energy with temperature and variations in reaction rate with gas velocity. Guerin and Bastick[18] explained the differences in reactivity of cokes and changes in reaction rates with burn off on the basis of diffusion within the pores.

Several workers, notably Dotson and coworkers,[19] Ergun,[20] Jolley and Poll,[21] and Walker and Nichols,[22] have ruled out film diffusion

[3] Mayers, M. A., I. The Physical Properties and Reactivity of Coke. Chemistry of Coal Utilization: John Wiley and Sons, Inc., New York, N.Y., 1945, vol. 1, pp. 895-919. II. Combustion in Fuel Beds. Vol. 2 pp. 1515-1520.

[4] Guerin, H., [The Problem of Reactivity of Solid Fuel]: H. Dunod, Paris, France, 1945, 222 pp.

[5] Scott, G. S., Mechanism of the Steam-Carbon Reaction: Ind. Eng. Chem., vol. 33, 1941, pp. 1279-1285.

[6] Warner, B. R., Mechanism of the Steam-Carbon Reaction: Jour. Am. Chem. Soc., vol. 65, 1943, pp. 1447-1451.

[7] Jolley, L. J., and Poll, A., Effects of Reactivity and some Other Variables on Gasification of Coke with Steam: Jour. Inst. Fuel, vol. 26, 1953, pp. 33-44.

[8] Blackwood, J. D., Gasification of Carbon: Reviews Pure Appl. Chem., vol. 4, 1954, pp. 251-274.

[9] Blayden, H. E., Reactivity of Cokes and Chars: Proc. Residential Conf. on Sci. in the Use of Coal, Univ. of Sheffield, Sheffield, England, Inst. of Fuel, April 1958, pp. E1-E7.

[10] Essenhigh, R. H., and Perry, M. G., Combustion and Gasification: Proc. Residential Conf. on Sci. in the Use of Coal, Univ. of Sheffield, Sheffield, England, Inst. of Fuel, April 1958, pp. D1-D12.

[11] Rossberg, M., [Experimental Results Concerning the Primary Reactions in the Combustion of Carbon]: Ztschr. Elektrochem., vol. 60, 1956, pp. 952-956.

[12] Hedden, K., and Wicke, E., About Some Influences on the Reactivity of Carbon: Proc. 3d Conf. on Carbon, Pergamon Press, New York, N.Y., 1959, pp. 249-301.

[13] Blyholder, G., and Eyring, H., Kinetics of Graphite Oxidation. II: Jour. Phys. Chem., vol. 63, 1959, pp. 1004-1008.

[14] Earp, F. K., and Hill, M. W., Oxidation of Carbon and Graphite: Conf. on Ind. Carbon and Graphite, Soc. Chem. Ind., London, England, September 1957, 1958, pp. 326-333.

[15] Day, R. J., Walker, P. L., and Wright, C. C., The Carbon-Oxygen Reaction at High Temperatures and High Gas Flow Rates: Conf. on Ind. Carbon and Graphite, Soc. Chem. Ind., London, England, September 1957, 1958, pp. 348-370.

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

[17] Pilcher, J. M., Walker, P. L., Jr. and Wright, C. C., Kinetic Study of the Steam-Carbon Reaction: Ind. Eng. Chem., vol. 47, 1955, pp. 1742-1749.

[18] Guerin, H. and Bastick, M., Some Results Relative to the Study of Coke Reactivity: Preprints 3d Internat. Conf. on Coal, Valkenburg, The Netherlands, 1959, IV C8, pp. 1-11.

[19] Dotson, J. A., Koehler, W. A., and Holden, J. A., Rate of the Steam-Carbon Reaction by a Falling Particle Method: Ind. Eng. Chem., vol. 49, 1957, pp. 148-154.

[20] Ergun, S., Kinetics of the Reaction of Carbon Dioxide With Carbon: Jour. Phys. Chem., vol. 60, 1956, pp. 480-485.

[21] Work cited in footnote 7.

[22] Walker, P. L., and Nichols, J. R., Some Factors Affecting the Reactivity of Sized Particle Carbons to Carbon Dioxide: Conf. on Ind. Carbon and Graphite, Soc. Chem. Ind., London, England, September 1957, 1958, pp. 334-347.

as a rate-controlling step in most cases because of the large magnitude of temperature coefficient, rate differences with different types of carbon, or a lack of dependence of rate upon particle size. From a critical analysis of the conventional use of partial pressure, specific reaction rate, activation energy, and order of reaction in flow systems, Ergun [23] concluded that most of the confusion about the role of physical factors such as diffusion and gas velocity resulted from attempts to interpret data on the heterogeneous gasification reactions in a manner analogous to homogeneous reactions. He illustrated that the specific reaction rate is not necessarily proportional to the rate of the slowest, that is, the rate-controlling step of the reaction, except under limiting conditions; hence, deviations from linearity of the specific reaction rate in an Arrhenius plot may not mean the onset of diffusion control. He further pointed out that an increase in gas velocity in a flow system is accompanied by an increase in the concentration of reactant gas and a decrease in the concentration of product gases in the gas phase and that the changes in the gas-phase concentrations could adequately explain the increase in the gasification rate of the solid without recourse to a diffusional phenomenon. Ergun calculated boundary diffusion rates and observed that the diffusion rates were several orders of magnitude larger than the gasification rates at temperatures at which reaction had been considered to be diffusion controlled. Goring and coworkers [24] also had earlier ruled out boundary diffusion control on the basis of comparative considerations of diffusion and gasification rates. In a recent review article Essenhigh and Perry [25] concluded that the importance of diffusion at high temperatures (film-boundary diffusion) has been overestimated and that at low temperatures (pore diffusion) has been underestimated.

Though there has been some conflict in attempting to explain reaction rates largely by physical factors, physical chemical considerations also drew attention, and attempts in this direction also proved to be equally controversial. In 1912, Rhead and Wheeler [26] showed that carbon surfaces were capable of holding oxygen even at combustion temperatures. They introduced the concept of the C_xO_y complex on the surface. Later Langmuir [27] discovered that carbon dioxide reacts on an initially cleaned carbon surface without causing any increase in pressure in a static system. Under the described conditions a molecule of carbon dioxide yielded a molecule of carbon monoxide, and an oxygen atom was retained by the solid. The findings of Rhead and Wheeler and of Langmuir clearly demonstrated the heterogeneity of the reaction of carbon and indicated that the initial step leading to the formation of surface oxide was not necessarily slow. Yet in many later and recent publications these findings were not considered. Data obtained were correlated on the basis of the assumption that the reaction rate had some order with respect to carbon dioxide or steam, and the reactions of the products were either neglected or were assumed to have rate orders based largely on the stoichiometry of the reactions. The apparent rate orders reported varied with temperature and ranged between zero and one. In a discussion of interpretation of kinetic data, Ergun [28] considered such treatments as empirical and often leading to meaningless, if not erroneous, conclusions.

Following Rhead and Wheeler many other workers have shown the ability of carbons to detach oxygen atoms from gaseous oxygen, steam, carbon dioxide, nitrous oxide, and other oxides and to retain them strongly. The questions that concerned the kineticists were multiple: (1) The nature of the primary reaction leading to the formation of carbon-oxygen complexes; (2) the nature of the carbon-oxygen complexes; (3) the products obtained from the decomposition or evaporation of carbon-oxygen complexes; (4) the effects of the product gases on the reaction rate; and (5) the rate-controlling step in the reaction sequence. On virtually all of these questions conflicting views have been advanced.

With regard to the nature of the initial reaction of carbon dioxide with carbon, a great number of workers, notably Broom and Travers,[29] Semechkova and Frank-Kamenetski,[30] Gadsby and coworkers,[31] Bonner and Turkevich,[32] Marsh,[33] Ergun,[34] Boulangier and

[23] Ergun, S., Flow Experiments in Studying Kinetics: Ind. Eng. Chem., vol. 47, 1955, pp. 2075–2080.
[24] Goring, G. E., Currin G. P., Tarbox, R. P., and Gorin, E., Kinetics of Carbon Gasification by Steam. Effect of High Temperature Pretreatment on Reactivity of Low Temperature Char to Steam and Carbon Dioxide: Ind. Eng. Chem., vol. 44, 1952, pp. 1051–1057.
——, Effect of Pressure and Carbon Burnoff on Rate of Interaction of Low Temperature Char With Steam-Hydrogen Mixtures at 1,600° F., Ind. Eng. Chem., vol. 44, 1952, pp. 1057–1065.
[25] Work cited in footnote 10.
[26] Rhead, T. F. E., and Wheeler, R. V., Mode of Combustion of Carbon: Proc. Chem. Soc., vol. 29, pp. 51–53; Jour. Chem. Soc., vol 103, 1912, pp. 461–489.

[27] Langmuir, I., Chemical Reactions at Low Pressures: Jour. Am. Chem. Soc., vol. 37, 1915, pp. 1139–1167.
[28] Work cited in footnote 23.
[29] Broom, W. E. J., and Travers, M. W., The Reaction Between Carbon and Different Gases: Proc. Roy. Soc. (London), vol. A135, 1932, pp. 512–537.
[30] Semechkova, A. F., and Frank-Kamenetski, D. A., [Reduction of CO₂]: Acta Physicochim. U.S.S.R., vol. 12, 1940, pp. 876–898.
[31] Gadsby, J., Long, F. J., Sleightholm, P., and Sykes, K. W., The Mechanism of the Carbon Dioxide-Carbon Reaction: Proc. Roy. Soc. (London), vol. A193, 1948, pp. 357–376.
[32] Bonner, F., and Turkevich, J., Study of the Carbon Dioxide-Carbon Reaction Using C¹⁴ as a Tracer: Jour. Am. Chem. Soc., vol. 73, 1951, pp. 561–564.
[33] Marsh, J. D. F., Some Aspects of the Mechanism of the Gasification of Carbon by Carbon Dioxide and Steam: Inst. Gas Eng. (London), Communication 393, 1951, 21 pp.
[34] Work cited in footnote 20.

coworkers,[35] and Harker and coworkers [36] have agreed with Langmuir's results. Though most of these workers postulated some sort of initial sorption of carbon dioxide as a prerequisite step for the Langmuir reaction. studies by Bonner and Turkevich, Brown,[37] and Orning and Sterling,[38] employing a radioactive isotope of carbon in the gas phase, revealed the exchange of oxygen between carbon dioxide and monoxide and negligible transfer of carbon from gas to solid phase. These results and other considerations led Ergun to postulate a direct gas-solid interaction between carbon dioxide and reaction sites for the Langmuir reaction. Similarly, initial reaction of steam with carbon has been postulated to lead to the formation of surface oxygen and gaseous hydrogen by Gadsby and coworkers,[39] Strickland-Constable,[40][41] Long and Sykes,[42] and recent workers. Gadsby and coworkers postulated an adsorption-desorption mechanism to derive their well-known equation. Strickland-Constable proposed the adsorption of water in molecular form largely because of reversible adsorption of water on charcoal below 700° C. Long and Sykes and Binford and Eyring [43] proposed predissociation of steam into hydrogen and oxygen which are then adsorbed separately on different reaction sites, whereas Johnstone and coworkers [44] proposed dissociation of water into H and OH radicals. Ergun [45] proposed a direct gas-solid interaction between water vapor and carbon similar to that between carbon dioxide and carbon.

The nature of carbon-oxygen complexes has been the subject of much speculation but not many direct examinations. Rhead and Wheeler,[46] Eucken,[47] Meyer,[48][49] Sihvonen,[50-52]

and Blackwood and McGrory [53] postulated that oxygen is held on the surface through primary and secondary valences. Sihvonen proposed a carboxyl theory of combustion which postulates the formation of keto and ketene groups through primary valences. Strickland-Constable [54] observed that oxidation could be explained by intermediate surface complexes that are more reactive and less stable than the surface oxides that, he believed, formed the main part of the surface oxygen complexes. Several questions confronted the proponents of sorption-desorption theories of gasification concerning the distinction among the chemisorbed carbon dioxide, carbon monoxide, and surface carbon-oxygen complexes. Semechkova and Frank-Kamenetski [55] and Harker and coworkers [56] considered the surface oxide to be identical with chemisorbed carbon monoxide. Since carbon monoxide retards the reaction, these authors concluded that gasification is inhibited by surface oxygen. Such a conclusion, however, is inconsistent with their other postulate that the critical step of the reaction is conversion of surface oxide to carbon monoxide. Gadsby and coworkers [57] differed from the Frank-Kamenetski view in that they made a distinction between adsorbed oxygen and adsorbed carbon monoxide.

Surface properties of solids generally are complex and require careful study. Carbons have been found to absorb microwaves in a magnetic field, suggesting the presence of free radicals or electrons in the triplet state. Both reversibly adsorbed (physical) and chemisorbed oxygen alter the absorption spectra,[58-60] in the different manners that were expected. Further studies like these should be promising for elucidating the nature of carbon-oxygen complexes.

Different views have been also expressed concerning the primary product of the decomposition of the carbon-oxygen complex.

[35] Boulangier, F., Duval, X., and Letort, M., The Kinetics of the Reactions of Carbon Filaments With Carbon Dioxide and Water Vapor at High Temperatures and Low Pressures: Proc. 3d Conf. on Carbon: Pergamon Press, New York, N.Y., 1959, pp. 257-64.
[36] Harker, H., Marsh, H., and Wynne-Jones, W. F. K., The Carbon-Carbon Dioxide Reaction: Proc. Conf. on Ind. Carbon and Graphite, London, England, September 1957: Soc. Chem. Ind., 1958, pp. 291-301.
[37] Brown, F., The Exchange of C14 Between Carbon and Its Oxides: Trans. Faraday Soc., vol. 48, 1952, p. 1005.
[38] Orning, A. A., and Sterling, E., Oxygen Transfer Between Carbon Dioxide and Carbon Monoxide in the Presence of Carbon: Jour. Phys. Chem., vol. 58, 1954, p. 1044.
[39] Gadsby, J., Hinshelwood, C. N., and Sykes, K. W., The Kinetics of the Reactions of the Steam-Carbon System: Proc. Roy. Soc. (London), vol. A187, 1946, pp. 129-151.
[40] Strickland-Constable, R. F., Part Played by Surface Oxides in the Oxidation of Carbon: Trans. Faraday Soc., vol. 34, 1938, pp. 1074-1084.
[41] ———, Interaction of Steam and Charcoal at Low Pressures: Proc. Roy. Soc. (London), vol. A189, 1947, pp. 1-10.
[42] Long, F. J., and Sykes, K. W., The Mechanism of the Steam-Carbon Reaction: Proc. Roy. Soc. (London), vol. A193, 1948. pp. 377-399.
[43] Binford, J. S., Jr., and Eyring, H., Kinetics of the Steam-Carbon Reaction: Jour. Phys. Chem., vol. 60, 1956. pp. 486-491.
[44] Johnstone, H. F., Chen, C. Y., and Scott, D. S., Kinetics of the Steam-Carbon Reaction in Porous Graphite Tubes: Ind. Eng. Chem., vol. 44, 1952, pp. 1564-1569.
[45] Hottel, H. C., Altman, D., Ergun, S., and Williams, G. C., Heterogeneous Burning, Panel Discussion, Fifth Symposium (Internat.) on Combustion: Reinhold Publishing Co., New York, N.Y., 1955, pp. 795-798.
[46] Work cited in footnote 26.
[47] Eucken, A., [The Mechanism of Carbon Combustion at Very Low Pressures]: Ztschr. angew. Chem., vol. 43, 1930, pp. 986-993.
[48] Meyer, L., The Surface Reaction of Graphite With Oxygen, Carbon Dioxide, and Water Vapor at Low Pressures: Trans. Faraday Soc., vol. 34, 1938, pp. 1056-1061.
[49] ———, [The Mechanism of the Primary Reaction Between Oxygen and Graphite]: Ztschr. Phys. Chem., vol. B17, 1932, pp. 385-404.

[50] Sihvonen, V. [Primary Reactions in the Oxidation of Graphite]: Ztschr. Electrochem., vol. 40, 1938, pp. 456-460.
[51] ———, [The Reaction Mechanism of the Combustion of Carbon According to Carboxyl Group Theory: Suomen Kimistilehti, vol. 12B] 1939, pp. 20-23.
[52] ———, The Influence of Keto and Ketene Groups, Adsorbed Molecules, and Ions on the Mechanism of Oxidation of Carbon: Trans. Faraday Soc., vol. 34, 1938, pp. 1062-1074
[53] Blackwood, J. D., and McGrory, F., The Carbon Steam Reaction at High Pressure: Australian Jour. Chem., vol. 11, 1958, pp. 16-33.
[54] Work cited in footnote 41.
[55] Work cited in footnote 30.
[56] Work cited in footnote 36.
[57] Work cited in footnote 31.
[58] Uebersfeld, J., and Erb, E., Paramagnetic Resonance of Carbons. Detection of Free Radicals That Are Unstable in Air: Jour. Phys. Radium, vol. 16, 1955, p. 340.
[59] Ingram, D. J. E., and Austen, D. E. G., Investigations on the Trapping of Free Electrons in Carbon: Conf. on Ind. Carbon and Graphite, Soc. Chem. Ind., London, England, September 1958, pp. 19-27.
[60] Harker, H., Catalysis by Alkali-Metal Salts in Carbon Gasification Reactions: Proc. 4th Conf. on Carbon, Pergamon Press, New York, N.Y., 1960, pp. 125-139; Fuel, vol. 38, 1959, p. 509.

Whereas many workers [61-70] deduced carbon monoxide to be the primary product, some have stated that carbon dioxide may also be a primary product of reaction, being formed in small amounts under special conditions of temperature and pressure.[71-76] Recently Deitz [77] reported the formation of carbon suboxide. The formation of carbon dioxide is explained by the reaction of carbon monoxide with oxygen of the carbon-oxygen complex. Steam-carbon reactions are complicated by the water-gas shift, in itself a heterogeneous reaction taking place in the presence of carbon or metal oxides. However, the question of primary products has been found to be more complicated in the case of oxygen-carbon reaction wherein both CO and CO_2 are regarded as primary reaction products.[78 79] In a study involving the reaction of atomic oxygen with carbon films, Streznewski and Turkevich [80] reported carbon dioxide as the sole product of reaction as determined by mass spectrometric analysis.

The inhibiting influence of the product gases, that is carbon monoxide and hydrogen on gasification rate, is well known. An explanation of the inhibition is intimately tied with the reaction mechanism postulated. However, the inhibition effects of trace amounts of retardants, as for example water vapor and hydrogen, on the combustion of carbon, observed by Hoynant and coworkers,[81] is difficult to explain in the absence of knowledge of the absolute rate constants of each step in the reaction sequence. The proponents of sorption theories explained retardation by sorption of these gases on the reaction sites. For such an explanation to be valid it must be assumed that the reaction rate is largely determined by the concentration

of the adsorbed reactants on the surface,[82-84] and a distinction must be made between chemisorbed oxygen and carbon monoxide.[85] Ergun [86 87] explained the retardation effect by a dynamic oxidation-reduction equilibrium between the gas and solid phases. For this explanation to be valid the slowest step of the reaction must be the transfer of carbon from the solid to the gas phase.

Virtually every investigator of the reactions of carbon has been interested in determining the rate-controlling step, for a knowledge of this step has a practical as well as a theoretical consequence. Several workers proposed adsorption of carbon dioxide or steam [88-90] as the rate-determining step; some suggested the rate of formation of surface oxide [91-95]; however, a great many investigators proposed the breakdown of the surface complex. As mentioned earlier, several workers postulated two or three processes effective in different temperature ranges, the reactions being diffusion controlled in the higher ranges.

Possibly the major cause of the disagreements and confusion is the inadequate consideration of the solid state of carbon by most of the investigators. Since most of the carbons contain impurities, Arthur,[96] Long and Sykes,[97-99] Wicke,[1] Hennig,[2] and others have studied the catalytic effect of impurities on the gasification of carbon. Under certain conditions reaction rates of carbons undergo changes with burn off. Since some porosity is also developed with burn off, several workers, more recently Guerin and coworkers,[3-5] Cameron and Stacy,[6] Jolley and

[61] Work cited in footnote 47.
[62] Work cited in footnote 49.
[63] Work cited in footnote 41.
[64] Arthur cited in footnote 30.
[65] Work cited in footnote 31.
[66] Work cited in footnote 33.
[67] Reif, A. E., The Mechanism of Carbon Dioxide-Carbon Reaction: Jour. Phys. Chem., vol. 56, 1952, p. 785.
[68] Work cited in footnote 7.
[69] Work cited in footnote 53.
[70] Work cited in footnote 20.
[71] Work cited in footnote 26.
[72] Work cited in footnote 40.
[73] Arthur, J. R., Reactions Between Carbon and Oxygen: Trans. Faraday Soc., vol. 47, 1951, pp. 164-178.
[74] Wicke, E., and Rossberg, M., [Primary and Secondary Reactions in the Gasification of Coal with Steam]: Ztschr. Elektrochem., vol. 57, 1953, pp. 641-645.
[75] Goring, G. E., Curran, G. P., Zielke, C. W., and Gorin, E., Kinetics of Carbon Gasification by Steam. Mechanism of Interaction of Low-Temperature Char and Steam-Hydrogen Mixtures at 1600° F.: Ind. Eng. Chem., vol. 45, 1953, pp. 2586-2591, 2792.
[76] Bonnetain, L., Duval, X., and Letort, M., On the Role of Surface Oxides in the Graphite-Oxygen Reaction, Proc. 4th Biennial Conf. on Carbon, Pergamon Press, New York, N.Y., 1960, pp. 107-114.
[77] Deitz, V. R., and Prosem, E. J., Reaction of Carbon Monoxide With Graphitic Carbon at 450° C.: Nature, vol. 181, 1958, pp. 109-110.
[78] Work cited in footnote 11.
[79] Work cited in footnote 15.
[80] Streznewski, J., and Turkevich, J., The Reaction of Carbon With Oxygen Atoms: Proc. 3d Conf. on Carbon, Pergamon Press, New York, N.Y., 1958, pp. 273-278.
[81] Hoynant, G., Collart, F., Duval, X., and Letort, M., The Inhibitory Effect of Water Vapor and Hydrogen on the Combustion of Carbon: Compt. rend., vol. 246, 1958, pp. 2889-2892.

[82] Work cited in footnote 74.
[83] Warner, B. R., Pressure Dependence of the Rate of Gasification of Carbon: Jour. Am. Chem. Soc., vol. 66, 1944, pp. 1306-1309.
[84] Work cited in footnote 31.
[85] Work cited in footnote 30.
[86] Work cited in footnote 20.
[87] Work cited in footnote 45.
[88] Work cited in footnote 74.
[89] Work cited in footnote 83.
[90] Work cited in footnote 17.
[91] Work cited in footnote 75.
[92] Work cited in footnote 49.
[93] Paleev, I. I., and Yudin, V. F., The Reaction of Steam With Carbon-Containing Fuels; Gazovaya Prom., No. 5, 1957, pp. 10-16.
[94] Puri, B. R., Myer, Y. P., and Sharma, L. R., Oxygen Complexes of Charcoal; Chem. and Ind., British Ind. Fair Rev., April 1956, pp. R30-R31.
[95] Sihvonen, V., and Vuorela, A. A., Surface Reactions in the Combustion of Graphite; Ann. Acad. Sci. Fennicae, vol. A36, No. 8, 1933, 8 pp.
[96] Work cited in footnote 73.
[97] Long, F. J., and Sykes, K. W., The Catalysis of the Oxidation of Carbon; Journ. Chim. Phys., vol. 47, 1950, pp. 361-378.
[98] ———, The Effect of Specific Catalysts on the Reactions of the Steam-Carbon System; Proc. Roy. Soc. (London), vol. 215A, 1952, pp. 100-10.
[99] ———, The Catalysis of the Carbon Monoxide-Steam Reaction; Proc. Roy. Soc. (London), vol. 215A, 1952, pp. 111-119.
[1] Wicke, E., Contributions to the Combustion Mechanism of Carbon, Fifth Symposium (International) on Carbon; Reinhold Publishing Co., New York, N.Y., 1955, pp. 245-252.
[2] Hennig, G., Catalysis of Graphite Oxidation; Proc. 3d Conf. on Carbon, Pergamon Press, New York, N.Y., 1958, pp. 265-271.
[3] Bastick, M., Moutach, M., and Guerin, H. [The Variation of the Porous Structure of Cokes During Their Gasification With Carbon Dioxide and Water Vapor]: Compt. rend., vol. 243, 1956, pp. 1764-1766.
[4] Moutach, M., and Guerin, H. [On the Hydroreactivity of Cokes. I. Refinement of a Method for Measuring Hydroreactivity and Study of the Influence of Operating Conditions]: Bull. Soc. Chim. France, 1958, pp. 1008-1019.

Stantan,[7] Wicke,[8] and Walker and coworkers,[9] have focused their attention on the macrostructure of carbons and attempted to determine its significance on gasification. Although the influence of the macrostructure upon reaction rates, especially for massive pieces of solids, cannot be denied, parameters describing the macrostructure, that is, surface area and porosity, are not always relatable to reaction rates.

The importance of the solid state of carbon was stressed by Strickland-Constable[10] when he observed striking similarities among the reactions of nitrous oxide, carbon dioxide, water, and oxygen with carbon filaments. He attributed the similarities to the nature and behavior of carbon rather than to any specific similarities among the gases. Sihvonen[11][12] was first to observe that reaction rate of carbon filaments with oxygen decreased above 1,200° C. Eucken[13] and Meyer[14] confirmed this decrease and explained it by the theory of oxygen dissolved in the carbon lattice. According to the theory, below 1,200° C., the reaction rate is proportional to the amount of oxygen dissolved which, in turn, is proportional to the pressure; hence, it is a first order reaction. Above 1,200° C., the solution of oxygen in carbon diminishes; consequently, less and less of the combustion is affected by the process until ultimately the slower surface reaction becomes controlling. Meyer postulated that the reaction rate of carbon filament would be of zero order under these conditions. Strickland-Constable also observed a diminution of the reaction above 1,200° C., but he found the reaction to be of first order above 1,200° C., and fractional at the lower temperatures. He advanced the theory that N_2O, CO_2, and H_2O molecules react with carbon atoms on the edges of graphite planes. Above 1,200° C., edge carbon atoms would tend continually to take up more stable configurations in which they are less reactive, a process which he termed "healing." He further advanced the theory that oxygen behaves differently than the other gases because it can also react by

direct attack on the basal planes. Strickland-Constable further observed hysteresis effects, indicating that the reaction rate of a carbon filament also depended on the reaction temperature to which the filament was previously exposed. His theory of "healing," that is, change in the state of the terminal carbon atoms, explained the hysteresis effect satisfactorily.

In a detailed study of the reaction of carbon filaments with oxygen, Duval[15] also observed hysteresis effects when temperature or pressure was changed. He found the reaction rate to be of first order, both below and above 1,200° C., and carbon monoxide to be the sole product. He also observed that the surface area of a filament subjected to reactions at different temperatures and oxygen partial pressures remained the same. Like Strickland-Constable, Duval explained the hysteresis effects and the diminution of the reaction rate above 1,200° C. by changes in the solid state. He postulated that the attack of oxygen on the surface produces carbon atoms less tightly bound to the lattice, which are ready to react. Such a carbon atom would react with a colliding oxygen molecule or be "deactivated" by finding a more stable position in the lattice by surface migration, the latter course becoming more and more probable with increase in temperature. From the influence of oxygen on the thermionic emission of carbon, he concluded that no chemisorbed oxygen film was formed on the carbon.

L. Meyer had observed that the reaction rate of carbon filament with oxygen showed a second increase above 1,600° C., that is, following a minimum in reaction rate as a result of decrease in rate above 1,200° C. Duval found that this increase was caused by photoelectric discharge in the reaction chamber due to presence of mercury vapor. Upon eliminating the discharge by cooling with dry ice the traps separating the reaction chamber from other parts of the apparatus containing mercury vapor, he observed that the reaction rate above 1,600° C. remained constant, independent of temperature, and exactly of the first order.

With the advent of nuclear reactors, the use of graphite as a moderator caused a great impetus in research on carbon. Graphite became one of the most intensely studied materials and one of the few crystals whose electron energy band structure has been determined.[16] Conferences on carbon have been held in France,[17] Great Britain[18] and the United States.[19]

[5] ——— [The Hydroreactivity of Cokes. II. Comparative Study of the Reactivity of Cokes and of Their Microporosity]: Bull. Soc. Chim. France, 1959, pp. 102–115.
[6] Cameron, A., and Stacy, W. O., Changes in the Pore Structure of Coke During Carbonization and Gasification; Australian Jour. Appl. Sci., vol. 9, 1958, pp. 283–302.
[7] Jolley, L. J., and Stantan, J. E., Reactivity to Steam and Air of Coke made from Coals of Different Caking Properties and Rank; Conf. on Sci. in the Use of Coal, Univ. Sheffield, Sheffield, England, April 1958, Institute of Fuel, London, England, 1958, pp. E22–E26.
[8] Wicke, E., and Hedden, K. [The Significance of Inner Surfaces and of Diffusion Through Pores for the Combustion and Gasification of Porous Coals], Ztschr. Elektrochem, vol. 57, 1953, pp. 636–641.
[9] Walker, P. L., Jr., Rusinko, F., Jr., and Raats, E., Changes of Macropore Distributions in Carbon Rods Upon Gasification With Carbon Dioxide; Jour. Phys. Chem., vol. 59, 1955, pp. 245–249.
[10] Strickland-Constable, R. F., Interaction of Carbon Filaments at High Temperatures With Nitrous Oxide, Carbon Dioxide, and Water Vapor: Trans. Faraday Soc., vol. 43, 1947, pp. 769–778.
[11] Sihvonen, V., [On the Primary Reactions in the Oxidation of Graphite]: Ztschr. Elektrochem, vol. 40, 1934, pp. 456–460.
[12] ———, [The Reaction Mechanism of the Oxidation of Carbon at Low Pressures]: Ztschr. Elektrochem., vol. 36, 1930, p. 806.
[13] Work cited in footnote 47.
[14] Work cited in footnote 48.

[15] Duval, X., [Kinetics of the Combustion of Carbon at High Temperatures and Low Pressures]: Ann. chim., vol. 10, 1955, pp. 903–967.
[16] McClure, J. W., The Relation Between the Electron Energy Band Structure and the Electronic Properties of Graphite: Proc. 4th Biennial Conf. on Carbon, Pergamon Press, New York, N.Y., 1960, pp. 117–181.
[17] International Conference on the Combustion of Carbon, May 1949. University of Nancy, Nancy, France; International Conference on Carbon, May 1960, Paris, France.

Antal and coworkers [20] and Carter and Eggleston [21] have observed that neutron-induced changes in graphite may largely be healed by thermal annealing at temperatures of the order of 500° C. As stated earlier, thermal annealing was proposed by Strickland-Constable [22] and Duval [23] as an explanation of the decrease in the rate of combustion of carbon filaments above 1,200° C. Studies of thermal annealing of neutron-induced damage in graphite lattices suggest that thermal annealing would occur during gasification. Indeed, the present work supports this view.

A complicating factor is that the structure of amorphous carbons still remains a mystery. Until recently X-ray diagrams of amorphous carbons were interpreted to reveal that they are composed largely of graphitelike layers arranged turbostratically.[24] Therefore graphitelike layers were used as a model in explaining the role of the solid state in its physical and chemical properties. A recent study by Ergun and Tiensuu [25] revealed that the X-ray evidence on the graphitelike nature of amorphous carbons is by no means conclusive. Small tetrahedral (diamondlike) structures were found to yield X-ray patterns overlapping those of graphitelike layers. Hardness and nongraphitizability of some amorphous carbons tend to support their view. These findings show that the solid state of amorphous carbons is not yet fully understood.

[18] Conference on Industrial Carbon and Graphite, Society of Chemical Industry, London, England, September 1957.

[19] Conference on Carbon, University of Buffalo, Buffalo, N.Y., June 1953, June 1955, June 1957, June 1959.

[20] Antal, J. J., Weiss, R. J., and Dienes, G. J., Long Wavelength Neutron Transmission as an Absolute Method for Determining the Concentration of Lattice Defects in Crystals: Proc. 1st and 2d Conf. on Carbon, Univ. of Buffalo, Buffalo, N.Y., 1956, pp. 137–141.

[21] Carter, R. L., and Eggleston, R. R., Moderator Graphite for High Temperature Reactors: Proc. 1st and 2d Conf. on Carbon, Univ. of Buffalo, Buffalo, N.Y., 1956, pp. 149–153.

[22] Work cited in footnote 10, p 8.

[23] Work cited in footnote 15, p 8.

[24] Franklin, R. E., The Interpretation of Diffuse X-Ray Diagrams of Carbon: Acta Cryst., vol. 3, 1950, pp. 107–121.

[25] Ergun, S., and Tiensuu, V. H., Tetrahedral Structures in Amorphous Carbon: Acta Cryst., vol. 12, 1959, pp. 1050–1051.