[Contribution of the Research and Development Branch, Office of Synthetic Liquid Fuels, Bureau of Mines]

Mode of Transition from Hägg Iron Carbide to Cementite[1]

By E. M. Cohn and L. J. E. Hofer

In a previous publication,[2] the reaction

$$\underset{\text{Hägg carbide}}{3Fe_2C} \longrightarrow \underset{\text{Cementite}}{2Fe_3C} + \underset{\text{Free carbon}}{C}$$

has been noted to go to completion at 550° in about one hour, but the mode of transition from one carbide to the other was not known. The study of this transition by means of X-ray diffraction powder patterns appeared to present a formidable problem in view of the fact that the X-ray diffraction patterns of the two carbides are similar in many respects[2] and are very complex. Furthermore, the pattern of Hägg carbide is rather diffuse when obtained with preparations of small crystallite size. It has been possible, however, to follow this reaction by means of careful thermomagnetic measurements. A discontinuous precipitation was clearly shown by the invariance of the Curie points of the two ferromagnetic phases: The Curie point of cementite appeared at 209° initially and became more pronounced (at the expense of that of Hägg carbide, 245°) as the amount of cementite increased.

Experimental

Preparation of Hägg Carbide.—A precipitated iron oxide containing Fe:Cu:K_2O::100:10:0.32 (Bureau of Mines No. P3003.1)[2] was reduced with hydrogen at 208° for 1164 hours and then carburized with carbon monoxide at 170° for 464 hours. The final carbon:iron weight ratio was 0.1075, corresponding almost exactly to the stoichiometric ratio for Fe_2C. X-Ray analysis of the product showed the presence of hexagonal close-packed Fe_2C[2] and metallic copper. The thermomagnetic curve revealed that all the iron had been carburized, the main ferromagnetic constituent being hexagonal close-packed carbide, and that a very small amount of Hägg carbide was present.[3] This fact is brought out more clearly by the differential thermomagnetic curve of Fig. 1, where the change of magnetic moment between successive readings is plotted as a function of temperature, so that Curie points appear as maxima rather than as points of inflection. The sample was heated to 420° and then cooled slowly; this treatment sufficed to convert the hexagonal carbide quantitatively to Hägg carbide.

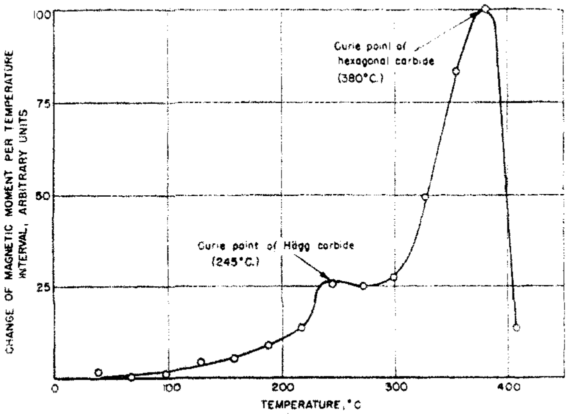

Fig. 1.—Differential thermomagnetic curve of carburized iron.

Conversion of Hägg Carbide to Cementite.—Conversion of the Hägg carbide to cementite was accomplished by successive heat treatments at 525°; the heating schedule is shown in Table I. After each heat treatment, the sample was cooled rapidly to about 300° to suppress further reaction, and then cooled very slowly while the magnetic moments were determined at intervals of 7° between 258° and 187° at a constant field strength of 550 gauss. This field strength was probably insufficient for magnetic saturation of the carbides, but the low value was chosen to accentuate the Curie points.[4] There was still a small amount of Hägg carbide left at the end of the experiment, as evidenced by a slight inflection of the thermomagnetic curve near 245°. The results of the measurements are plotted in Fig. 2, which shows that the greatest change of magnetic moment occurs near 225° (about midway between the two Curie points), so that measurements at that temperature are most sensitive for following the course of the transformation. Kinetic studies of this system are planned.

Table I

Heating Schedule for Conversion of Hägg Carbide to Cementite

Heating period	Time at 525° minutes	Total time at 525°, minutes
I	0	0
II	10	10
III	10	20
IV	20	40
V	30	70
VI	60	130
VII	120	250
VIII	240	490

Discussion

The data of Fig. 2 are most readily interpreted when represented in differential form as in Fig. 3. Here (as in Fig. 1) the change of magnetic moment per 7° temperature interval is plotted as a function of temperature. To avoid confusion, runs I, IV and VIII only are shown completely. In all runs, only the characteristic Curie points of Hägg carbide and of cementite were observed, the peaks of the latter becoming more pronounced at the expense of those of the former as the reaction proceeded. This behavior is indicative of discontinuous transformation, as pointed out, for example, by Mehl and Jetter[5]; and it is consistent with the fact that the Hägg carbide (the iron percarbide of Jack) has a narrow range of composition near 31 atom-per cent. carbon,[6] while the narrow range of

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[1] Article not copyrighted.

[2] Hofer, Cohn and Peebles, This Journal, **71**, 189–195 (1949).

[3] The mode of transition from hexagonal iron carbide to Hägg carbide will be described elsewhere.

[4] Hofer and Cohn, *Anal. Chem.*, **22**, 907-910 (1950).

[5] Mehl and Jetter in Sympos. on Age Hardening of Metals, 380–382 (1939); published by Am. Soc. Metals, Cleveland, Ohio.

[6] Jack, *Proc. Roy. Soc. (London)*, **195A**, 34–61 (1948).

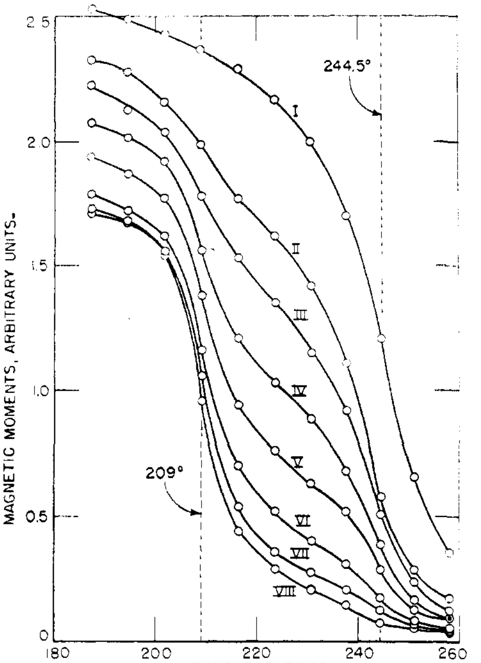

Fig. 2.—Thermomagnetic curve showing discontinuous transition from Hägg carbide to cementite.

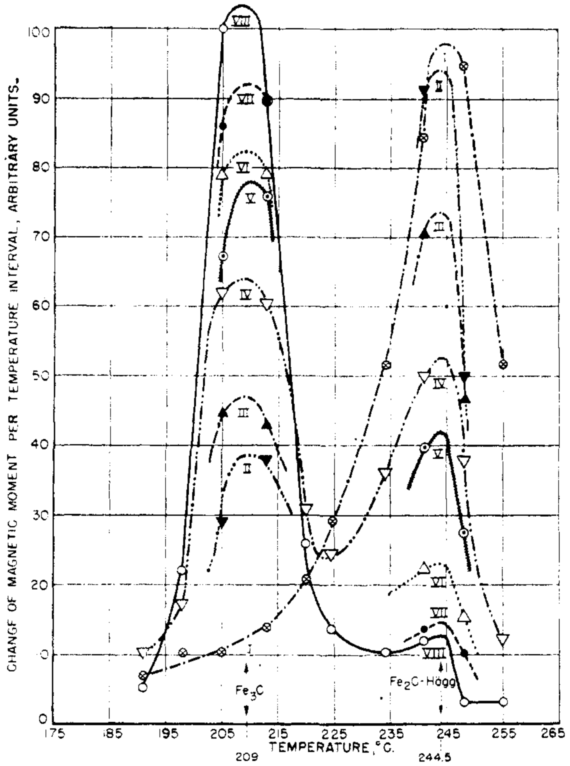

Fig. 3.—Differential curve derived from Fig. 2.

composition of cementite does not approach the lower limit of that of Hägg carbide. The constancy of the Curie points supports these data; it demonstrates the coexistence of these two carbides without the formation of intermediate solid solutions during the transition; and it makes very improbable Kölbel, Ackermann, Juza and Tentschert's[7] assumption of possible solid solutions of the carbides in each other during the Fischer–Tropsch synthesis. These authors also state that the Curie points of the carbides are probably functions of the carbon content of the carbides. However, the ranges of the Curie points of Hägg carbide and of cementite are sufficiently narrow (because of the narrow limits of composition) so that both can be determined in mixtures of the two phases, in spite of their proximity, by the use of a suitable experimental technique. Unless proper conditions are chosen (low field strength, slow rate of cooling or heating near Curie points, and measurement of magnetic moments at narrow temperature intervals), a resolution of the Curie points is virtually impossible, and the transition may seem to be continuous.

The work of Kölbel, *et al.*, is rather misleading in its interpretation of the iron carbides. In the first published account,[8] Hägg carbide was referred to as "unstable cementite" (see also ref. 2). In their formal publication,[7] the authors postulate the existence of a "labile" carbide with a Curie point near 220°. This is again the Hägg carbide, and their experimental results clearly show the Curie point of about 245°. It is difficult to understand why these authors were unable to deduce the correct Curie points from their thermomagnetic curves, and why they should have misquoted LeClerc and Lefebvre[9] who—while admittedly misinterpreting their results—specifically mentioned the Curie point as 250° and not 220°, as stated by Kölbel, *et al.* There is thus no basis for the assumption of an "unstable" cementite or a "labile" carbide. The disappearance of small quantities of "labile" Hägg carbide during thermomagnetic analysis is due to chemical reactions which will be described elsewhere. Kölbel, *et al.*, obtained the Curie point of the hexagonal iron carbide in two cases (their Fig. 7) but did not identify this compound, because they were not aware of its magnetic characteristics.[2]

It is interesting to note that the reaction $3Fe_2C$–Hägg → $2Fe_3C+C$ becomes appreciable only around 450°, while the reaction Fe_2C–Hägg+Fe → Fe_3C is noticeable already above 260°.[10]

Acknowledgment.—The authors wish to thank E. H. Bean for preparing the hexagonal carbide.

Summary

1. The reaction of Hägg carbide, Fe_2C, to yield cementite, Fe_3C, and free carbon is a discontinuous (or heterogeneous) precipitation.

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(7) Kölbel, Ackermann, Juza and Tentschert, *Erdöl und Kohle*, **2**, 278–285 (1949).

(8) FIAT Reel 116, frames 1678–1688.

(9) Lefebvre and LeClerc, *Compt. rend.*, **203**, 1378 (1936); **207**, 1099 (1938); *Congr. Chim. Ind. Nancy*, **18**, 725 (1938).

(10) Hofer and Cohn, Synthesis of Cementite, *J. Chem. Phys.* **18**, 766–767 (1950).

2. Hägg carbide and cementite have narrow ranges of composition and apparently do not form intermediate metastable solid solutions.
3. The reaction $3Fe_2C$–Hägg $\rightarrow 2Fe_3C+C$ becomes appreciable only at about 450°, while the reaction Fe_2C–Hägg$+Fe \rightarrow Fe_3C$ (described elsewhere) starts below 300°.
4. The "unstable" or "labile" carbide of Kölbel and co-workers is simply Hägg carbide.

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[Contribution No. 19 from the Thermodynamics Laboratory, Petroleum Experiment Station, Bureau of Mines]

Spiropentane: Heat Capacity, Heats of Fusion and Vaporization, Vapor Pressure, Entropy and Thermodynamic Functions[1]

By D. W. Scott, H. L. Finke, W. N. Hubbard, J. P. McCullough, M. E. Gross, K. D. Williamson, Guy Waddington and H. M. Huffman[2]

The hydrocarbon spiropentane, first prepared in a relatively pure state by Murray and Stevenson,[3] is of interest because of its highly condensed structure, and it seemed desirable to have accurate values of certain of its thermodynamic properties. Therefore, an investigation of spiropentane was included in the program of the Bureau of Mines for studying the thermodynamic properties of hydrocarbons and related substances. The present paper reports experimental values of the heat capacity in the solid, liquid, and vapor states, heats of fusion and vaporization, vapor pressure, and entropy, and in addition gives values of the thermodynamic functions calculated from spectroscopic and molecular structure data for selected temperatures up to 1500° K.

Experimental

The Material.—The spiropentane used for the calorimetric and vapor-pressure studies was purified from crude material, most of which was prepared in this Laboratory but which also included two smaller quantities obtained from outside sources. The preparation was carried out by reducing pentaerythrityl tetrabromide with zinc in an ethanol–water mixture containing sodium carbonate and sodium iodide, as described by Slabey.[4] Batchwise reduction of 44.2 moles (17.2 kg.) of pentaerythrityl tetrabromide in this manner yielded 2.47 kg. (3.36 l.) of hydrocarbon product, which was then distilled in an efficient fractionating column to separate the spiropentane from the methylenecyclobutane, 2-methyl-1-butene, and other byproducts of the reduction. Distillation fractions having refractive indices, $n^{20}D$, between 1.399 and 1.418 were combined to give 870 ml. of crude spiropentane. To this was added about 75 ml. of spiropentane obtained in part from Dr. Ralph Spitzer, of the State College of Oregon, and in part from the Automotive Section of the National Bureau of Standards through the courtesy of Frank L. Howard. The combined material was treated with bromine to convert the olefinic impurities into higher-boiling brominated compounds. (Bromine was added until the yellow color would persist for a number of seconds after the addition of a single drop.) The spiropentane was then separated from the brominated materials by a second fractional distillation. Center cuts from this distillation, all having refractive indices, $n^{25}D$, between 1.41198 and 1.41201, were combined into two samples. Sample A, having a volume of about 160 ml., was used for the heat-of-vaporization measurements and the initial series of vapor-heat-capacity measurements. Its purity, as determined by the time–temperature freezing-point method, was 99.67%. Sample B, having a volume of about 65 ml., was used for the first series of low-temperature studies and for the vapor-pressure measurements. From observations of the melting point as a function of the fraction melted, its purity was found to be 99.69%. In the ebulliometric vapor-pressure studies, the difference between the boiling and condensation temperatures of this sample at the normal boiling point was observed to be 0.009°. After completion of the measurements with these two samples, they were combined and further purified by repeated fractional crystallization. The crystallization was done in a closed, all-glass apparatus, which will be described in detail in a forthcoming publication from the Chemistry and Refining Section of this Station. The product from the fractional crystallization, Sample C (about 70 ml.), was used for the second series of low-temperature studies. Its purity was 99.87%, as determined by the change of melting point with fraction melted. A summary of the melting-point data for Sample C is given in Table I. The larger volume of less pure material rejected in the fractional crystallization, Sample D, was used for the final series of vapor-heat-capacity measurements.

Table I

Spiropentane Melting Point Summary

0°C. = 273.16°K., $N_2/F = 0.0280\Delta T$[a]

Melted, %	T, °K. Obsd.	T, °K. Calcd.
10.3	165.6969	165.6848
50.4[b]	166.0450	166.0450
70.8	.0722	.0716
91.1[b]	.0860	.0860
100		.0907
Pure		.1373

Triple point = 166.14 ± 0.05°K.
Impurity = 0.13 mole %.

[a] N_2 = mole fraction of impurity; F = fraction of sample in liquid form. [b] These points used to obtain calculated values.

Low-Temperature Heat Capacity.—The low-temperature measurements were made in the apparatus described by Ruehrwein and Huffman.[5] Very briefly, the method is as follows: About 0.61 mole of the material under investigation was contained in a sealed copper calorimeter, which was mounted in the adiabatic calorimetric system. A measured amount of electrical energy was supplied to the calorimeter, and at all times the temperature of the

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[1] Not subject to copyright.

[2] Deceased.

[3] Murray and Stevenson, This Journal, 66, 314 (1944); *ibid.*, p. 812.

[4] Slabey, *ibid.*, 68, 1335 (1946)

[5] Ruehrwein and Huffman, *ibid.*, 65, 1620 (1943).