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THE STABILITY OF IRON CARBIDE AND CALCULATIONS OF ITS HEAT OF FORMATION FROM EQUILIBRIUM STUDIES

by

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for the Degree of
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Approved

Signature was redacted for privacy.

In Charge of Major Work.

Signature was redacted for privacy.

Head of Major Department.

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Graduate Dean.

Iowa State College
1924

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The writer wishes to express his sincere thanks to Professor Anson Hayes who suggested and directed this problem and gave valuable suggestions throughout the progress of the work.

The three double line iron-carbon diagrams in most general use at present are those of Benedict(1), of Ruff(2), and of Wittorf(3). The portion of these three diagrams, which is important in explaining the graphitizing properties of pure iron-carbon alloys below the solidification range, i.e., below about 1134° C, differ only in the relative slopes of the carbon solubility and of the cementite solubility lines. (The latter will be called the Acm line.)

Benedict's diagram shows the slope of the Acm line to be greater than that of the carbon solubility line. Wittorf indicates that the two lines are parallel while Ruff has drawn them with the carbon solubility line having the greater slope.

Benedict's diagram would require also, as would Wittorf's as well, that pure iron-carbon alloys should graphitize completely on cooling slowly since the carbon solubility line lies to the left of the cementite solubility line. Ruff's diagram, however, offers the possibility of an intersection of these two lines. At this point of intersection, and for temperatures below it, iron-carbide should be stable.

It is therefore evident that a knowledge of the stability of Fe_3C in the vicinity of the lower critical range is of very great importance.

(1) Metallurgie, 5, page 45 (1908).
(2) Metallurgie, 8, page 457 (1911).
(3) J. Russ. Physical Chem. Soc. 43, 1613 (1911). (Original article not read.)

Equilibrium values obtained by methods similar to those of Schenck(5) make possible the calculation of the heat of formation of Fe_3C, as well as the determination of the stability or metastability of iron carbide at temperatures immediately below the lower critical.

Campbell(4) reported a value of 8494 cal. which he obtained by dissolving iron and iron-carbide in cupric chloride solution, according to the reactions:

$$3\,Fe + 6\,CuCl_2 = 3\,FeCl_2 + 6\,CuCl \text{ and}$$

$$Fe_3C + 6\,CuCl_2 = 3\,FeCl_2 + 6\,CuCl + C.$$

His method of calculation demands that the carbon be left wholly in the form of the element carbon.

Since he found it necessary to use considerable hydrochloric acid in order to bring about complete solution of the iron-carbide, and, since considerable portions of the combined carbon is converted into hydrocarbons under such conditions, it is to be expected that his result would be in error. Ruff pointed out this objection.

Schenck, Semiller and Falke(5) calculated the value 8940 from data which they obtained from their work on CO and CO_2 equilibria with various groupings of the solid phases, iron, carbon, iron carbide, and the oxides of iron. The near agreement of their value with that of Campbell, they considered evidence of the correctness of their work. It is not

(4) Jour. Iron & Steel Institute, No. 1, page 211 (1901).
(5) Berichte, Vol. 40, page 1709 (1907).

evident from Schenck's work wherein his error was made, but it is entirely possible that he assumed the presence of phases which did not exist when he took his equilibrium values for the gas phase.

Ruff (6), by direct combustion in a bomb colorimeter, obtained a value of -15100 calories, a value in wide disagreement with that of Campbell and Schenck.

It seems significant that the difference between the values of Campbell and Ruff is near the value of the heat of formation of the hydrocarbons, methane and ethane. In his work, Ruff analyzed the oxides of iron produced during the combustion to determine the portions of ferrous and ferric oxides resulting. Though he does not give details of his method, it would appear that this value of -15100 is of the correct order of magnitude.

A number of workers, of whom Schenck(7) was the first, pointed out the catalytic action of CO and CO_2 as a carrier of carbon. They represent the action as being:

$$C + CO_2 \rightleftharpoons 2\ CO$$

$$3\ Fe + 2\ CO \rightleftharpoons Fe_3C + CO_2$$

The net result of these reactions in one direction produces carbonizing while in the other direction they produce graphitization.

It is plain from the foregoing reactions that so long as the solid phases iron, carbon and iron-carbide exist the ac-

(6) Berichte, Vol. 45, Part 1, page 63 (1912).
(7) loc. cit. Berichte, 40, page 1709 (1907).

tion is strictly that of a catalyst since the gas composition does not change and the initial substances are carbon and alpha iron with the product Fe_3C resulting.

One of the greatest difficulties in determining the stability of iron-carbide and of austenite has been the extreme slowness of actions in the vicinity of the lower critical range. Since the equilibria determined by Schenck and co-workers were obtained in comparatively short times, it seemed that a mixture of carbon monoxide and carbon dioxide would offer possibilities of arriving at some very important conclusions as to the position of the carbon solubility line in the vicinity of the lower critical range.

Because of the discrepancy between Schenck's and Ruff's values for the heat of formation of iron-carbide, no credence could be given the results of the more extensive use of this catalyst in solving this important problem until it was shown that the results obtained from direct calorimetric determination and by methods based upon the actions of carbon monoxide and carbon dioxide were brought into agreement.

The present investigation was taken up in an attempt to establish the correctness of one or the other values for the heat of formation of iron-carbide by use of the Vant Hoff equation and equilibria between iron, iron-carbide, and carbon monoxide, and carbon dioxide.

A value in fair agreement with Ruff has resulted and some definite conclusions as to the stability of iron-carbide at temperatures as low as 650° C have been reached.

PREPARATION OF ALLOYS.

Pure iron-carbon alloys were made by melting Armco iron rods in contact with 200 mesh graphite in a magnesia lined graphite crucible in a resistor furnace. The magnesia linings were made from Baker's Analyzed highest purity MgO. The melt was allowed to solidify in the furnace and then removed to cool to room temperature from white heat. The alloy prepared as described and weighing 150 grams was annealed at 750° C for an hour. After a microscopic examination proved the absence of graphitic carbon the sample was freed from scale and made into turnings on the lathe.

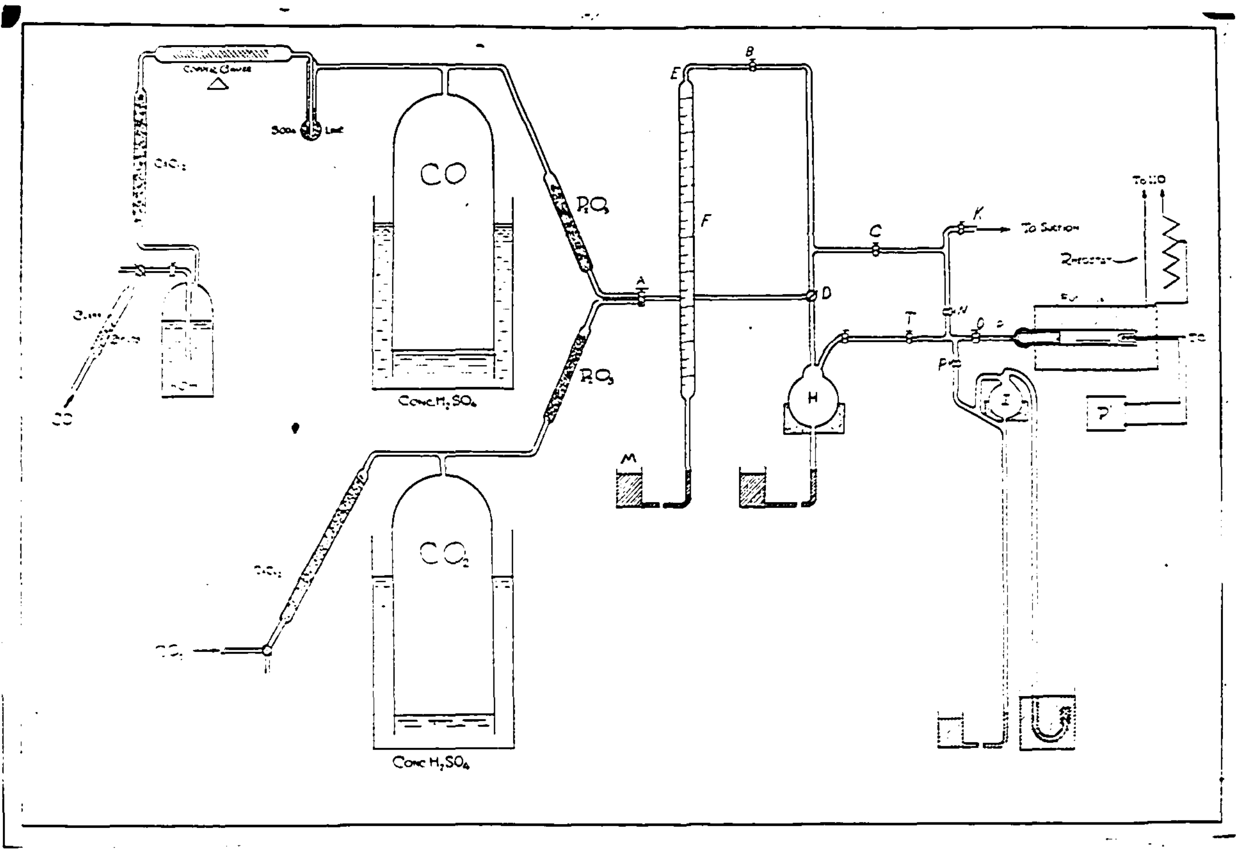
A chemical analysis was made of one of the alloys which gave the following composition:

C	S	Si	P	Mn
1.05%	0.027%	0.04%	0.0048%	0.043%

Silicon determinations made on alloys prepared at different times resulted in remarkably close agreement. For that reason a complete analysis on each alloy was not made.

The apparatus used in this work was designed to meet the requirements of this particular problem. It was constructed of Pyrex glass with the exception of the large gas reservoirs which were of soft glass and the reaction chamber which was of fused quartz.

The carbon dioxide was generated by the action of 1:1 recently boiled C. P. sulphuric acid on sodium bicarbonate suspended in freshly boiled water in a Kipp generator. The gas was led thru a calcium chloride tube and stored over concentrated sulphuric acid.



The carbon monoxide was prepared by dropping concentrated sulphuric acid onto chemically pure sodium formate, moistened with water in a two liter flask, maintained at 95°-100° Centigrade. The gas was conducted thru a short distilling head to condense most of the water vapor. This was followed by passing slowly thru a six inch roll of fine copper gauze, heated to glowing, where the traces of oxygen were removed and the equivalent of carbon dioxide was formed. The traces of carbon dioxide were removed by soda-lime and the purified carbon monoxide stored over concentrated sulphuric acid.

Gas mixtures of definitely known composition were used in charging the reaction chamber. In preparing the mixtures the following procedure was carried out:

Evacuate at K with stop cock A closed but with B, C and D open. This draws the mercury of graduate tube F up to E. Close C and open A to the left until CO gas fills F at atmospheric pressure. Close A and raise mercury reservoir M, turn D a half turn and allow the gas to flow thru displacing the mercury in the storage chamber H. Adjust mercury levels to atmospheric pressure and close D from H. Evacuate as before to remove traces of carbon monoxide and repeat using CO_2 to bring the proportions to the desired value.

Eight grams of turnings from the F-C alloy were placed in a porcelain boat in the reaction chamber. This chamber was fitted into the Pyrex glass cap by a carefully made ground joint which was sealed on the outside by hard wax. The quartz reaction tube was similar to the one used by Schenk, with two slight changes, i.e., an identation for the thermocouple and a quartz plug to displace the gases in the cold end of the tube. Finally, the reaction chamber was connected with the remainder of the apparatus by sealing together at point R.

In order to insure against oxidation by air or water vapor, the reaction tube was evacuated at room temperature for

30 minutes by means of a high vac pump. Stop cocks C and P were closed while N and O were open. The furnace was heated at such a rate as to reach 750° C in an hour and a half. The pumping was continued and the temperature held at 750° C for about 20 minutes to remove the strain caused by machining the alloy. In order to guard against even traces of oxide the alloy was treated with pure carbon monoxide at this temperature for a few minutes. The gas was pumped out and N closed. This procedure for the reduction of the oxide gave uniformly good results. The surface of the metal was left silver white in color and free from traces of either graphite or oxide.

At this point, when the reaction tube was evacuated, freed from oxide and maintained at a uniform temperature of 750° C, the gas mixture was cautiously admitted thru T and O, and the furnace cooled to working temperature. The gases in H and the reaction tube were maintained at atmospheric pressure.

The time required for the gases to reach equilibrium was found to be dependent upon several different factors and was determined by trial. The period was considerably shortened if the gases were mixed from time to time during the first few hours by raising and lowering the mercury reservoir a few centimeters. When equilibrium had been established, the stop cocks C, T and O were closed while P and N were opened.

The method of removing the gas for analysis was that employed by Schenck. Suction was applied drawing the mercury up in the lower tubes of I. These tubes were made of sufficient length to provide a mercury column which exceeded the barometer height by several centimeters. N was then closed and C opened. The gases rushed out and the major portion collected in I. By closing P and raising the mercury reservoir, the gases were forced out thru the lower U-tube where they were collected for analysis. The volume collected from one heating averaged about 24 cubic centimeters.

The analysis of the gas was made by the Hempel method, using mercury as the trapping liquid in a small specially made gas burrette. The carbon dioxide was absorbed by 40% KOH solution and the CO was determined by absorption in cuprous chloride. The error in reading did not exceed 1 Cu M which is well within one-half of one percent.

Sample	Carbon Content	Initial Charge	Equilibrium Mixture		Time	Temp.
			CO	CO_2		
I	1.05	94% CO & 6% CO_2	76.27	23.73	10hrs	700°C
I	1.05	same	74.78	25.22	20hrs	700°C
I	1.05	same	74.66	25.33	20hrs	700°C
I	1.05	same	64.04	35.96	32hrs	650°C
I	1.05	same	64.64	35.35	34hrs	650°C
II	1.55	same	64.8	35.2	17hrs	650°C
II	1.55	same	64.28	35.71	24hrs	650°C
II	1.55	same	64.42	35.57	43hrs	650°C

Note: This equilibrium was reached by holding the temperature at 675° C for ten hours and then raising to 700° C for the remainder of the reaction period. The purpose of this was to approach equilibrium from the CO_2 side. The good agreement between these values for 20 hours at 700° C was taken as substantial evidence that equilibrium had been reached.

The ten hour run had evidently not reached equilibrium. These values were not used in the calculation.

The equilibrium of the gases in contact with the 1.55% carbon alloy at 650° C gave uniform values. Free graphite was not found.

Two determinations were made with the high carbon alloy at 700° C. Both resulted in a small amount of free graphite. These results were likewise discarded.

DISCUSSION OF RESULTS.

The average values of those shown in the table were used in the calculation. Equilibrium values were taken at 700° C, as 25.27% CO_2 and 74.73% CO. The average values at 650° C were 35.58% CO_2 and 64.42% CO.

Knowing the purity of the iron-carbon alloy and having the assurance that equilibrium was established, the equation may be written:

(1) $$Fe_3C + CO_2 \rightleftharpoons 3\,Fe + 2\,CO$$

The equilibrium constant for the above reaction may be written $K = \frac{P^2_{CO}}{P_{CO_2}}$. Knowing the values for K_1 and K_2 at the temperatures 650° C and 700° C respectively, it is possible, by means of the Van't Hoff equation, to calculate a mean of the heat of this reaction.

$$\ln \frac{2.21}{1.166} = \frac{\Delta H}{R}\left[\frac{1}{923} - \frac{1}{973}\right]$$

Solving for ΔH and changing to common logarithms,

$$\Delta H_{675^\circ C} = 22800 \text{ calories}$$

or writing the thermo-chemical equation

$$Fe_3C + CO_2 = 3\,Fe + 2\,CO - 22800$$

The assumption was made that the heat of reaction was nearly constant over a fifty degree interval. The term $\Delta H_{675^\circ C}$ therefore represents the mean value.

In order to calculate the heat of formation of Fe_3C at room temperature it is necessary to correct the value of 22800 for the difference in heat capacity between the factors and resultants in the above reaction. The heat of reaction at 650° C, which is 22800, will be designated as ΔH_2. The heat of reaction at 20° C, to be solved for, will be represented by ΔH_1. The principle of the conservation of energy requires that:

$$\Sigma C_F + \Delta H_2 = \Sigma C_R + \Delta H_1$$

where ΣC_F represents the heat capacity of the factors entering the reaction and ΣC_R the same for the resultants of the reaction, both being raised thru the temperature interval, 20° C to 675° C.

Solving for ΔH_1 and substituting the determined value for ΔH_2:

$$\Delta H_1 = 22800 + \Sigma C_F - \Sigma C_R$$

Assuming the molecular heat of Fe_3C to be equal to the sum of the atomic heats, then 3 Fe may be cancelled from both sides of equation (1). This makes the variation of the heat of reaction identical with that of $C + CO_2 = 2\ CO$. Then expressing the heat capacities as functions of T, as taken from Landolt-Bornstein tables and setting up the equation, we have

$$\Delta H_{20} = 22800 + \int_{293}^{T}(7.0 + 7.1 \times 10^{-3}T - 1.86 \times 10^{-6}T^2)dt + \int_{293}^{T}(0.31 \times 12)dt - 2\int_{293}^{T}(6.5 + 1 \times 10^{-3}T)dt.$$

Solving, $\Delta H_{20^\circ C} = 22800 + 69 = 22869.$

The heat of the reaction at 20° C was shown to be 22869 cal.

By setting this value in the thermo-chemical equation and substituting for CO and CO_2 their heats of formation from graphite,

$$Fe_3C + CO_2 = 3\ Fe + 2\ CO - 22869$$

$$18331 + -94800 = \quad - 53600$$

the heat of formation of Fe_3C is shown to have the negative value, -18331 cal.

When the values for CO and CO_2 are those corresponding to formation from amorphous carbon, the equation becomes

$$Fe_3C + (-97,000) = -58,000 + (-22,869),$$

which gives the heat of formation of Fe_3C as -16,131.

As was stated earlier in the paper, the value obtained by Ruff by a direct calorimetric method was -15,100. It should be stated that when calculations are made from individual observations of Ruff, values ranging from -14,000 to -18,100 result.

From the fact that the equilibrium constants at 650° C and 700° C for the gases in contact with Fe_3C and ferrite, are greater than those for carbon at the same temperature, it must be concluded that Fe_3C is meta stable toward carbon and alpha iron at these temperatures. Since Fe_3C is metastable immediately below the lower critical, it is concluded that the carbon solubility line and the Acm line do not intersect immediately above the A_1 point.

When values were taken from Falcke's data and calculations made by use of the Van't Hoff equation as was done above, a heat effect corresponding rather closely to that for the reaction $C + CO_2 = 2\ CO$ was obtained. This is true whether data are taken from table "Reines Eisen" or "Gekoltes Eisen". This appears to indicate that the equilibria which he reported were those of these gases in contact with carbon, instead of the metal which he assumed. This carbon probably resulted either from the deposition of soot or from the break down of the iron carbide in the alloy used in his work.

If it is assumed that the values given by Falcke for CO, CO_2, Fe and Fe_3C are correct, then the close agreement between the two heat effects may be used to predict the heat of formation of Fe_3C as follows:

$$Fe_3C + CO_2 = 2\ CO + Q_1$$

$$C + CO_2 = 2\ CO + Q_2$$

If, as was calculated, Q_2 is approximately equal to Q_1, then the heat of formation of Fe_3C must be nearly zero.

SUMMARY.

1. Equilibrium values for CO and CO_2 in contact with Fe and Fe_3C at 650° C and 700° C have been determined.
2. By means of these data values of -18,331 and -16,131 were obtained for the heat of formation of Fe_3C from alpha Fe and carbon, assuming graphitic carbon in the first case and amorphous carbon in the second.
3. Fe_3C is found to be metastable at temperatures of 650° C and 700° C.
4. It is concluded that the carbon solubility and the Acm line do not intersect in the immediate vicinity of A_1.