CHEMICAL AND THERMOMAGNETIC STUDIES ON IRON CATALYSTS FOR SYNTHESIS OF HYDROCARBONS

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## INTRODUCTION

In their early work on the reaction of carbon monoxide with hydrogen in the presence of iron catalysts, F. Fischer and H. Tropsch used alkalized iron filings. At 100 atmospheres pressure and temperatures between 350° and 450°C., they obtained a mixture of different types of oxygenated compounds, named synthol. For synthesis at atmospheric pressure, Fischer and Tropsch used iron catalysts (prepared, for instance, by decomposition of iron nitrate) which were activated further by the addition of such substances as copper, manganese, or alkali. At atmospheric pressure, a yield of 30 to 40 grams of liquid aliphatic hydrocarbons per cubic meter of water gas was obtained with these catalysts. In the period from 1934 to 1936, Fischer and coworkers succeeded in doubling the yield by using precipitated iron catalysts having a maximum life of 4 to 6 weeks. When Fischer and Pichler used iron catalysts at medium pressure (1937 to 1940), they obtained yields of 130 to 150 grams of liquid and solid hydrocarbons per normal cubic meter of carbon monoxide–hydrogen mixture. The life of these catalysts ranged from many months to several years. The precipitated iron catalysts were pretreated with carbon monoxide-rich gas at atmospheric or lower pressure, and then operated in the synthesis at pressures between 10 and 30 atmospheres. An especially active catalyst, for instance, was formed by pretreating with carbon monoxide at 0.1 atmosphere and 325°C. and subsequently operating the synthesis with water gas at 15 atmospheres and at 210° to 230°C.

Fischer and Pichler's pretreatment of iron catalysts for synthesis at medium pressure differs fundamentally from that of catalysts containing nickel or cobalt. The latter may be pretreated by reduction with hydrogen. The activity of iron catalysts reduced with hydrogen at different temperatures to Fe_3O_4 or to metallic iron was no greater than that of untreated iron catalysts when used in the hydrocarbon synthesis at atmospheric or at higher pressures.

Pressures of 10 to 30 atmospheres were particularly suitable for the synthesis. If an iron catalyst were used at this pressure without pretreatment, however, satisfactory reactivity of carbon monoxide–hydrogen mixtures would be obtained only at high temperatures, that is, 280° to 300°C.; and at these temperatures the fraction of undesirable gaseous hydrocarbons would be large. When, however, iron catalysts were treated with carbon monoxide-rich gas (for example, pure carbon monoxide or water gas) at pressures lower than those used for the synthesis (atmospheric pressure or preferably lower), the high activity of the catalysts resulted in satisfactory synthesis of chiefly liquid and solid aliphatic hydrocarbons at temperatures between 220° and 230°C.

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Thus, carburization made it possible to lower the synthesis temperature by 60° to 80°C. The increased activity persisted even after the catalyst had been used over a period of months.

The hydrocarbon synthesis occurs according to the following generalized equations:

$$2xCO + xH_2 = (CH_2)_x + xCO_2$$
$$xCO + 2xH_2 = (CH_2)_x + xH_2O$$
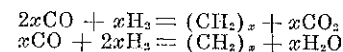
Carbon dioxide and water are formed in addition to hydrocarbons (paraffins and olefins in varying proportions, depending on the conditions of the reaction). Lowering the synthesis temperature, increasing the synthesis pressure, and increasing the hydrogen content of the synthesis gas favor the formation of water. An increase in temperature, a decrease in pressure, and an increase in the carbon monoxide content of the synthesis gas favor the formation of carbon dioxide. The consumption of carbon monoxide is generally somewhat higher than that of hydrogen. The two components in the synthesis gas should be present in the same ratio in which they react for optimum efficiency.

REVIEW OF LITERATURE

HETEROGENEOUS CATALYSIS

In their earliest publication on the gasoline synthesis, Fischer and Tropsch[59] discussed the mechanism of the reaction between carbon monoxide and hydrogen to form hydrocarbons. It was assumed that carbon monoxide and metal react first to form carbides (the formation of higher carbides is thus to be expected) and that hydrogen then reacts with carbidic carbon to form (CH_2) radicals. These methylene groups polymerize to form more or less saturated hydrocarbon chains.

The synthesis proceeds by way of heterogeneous catalysis. It is known that, when a gaseous reaction is catalyzed by a solid, condensation of the gaseous substances on the catalyst surface (that is, physical adsorption) is a necessary but not always sufficient condition for catalytic activity. Of great importance is the selective chemical effect exercised by the specific molecular forces of the catalyst surface on the reacting molecules and resulting in a decrease of the activation energy. According to Taylor,[60] a specific effect on the reacting molecules is exerted only by certain well-defined areas of the macroscopic surface. Eckell[61] observed that the specific catalytic structure is intimately related to lattice deformation.

For highly dispersed substances, the configuration of the inner surfaces is extremely significant, since their active centers are accessible to gases only by diffusion (Schwab and Zorn[62]). Graue and Riehl[63] have shown that gases do not penetrate into catalysts

[59] Fischer, F. and Tropsch, H., work cited in footnote 8 (p. 3).
[60] Taylor, S. [Active Centers and Catalysts]: Ztschr. Elektrochem., vol. 35, 1929, pp. 542–548.
[61] Eckell, J. [Relationship between Catalyst Structure and Chemical Reaction]: Ztschr. Elektrochem., vol. 39, 1933, pp. 433–439.
[62] Schwab, G., and Zorn, H. [Kinetics of Hydrogenation of Ethylene on Skeletal Catalysts]: Ztschr. physik. Chem., vol. B32, 1936, pp. 169–201.
[63] Graue, G., and Riehl, N. [Pore Diameter and Internal Volume of Amorphous and Crystalline Substances]: Ztschr. anorg. allgem. Chem., vol. 233, 1937, pp. 365–375.

through the large pores alone. Where there is random distribution or where the arrangement of the lattice lacks regularity, the irregular spacing of the atoms allows penetration even through openings of atomic dimensions. According to Graue and Koch,[64] the atomic pores of highly dispersed materials remain accessible by the addition of certain substances.

The catalyst surface is important not only because of its geometrical configuration but even more because of its electric fields. The influence of these specific fields (active centers) on the reagents is shown by the catalyst's affinity for them; this affinity constitutes the essential condition of catalytic activity. Thus, adsorption of hydrogen and carbon monoxide by a catalyst is a reversible chemical adsorption and much stronger than a physical adsorption. Moreover, the favorable relationship of catalyst to reagent does not depend solely on the material nature of the reacting substances but is a function of the atomic radii (or atomic distances) of the reagent and of the atomic spacings (or lattice structure) of the catalyst.

The effect of promoters in activated catalysts has been the subject of extensive research by numerous investigators. X-ray studies of ammonia catalysts were used by Wyckoff and Crittenden,[65] as well as by Brill,[66] to show that certain additions produce their activating effect by favoring the formation of numerous active points and by stabilizing these specifically active metal particles.

According to a theory formulated by Ipatieff,[67] increased activity is not explained satisfactorily as a purely physical effect of the promoters resulting in arrested recrystallization and preservation of the surface. Experiments with promoted catalysts led this author to the conclusion that a new source of energy contributes to catalysis. He assumes that contact of the metallic promoter with the basic catalyst produces electric energy. Ipatieff believes that the metallic oxide promoters participate in the reaction according to their chemical nature, thus assisting the catalyst in utilizing the reaction energy. This would mean, for instance, that thoria in a cobalt-thoria-kieselguhr catalyst acts not only by its stabilizing influence on the specific structure of the catalyst but actually takes part in the reaction as a dehydrating agent. An activating agent may thus operate by physical, chemical, or physicochemical means.

In certain cases a relationship is also known to exist between magnetic properties and catalytic activity. Thus, the conversion of ortho- and para-hydrogen is catalyzed by paramagnetic ions, the rate of conversion increasing with increasing magnetic moment of the ions.[68] The so-called magnetocatalytic effect is based on similar phenomena. From a large body of experimental evi-

* [64] Graue, G., and Koch, H. [Diffusion of Gases in Solids, Studies on Iron Oxide and Iron-Aluminum Oxide]: Ber. Deut. chem. Gesell., vol. 73, 1940, pp. 984–995.
[65] Wyckoff, R. W. G., and Crittenden, E. D., An X-ray Examination of Some Ammonia Catalysts: Jour. Am. Chem. Soc., vol. 47, 1925, pp. 2866–2876.
[66] Oppau Experimental Laboratory, unpublished work, 1925.
[67] Ipatieff, V. N., Mixed Catalysts: Petrol. Refiner, vol. 19, 1940, pp. 250–255.
[68] Farkas, A., and Farkas, L., Ortho-, Para-, and Heavy Hydrogen: MacMillan Co., New York, 1935, 215 pp.

dence, Hedvall[69] reported a change in catalytic activity above the Curie-point temperature. The magnetocatalytic effects of nickel–iron catalysts on the decomposition and hydrogenation of carbon monoxide are of particular interest in this connection. The change in activity that occurs at the Curie point is due to electronic changes.[70]

Fe-C-O SYSTEM (EXCLUDING HIGHER IRON CARBIDES)

It has already been stated that treatment of iron catalysts with carbon monoxide before synthesis is desirable. The study of the reactions that accompany this pretreatment is very closely related to the problem of carburization of iron and iron oxides.

Much has been written on the decomposition of carbon monoxide on iron. The literature will be considered here only to the extent to which it relates to iron carbides and explains the processes that occur during pretreatment.

It had long been assumed that the decomposition of carbon monoxide on iron results in formation of carbide,[71] but no particular importance was attached to this reaction. According to Boudouard,[72] the rate of the reaction,

$$2CO = CO_2 + C + 39 \text{ kcal.},$$

is increased by the presence of iron oxides. Schenck and Zimmermann[73] assume that the rate is increased only by the free metal, particularly when finely divided. According to them, the iron acts solely as a catalyst as long as sufficient carbon monoxide is present, whereas it takes part in the reaction when the equilibrium ratio of carbon monoxide to carbon dioxide is exceeded.

The problem of oxidation, reduction, and carburization equilibria of the system Fe–C–O, at temperatures ranging from 500° to 1,100°C., has been studied by Schenck.[74] In the solid phase, Fe_3O_4, FeO, Fe, Fe_3C, and C may coexist. Solid solutions of iron oxides in each other are known as wüstite, and those of a metallic character, formed by the solution of ferrous oxide in free iron, are known as oxoferrite. In contrast to the oxidation and reduction equilibria, the carburization equilibria were pressure-dependent, the carbiding reaction being accompanied by a change in the number of gas molecules. Cementite participates in the establishment of equilibrium even at temperatures below 400°C. On the other hand, reduction of iron oxides by free carbon does not begin until 680°C.

In connection with the action of promoters, it should be noted that oxides may cause a shift in the equilibrium between gas and

[69] Hedvall, J. A., and Gustavson, E. [Catalytic Activity and Ferromagnetism]: Svensk Kem. Tids., vol. 46, 1934, pp. 64–65; Chem. Abs., vol. 28, 1934, p. 4971[6].
[70] Reinäcker, G. [Heterogeneous Catalysis and Atomic Structure]: Die Chemie, vol. 57, 1944, pp. 85–90; Chem. Abs., vol. 40, 1946, p. 4593 (review).
[71] Stammer, K. [Phenomena Connected with Reduction, Especially of Iron by Carbon Monoxide]: Ann. Chem., vol. 82, 1851, pp. 136–141.
[72] Boudouard, O. [Decomposition of Carbon Monoxide on Metallic Oxides]: Bull. Soc. Chim., Paris, vol. 21, 1899, pp. 463–465 and 712–713.
[73] Schenck, R., and Zimmermann, F. [Decomposition of Carbon Monoxide and Equilibrium in Blast Furnaces]: Ber. Deut. chem. Gesell., vol. 36, 1903, pp. 1231–1251.
[74] Schenck, R., and Dingmann, T. [Reduction, Oxidation, and Carburization Equilibria for Iron, III]: Ztschr. anorg. allgem. Chem., vol. 166, 1927, pp. 113–154.
Schenck, R. [Reduction, Oxidation, and Carburization Equilibria for Iron, IV–V]: Ztschr. anorg. allgem. Chem., vol. 167, 1927, pp. 254–328.
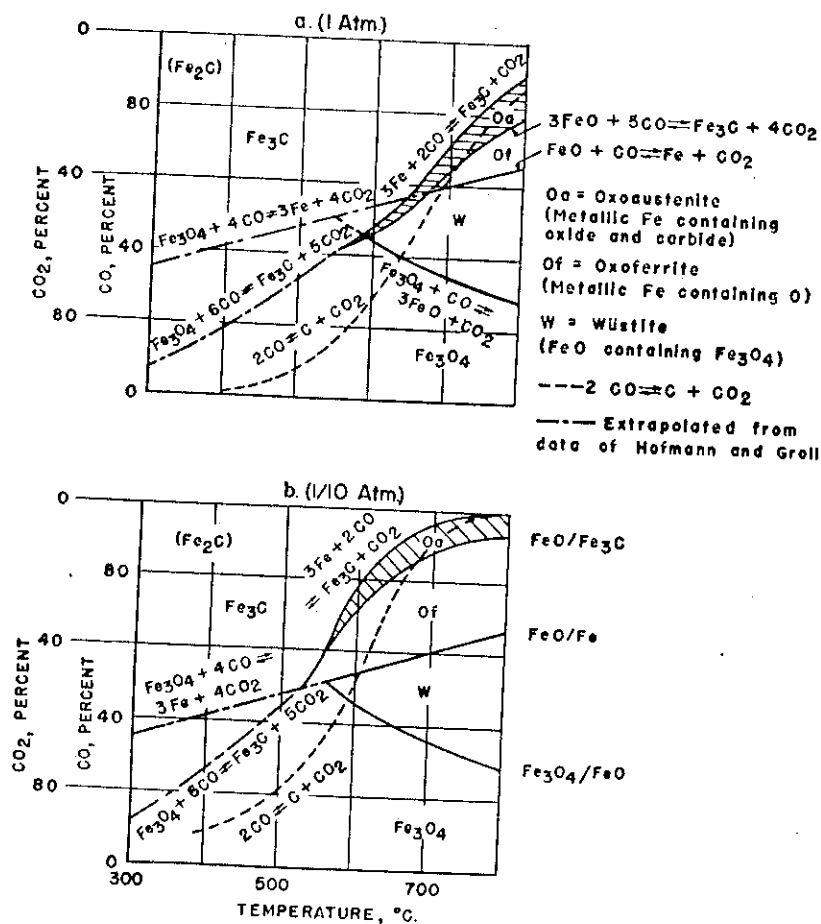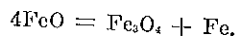
FIGURE 1.—Equilibria in the system Fe–C–O.

solid phase. Figure 1 shows the results of Schenck's equilibria studies. It will be seen from this equilibrium diagram that the lower limit of stability of FeO lies at 560°C.[75] Chaudron[76] had previously shown that this oxide decomposes below 560°C. according to the equation:

$$4FeO = Fe_3O_4 + Fe.$$

Using more recent data, Jänecke[77] also interpreted the system Fe–C–O quantitatively without taking the higher carbides into account.

[75] Editor's note. Figure 1 was incomplete and has been replaced by a complete diagram from Bureau of Mines Report 2774–Q:18 of September 1946, following p. 16, work cited in footnote 6 (p. 1).
[76] Chaudron, G. [Reversible Reactions of Hydrogen and of Carbon Monoxide with Metallic Oxides]: Ann. chim., vol. 16, 1921, pp. 221–281. [Reversible Reactions of Carbon Monoxide with Iron Oxides]: Compt. rend., vol. 172, 1921, pp. 152–155.
[77] Jänecke, E. [Equilibria in the System Fe–C–O]: Ztschr. anorg. allgem. Chem., vol. 204, 1932, pp. 257–290.

According to Tutiya,[78] who decomposed carbon monoxide in the presence of iron wire and powder, the catalytic effect of compact iron is very slight. During prolonged experiments there is a considerable increase in catalytic activity, accompanied by formation of iron carbide and disappearance of Fe–lines in the X-ray diagram. Consequently, the active catalyst is not iron itself but the carbide whose formation occurs upon decomposition of carbon monoxide:

$$3Fe + 2CO = Fe_3C + CO_2,$$
$$2CO = CO_2 + C.$$
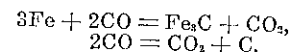
Similarly, Fischer[79] considered formation of carbide essential in the catalytic decomposition of carbon monoxide by iron. According to him, formation of carbide is associated with a disruptive action of carbon on iron, which results in a slow dispersion of iron in carbon. The favorable effect of iron carbide is neutralized by the deposition of a film of carbon on the crystals.

On the other hand, Baukloh[80] emphasized the catalytic action of metallic iron. A series of studies led him to the conclusion that carbon is deposited directly by carbon monoxide. For theoretical reasons, decomposition of carbon monoxide is considered to be a special case of adsorptive catalysis by metallic iron.

More recently, Körber, Wiemer, and Fischer[81] have given a clearer picture of the thermal decomposition of carbon monoxide on iron. They studied the decomposition of carbon monoxide streaming over powdered soft iron and over mixtures of powdered soft iron with graphite and cementite (in the form of crude iron powder) at temperatures from 300° to 1,200°C. Considerable decomposition of carbon monoxide by powdered soft iron was observed to start around 900°C. However, comparison with the equilibrium concentrations of the Boudouard curve indicates that this decomposition is to be attributed not to the catalytic action of the solid phase, but to chemical reaction between carbon monoxide and iron. Addition of graphite had no effect on the action of powdered soft iron. However, when cementite was added to the catalyst, carbon dioxide formation showed a sharp maximum between 500° and 600°C., the volume of gas depending on the amount of catalyst used. Because of their much smaller active surface, steel samples produced considerably less decomposition than powdered or pressed iron.

Results obtained with various catalysts in isothermal reactions are revealing. In the presence of pig-iron powder containing cementite, considerable carbon dioxide was evolved as soon as the operating temperature was reached, and a final value of about 65 percent of carbon dioxide was approached. However, when powdered soft iron was used, an induction period of several hours was always needed for the carbon dioxide content to attain the same final value.

[78] Tutiya, H., work cited in footnote 43.
[79] Fischer, F., and Dilthey, P. [Preparation of Pure Carbon at a Low Temperature]: Ges. Abhndl. Kenntnis Kohle, vol. 8, 1928, pp. 234–255.
[80] Baukloh, W., and Edwin, B. [Effect of Temperature and Pressure on the Decomposition of Carbon Monoxide and the Mechanism of Carbon Deposition]: Arch. Eisenhüttenw., vol. 16, 1942, pp. 197–200.
[81] Körber, F., Wiemer, H., and Fischer, W. [Thermal Decomposition of Carbon Monoxide on Iron and Its Alloys and Mixtures with Carbon]: Arch. Eisenhüttenw., vol. 17, 1943, pp. 43–52.

FORMATION OF HIGHER CARBIDES BY ACTION OF CARBON MONOXIDE ON IRON

Hilpert and Dieckmann[82] studied the course of carbon deposition on Fe_2O_3 at about 800°C. The results showed that the decomposition of carbon monoxide is catalyzed by the iron carbide, Fe_3C. Carburization of this carbide is assumed to give carbides with a higher carbon content, such as Fe_2C or FeC, which decompose with elimination of carbon. The authors believe that their theory is supported by the manner in which steels (quenched at 900°C. and tempered at 200° to 600°C.) behave on acid decomposition. Thermomagnetic study of the carburized product showed a Curie point of 200°C. The magnetic transition point (Curie point) is defined in this paper as the point of inflection on the specific magnetization-temperature (thermomagnetic) curve. At that time the recorded data concerning the magnetic transition point of the iron carbide, Fe_3C, showed considerable variation, thus leaving the authors in doubt as to the homogeneous nature of the product.

In an article on the carbon monoxide–carbon dioxide equilibrium obtaining during the decomposition of carbon monoxide on iron, Falcke[83] concurred with the Hilpert and Dieckmann theory on the formation of higher iron carbides, but without contributing any experimental evidence. Hilpert and Dieckmann received further support of a purely hypothetical nature from Schenck,[84] who assumed that higher carbides possess an unusually high vapor pressure of carbon to explain their high reactivity.

In contrast, Fischer and Bahr[85] were able to establish the existence of a higher iron carbide experimentally; by graphic determination of the amount of carbidic carbon in their carburization curves they found the formula Fe_3C_4. In evaluating the experimental results the iron combined with oxygen was assumed to be FeO. By reducing the carburized iron with hydrogen at 400°C., they arrived at the formula, Fe_2C. This discrepancy is attributed to the thermal instability of Fe_3C_4, which is said to decompose at higher temperatures:

$$Fe_3C_4 = Fe + 3C + Fe_2C.$$
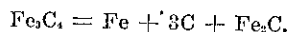
Mittasch and Kuss[86] likewise showed plausible experimental reasons for the formation of higher iron carbides. A nitrogen-hydrogen mixture acting on ferrous cyanide at 400°C. yielded a carbide to which they assigned the formula, Fe_2C. The compound is believed to decompose rapidly into iron, cementite, and carbon. Decomposition with sulfuric acid at 60°C. yielded a mixture consisting of 75 percent of hydrogen and 25 percent of hydrocarbons, calculated as methane.

[82] Hilpert, S., and Dieckmann, T., work cited in footnote 9 (p. —).
[83] Falcke, V. [Reactions of Iron Oxide with Coal and of Carbon Monoxide with Iron]: Ztschr. Elektrochem., vol. 22, 1916, pp. 121–133.
[84] Schenck, R. [The Relationships between Carbon and Oxygen]: Stahl u. Eisen, vol. 46, 1926, pp. 665–682.
[85] Fischer, F., and Bahr, H. [High-Carbon Carbides of the Iron Group]: Ges. Abhandl. Kenntnis Kohle, vol. 8, 1928, pp. 225–269; Chem. Abs., vol. 25, 1931, p. 2932.
[86] Mittasch, A., and Kuss, E. [Synthesis of Ammonia with Catalysts Made from Complex Iron Cyanides]: Ztschr. Elektrochem., vol. 34, 1928, pp. 159–170.

Gluud, Otto, and Ritter[87] investigated more thoroughly the formation of a higher iron carbide from iron oxide, using a current of carbon monoxide at low temperature, then passing a stream of hydrogen at 275°C. and atmospheric pressure over the surface, and determining the carbidic carbon as methane. The decarburization curves led the authors to postulate the formation of the carbide, Fe_2C. The same result was obtained when the authors distinguished free carbon from carbidic carbon in their carburization curves. According to these curves, 10 to 12 parts of carbon are associated as the carbide with 100 parts of iron. Bahr and Jessen,[88] upon repeating the work of Gluud and Ritter, found that the decarburization temperature should be carefully controlled. According to these authors, free carbon on iron oxide was hydrogenated at temperatures as low as 280°C., whereas free carbon deposited on pure iron reacted with hydrogen only at 320°C. Experiments in decarburization with hydrogen always produced 7 to 8 percent of carbidic carbon. Consequently, the quantity of carbon hydrogenated was always greater than that corresponding to the carbon content of cementite, but less than that corresponding to Fe_2C. At 225°C., however, metallic iron could be carburized to a point corresponding to Fe_2C; no further carbon was then taken up. At higher carburization temperatures, Bahr and Jessen again obtained products containing 7 to 8 percent of carbidic carbon. At temperatures above 400°C. the carbon content decreased to that of Fe_3C.

Tutiya[89] suggested that carbon monoxide decomposition on iron catalysts is accompanied by the formation of a higher iron carbide. In fact, he considers this compound to be the sole product of the carburization of magnetite at low temperatures. No cementite, ferrous oxide, and iron were found. At 280° to 320°C., carbiding of Fe_3O_4 by carbon monoxide yielded a mixture of Fe_3C and Fe_xC. As the carburization temperature was increased, the amount of cementite was increased at the expense of the higher carbide. From the point of view of the problems discussed in the present work, it is significant that at 270°C. the Fe_xC carbide is formed not only from iron and iron oxides but also from cementite.

Hofmann[90][91] studied the formation of carbon, iron oxide, and iron carbide during carburization. Using oxygen-free carbon monoxide and extremely pure iron, prepared from iron pentacarbonyl, this investigator found that when carbon monoxide was passed over iron at temperatures up to 560°C., magnetite was always present, together with carbon, cementite, and very small amounts of iron. From 560° to 655°C. the solid phase contained principally ferrous oxide and carbon, very little cementite, iron, and magnetite. The presence of the oxides was established by X-ray analysis and by determination of the oxygen content.

[87] Gluud, W., Otto, K. V., and Ritter, H. [Formation of Fe_2C During Reduction of Iron Oxide with Carbon Monoxide at a Low Temperature]: Ber. Deut. chem. Gesell., vol. 62, 1929, pp. 2483–2485.
[88] Bahr, H. A., and Jessen, V., work cited in footnote 48.
[89] Tutiya, H., work cited in footnote 44.
[90] Hofmann, U. [Carbon Deposition from Carbon Monoxide and Benzine on Iron]: Ber. Deut. chem. Gesell., vol. 61, 1928, pp. 1180–1195.
[91] Hofmann, U., and Groll, E., work cited in footnote 42.

Above 655°C. oxides were no longer found, but cementite was always present. An oxygen-free product was obtainable at 655°C. only at an extremely high rate of flow. At high rates of flow, the carbon dioxide produced during the carbiding reaction was carried away so rapidly that its concentration did not reach the value necessary for the iron–magnetite or iron–ferrous oxide equilibrium. Under these conditions Hofmann found only iron and cementite in the product.

It was determined, moreover, that whenever free carbon is deposited, cementite is present in the solid phase. However, decomposition of cementite accompanied by elimination of carbon at temperatures below 450°C. appears extremely unlikely, since cementite is not decomposed at this temperature in an atmosphere of nitrogen. A purely catalytic acceleration of the reaction,

$$2CO = CO_2 + C,$$
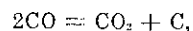
also appears unlikely. The properties of the carbon deposited from carbon monoxide on iron at low temperature indicate that elimination of carbon occurs (through slight supersaturation) from a primary iron carbide. The size of the carbon crystallites thus obtained is quite different from the size of lustrous carbon which forms at the same temperature by simple thermal decomposition of benzine vapor.

This assumption of a higher carbide receives additional support from the fact that X-ray analysis of iron preparations which were treated with carbon monoxide at temperatures below 400°C. (for example at 320°C.) showed interference lines indicative of an unidentified crystal lattice. The majority of these lines coincided with those obtained by Brill and Mark[92] for the decomposition of ferrous cyanide. In accord with Mittasch,[93] the lines were thought to be those of an unknown carbide. Hofmann believed this to be the higher iron carbide first described by Hilpert as an intermediate in carbon formation. Above 400°C. no lines of this carbide were observed, very probably because of its lack of stability in this region. The iron, which may be liberated (with formation of free carbon) by decomposition of the higher carbide, appears to react again rapidly, since X-ray analysis of the solid phase showed the iron content to be very low below 655°C. It is interesting to note that at low carbiding temperatures no ferrous oxide is formed, and that the interference lines observed for iron oxide are those of magnetite. In accord with observations made by Schenck, the limits of stability of ferrous oxide are between 560° and 660°C.

In his experiments on the role of catalysts in heterogeneous catalysis, Göthel[94] used the change in the electric resistance of powdered-metal catalysts during reaction. It was observed that carburization of powdered-iron catalysts was accompanied by an increase in electric resistance, which decreased again upon treatment with hydrogen. This increase in resistance was explained by carbide and oxide formation. The action of a carbon monox-

[92] Brill, R., and Mark, H., work cited in footnote 30.
[93] Mittasch, A., and Kuss, E., work cited in footnote 86.
[94] Kröger (editor) [Surface Catalysis]: Hirzel, Leipzig, 1933.

ide–hydrogen mixture also increased the resistance. Göthel arrived at an interpretation of the fundamental process of carbon monoxide decomposition, according to which carbon monoxide is chemisorbed by iron. The carbon-to-oxygen bond of these surface compounds was believed to be loosened so that adjacent carbon monoxide molecules react with each other to form carbon dioxide. The carbide thus formed was assumed to be Fe_2C.

THERMOMAGNETIC STUDY ON CARBURIZED IRON

Thermomagnetic studies of ferromagnetic substances have been used successfully in the determination of cementite, particularly in mixtures of iron and iron oxides. Early work in this field included the determination of iron and cementite in iron synthetic ammonia catalysts by Mittasch and Kuss,[95] and the above-mentioned work by Hilpert.[96] Magnetization curves, plotted as a function of temperature, showed that decomposition of complex iron cyanides resulted in the formation of cementite and iron. Magnetic studies by Körber, Wiemer, and Fischer[97] of the products obtained by carburization of iron catalysts are more directly concerned with the formation of such catalysts. From the thermomagnetic curve, which showed an inflection point above 250°C., the authors concluded that cementite was formed. The probable catalytic effect of this carbide on the decomposition of carbon monoxide was indicated by the fact that the quantity of carbide remained constant in spite of the formation of large amounts of carbon. However, the question remained as to whether carbon is deposited by way of higher carbides or directly from carbon monoxide. The thermomagnetic curves gave no evidence of the formation of other carbides. In addition, magnetic studies of the carburization of iron powder at 500°C. showed that all but 3.5 percent of the iron was converted to Fe_3C.

More recently Lange and Mathieu[98, 99] used the thermomagnetic method to study steels. Magnetic saturation was determined with remarkable accuracy by means of a suitable magnetic balance, thus making the quantitative determination of the carbide and ferrite content of steels readily possible.

An interesting variation of the magnetic method is the procedure reported by Westerhoff,[1] in connection with work on changes in magnetic properties of catalysts used for heterogeneous catalytic reactions. This method is based on the fact that the ferromagnetic catalyst forms part of a tuned electric circuit which is coupled with a second one having a constant frequency. Any change in the permeability of the catalyst is accompanied by a change in the self-induction and consequently a change in the frequency of its circuit.

[95] Mittasch, A., and Kuss, E., work cited in footnote 86.
[96] Hilpert, S., and Dieckmann, T., work cited in footnote 9 (p. —).
[97] Körber, F., Wiemer, H., and Fischer, W. A., work cited in footnote 81.
[98] Lange, H., and Mathieu, K. [The Progress of Austenite Transformation in the Undercooled State of Iron–Nickel–Carbon Alloys]: Mitt. Kaiser-Wilhelm Inst. Eisenforsch., Düsseldorf, vol. 20, 1938, pp. 125–134, 239–246; Chem. Abs., vol. 32, 1938, p. 7878[6].
[99] Mathieu, K. [Measurements of Specific Magnetization and Their Use in Problems of the Metallurgy of Iron]: Arch. Eisenhüttenw., vol. 16, 1943, pp. 415–423.
[1] Kröger (editor) [Surface Catalysis]: Hirzel, Leipzig, 1933.

The magnetic studies in the present work are concerned with iron and its ferromagnetic compounds. The known magnetic transition points of these substances are given in table 3.

TABLE 3.—*Curie points of iron and its ferromagnetic compounds*

Substance	Curie point, °C.	Investigator	Year
Fe	750	P. Curie	1891
	785	Jensen	1914
	769	Honda	1914
	768	Lange	1933
Fe₃C	180	Woloedine	1909
	215	Honda	1917
	215		1923
	215	Mittasch	1923
	210	Tammann	1922
	205	Lange	1933
Fe₃O₄	570	Huggett	1928
	510	Ischiwara	1917
	575	Takagi	1913
	565	Mathieu	1933
Fe₂O₃ (cubic)	500	Hilpert	1909
	650	Abraham	1925
	600	Chevallier	1927
	675	{Huggett / Chaudron}	1928
K₂O·Fe₂O₃	150	Hilpert	1909
CuO·Fe₂O₃	455	{Forestier / Chaudron}	1925

SUMMARY

Definite information is available concerning the equilibria between the gas and solid phases during the decomposition of carbon monoxide by iron and iron oxides. On the other hand, interpretations of the reactions occurring in the solid phase are not consistent. In evaluating the experimental results, it is convenient to differentiate among carbide reactions at high (above 900°C.), medium, and low (below 320°C.) temperatures.

The range of medium temperatures (400° to 500°C.) is characterized by the deposition of large amounts of free carbon, whereas the conditions existing at lower temperatures favor formation of carbide. Below 900°C., iron is generally thought to catalyze the decomposition of carbon monoxide in either one or both of two possible ways: (1) Surface catalysis of the decomposition of carbon monoxide by iron; and (2) formation of intermediate, unstable higher iron carbides from carbon monoxide, which decompose to yield free carbon. Iron carbide and/or metallic iron can be considered the active catalytic agent. The theory of catalytic higher carbides was at first hypothetical in character but has since received support from the observation of unfamiliar interference lines in X-ray patterns of iron preparations treated with carbon monoxide at low temperatures. Formation of iron carbides higher in carbon content than cementite is also suggested by the easily reducible carbon obtained by hydrogen reduction of iron preparations that had been carburized at low temperatures. However, the evidence available cannot be con-

sidered as proof of the existence of higher iron carbides. It should be noted, for instance, that activated carbon, located in the interstices of the iron lattice, reacts with hydrogen at low temperatures to yield methane. The problem of whether the product obtained upon carburization at low temperatures is a single carbide or mixture of carbides deserves further consideration. As long as this question remains unsolved, there is no justification for the derivation of carbide formulas from carburization and decarburization curves. Although the results of magnetic studies have proved the formation of cementite from the decomposition of carbon monoxide over iron, they have as yet produced no information about the formation of higher carbide nor about the mechanism of carburization.