[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF IOWA STATE COLLEGE]

THE FREE ENERGY AND HEAT OF FORMATION OF IRON CARBIDE FOR THE TEMPERATURE INTERVAL 650° TO 700°

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The literature contains many conflicting statements of the stability of iron carbide, Fe_3C and its heat of formation at temperatures below the solidification range.[1]

The confusion that is so evident in the references cited is further emphasized when the various forms of the equilibrium diagrams for the iron–carbon system are interpreted with reference to the stability and heat of formation of the carbide.

Benedicks' diagram,[2] (see Fig. 1), would require, as would Wittorff's,[3] as well, that the iron carbide should break down completely into iron and carbon on cooling slowly, since the carbon solubility line lies, throughout its length, to the left of the iron carbide solubility line.

Ruff's diagram,[4] however, offers the possibility of an intersection of the carbon solubility and A_{cm} lines before the A_3 or A_{2-3} lines are reached (Fig. 1). If such an intersection should occur, iron carbide would become a stable phase for this temperature. According to Ruff's diagram pure iron-carbon alloys would graphitize completely or not, depending upon the intersection of the carbon solubility line with the A_3 or A_{2-3} line in one case or with the A_{cm} line in the other. At the intersection of the carbon solubility line with the A_{2-3} line, alpha iron, carbon and solid solution saturated with carbon, would be in equilibrium. Extraction of heat at the temperature of this intersection should result in the decomposition of the solid solution into alpha iron and carbon.

At the intersection of the carbon solubility line with the A_{cm} line, carbon, iron carbide and solid solution saturated with carbon would be in equilibrium. Extraction of heat at this temperature would result in the formation of iron carbide from carbon and solid solution.

The relative slopes of these two lines in the vicinity of 700° can be shown to be determined by the relative values of the heats of solution of carbon and of iron carbide in the saturated solid solution, if the difference between the solubilities of carbon from carbon, and of carbon from iron carbide, is not great.

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[1] Honda and Murakami, *J. Iron Steel Inst.*, **102**, No. 2, 287 (1920). Honda, *Sci. Repts. Tôhoku Imp. Univ.*, [1] No. 11, 119 (1922). Upton, *J. Phys. Chem.*, **12**, 507 (1908). Schwartz, *Trans. Am. Inst. Mining Met. Eng.*, **69**, 794 (1923). R. Ruer, *Z. anorg. allgem. Chem.*, **117**, 249 (1921).

[2] Benedicks, *Metallurgie*, **5**, 45 (1908).

[3] Wittorff *J. Russ. Phys.-Chem. Soc.*, **43**, 1613 (1911).

[4] Ruff, *Metallurgie*, **8**, 456, 497 (1911).

If the formation of iron carbide is accompanied by a heat evolution of considerable magnitude, it can be shown that the slope of the carbon solubility line is less than that of the A_{cm} line as is the case in Benedicks' diagram. Conversely, if the formation of iron carbide is accompanied by a heat absorption of considerable magnitude, the carbon solubility line will have the greater slope, as is shown by Ruff's diagram.

Values obtained for ΔH_{Fe_3C} are in wide disagreement, as the following summary of the work indicates.

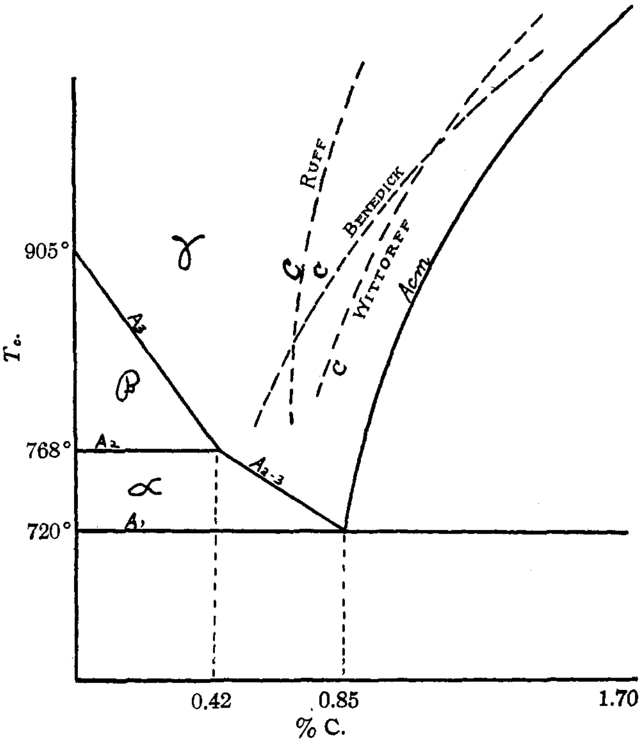

Fig. 1.

Campbell,[5] reported a value of 8494 calories for the heat of formation of iron carbide. He dissolved iron and iron carbide in cupric chloride solution, assuming that the reactions, $3Fe + 6CuCl_2 = 3FeCl_2 + 6CuCl$, and $Fe_3C + 6CuCl_2 = 3FeCl_2 + 6CuCl + C$, take place and from the measured heat effect calculated the heat of formation of the iron carbide. Campbell's method of calculation requires 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 a considerable portion of the combined

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[5] Campbell, *J. Iron Steel Inst.*, **59**, No. 1, 211 (1901).

carbon is converted into hydrocarbons under such conditions, it is to be expected that his results would be in error. Ruff pointed out this objection.

Schenck, Semiller and Falcke[6] calculated the value 8940 from data which they obtained from their work on carbon monoxide and dioxide equilibria with various groupings of the solid phases, iron, carbon, iron carbide and the oxides of iron. The near agreement of the value of Schenck, Semiller and Falcke with that of Campbell was considered by them as evidence of the correctness of their work. From the fact that Schenck used gas equilibrium values to calculate this heat of formation of iron carbide, which value has since been found to be erroneous, it follows that his equilibrium values were not correct. Experience in the present work shows that it is extremely difficult to identify the solid phases which Schenck assumed to be present. The assumption of solid phases which did not exist is probably the cause of his error.

Ruff and Gestern[7] determined the heat of the reaction, $Fe_3C + 3O_2 = Fe_3O_4 + CO_2$, by burning the iron carbide in a bomb calorimeter. They analyzed the oxide residue and corrected the heat effect for the excess of ferrous oxide that had not been oxidized to ferro-ferric oxide. They obtained a value of —15,300 calories.

The direct method of Ruff offers fewer possibilities of error and a recalculation of the data he obtained reveals no discrepancy. The obvious error made by Campbell and the wide disagreement between his value and that of Ruff indicate that Schenck's values are also in error.

The apparent failure of iron carbide to decompose completely into carbon and iron in the vicinity of 700° would point to one or the other of two conclusions. Either iron carbide is stable at this temperature, or it represents a very persistent case of metastability. No matter which of these conclusions is correct, it would appear feasible to determine equilibrium data directly for the system, Fe_3C, Fe(alpha), CO, CO_2.

It has been shown by Carpenter and Smith[8] that a carbide exhibiting six of the chemical and physical characteristics of iron carbide is formed by the action of carbon monoxide on iron at 650° when suitable experimental conditions are provided.

These workers found that the substance studied resembled the carbide, Fe_3C, in the following respects. It was darkened by boiling sodium picrate, but not by alcoholic nitric acid. It evolved hydrocarbons when treated with hot hydrochloric acid. Scratches across ferrite grains terminated at its boundaries, showing it to be a hard constituent. Stead's reagent does not precipitate copper upon it. When this carbide and the ferrite

[6] Schenck, Semiller and Falcke, *Ber.*, **40**, 1709 (1904).

[7] Ruff and Gestern, *Ber.*, **45**, 63 (1912).

[8] Carpenter and Smith, *J. Iron Steel Inst.*, **98**, No. 2, 139 (1918).

upon which it is formed are heated to 985°, a solid solution results which precipitates pearlite on cooling.

Unfortunately, they were unable to obtain sufficient quantities of their carbide to isolate it and prove its composition by direct analyses. The writers recognize the desirability of such final evidence. However, the experimental difficulties in obtaining such a proof of the identity of the iron carbide, Fe_3C, and of the carbide of Carpenter and Smith are of sufficient magnitude to constitute a separate investigation. This is planned for the immediate future.

The foregoing corroborative evidence, all of which is in accord with the conclusion that their carbide is Fe_3C, together with the absence of proof of the existence of any other carbide within this temperature range, are considered of sufficient weight to warrant the assumption that the two carbides are identical.

Under these circumstances the use of samples of somewhat different weight and of widely different carbon content, the treatment of the sample before equilibrium was established (as set forth later in this paper) to make certain that the alpha iron phase was saturated with carbon from the carbide Fe_3C, and the known low solubility in alpha iron of carbon from carbon and from the carbide, Fe_3C, are believed to justify the conclusion that the reaction with which the present equilibrium is concerned is $3Fe(alpha) + 2CO = Fe_3C + CO_2$.

The object of the present investigation was to determine the metastability or stability of the carbide Fe_3C in the vicinity of the lower critical temperature of pure iron-carbon alloys. A study of the equilibrium for the system, iron, iron carbide, carbon monoxide, carbon dioxide, was undertaken because it furnishes data from which the change in the free energy content ΔF, and in the heat content ΔH accompanying the reaction,

$$3\ Fe(alpha) + C(graphite) = Fe_3C(solid) \qquad (1)$$

may at once be calculated.

A study of System 1 has been made in this Laboratory at temperatures of 650° and 700°, and at a pressure of one atmosphere. These temperatures were chosen for a number of reasons. First, it was desirable to work at temperatures as high as possible in order to reach equilibrium in a relatively short time. Second, it seemed advisable to avoid the complicating factors of solid solution formation and graphitization. Third, temperatures below 650° were not used because Matsubara[9] has shown that oxidation of iron takes place at these lower temperatures.

Materials and Apparatus

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

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[9] Matsubara, *Trans. Am. Inst. Mining Met. Eng.*, **67**, 1 (1922).

linings were made from Baker's Analyzed highest purity magnesium oxide. 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 g. was annealed at 750° 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 of one of the alloys gave the following composition: carbon, 1.05%; sulfur, 0.027%; phosphorus, 0.0048%; manganese, 0.043%; silicon, 0.04%.

Except for carbon this analysis applies to both alloys.

The apparatus, Fig. 2, 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. sulfuric acid on sodium bicarbonate suspended in freshly boiled water in a Kipp generator. The gas was led through a calcium chloride tube and stored over concd. sulfuric acid.

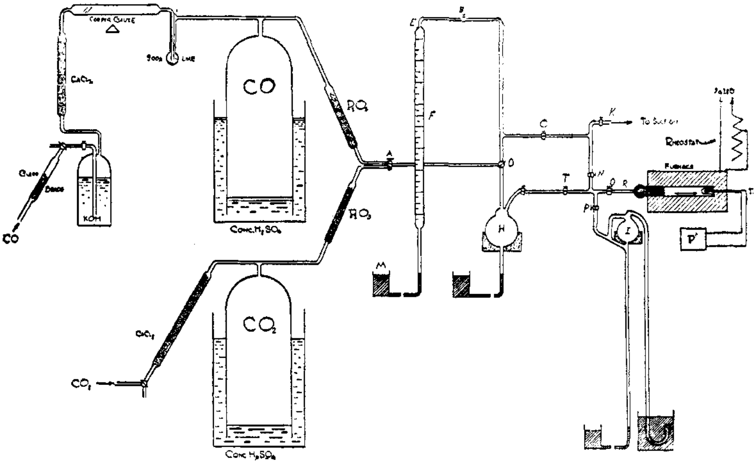

Fig. 2.

The carbon monoxide was prepared by dropping concd. sulfuric acid onto chemically pure sodium formate, moistened with water in a 2-liter flask, maintained at 95–100°. The gas was conducted through a short distilling head to condense most of the water vapor. This was followed by potassium hydroxide solution and solid calcium chloride. It was then passed slowly through a 15cm. 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 was stored over concd. sulfuric 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 Stopcock 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 carbon monoxide gas fills F at atmospheric pressure. Close A and raise mercury reservoir M, turn D a half turn and allow the gas to flow through, 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 carbon dioxide to bring the proportions to the desired value.

Approximately 8 g. of turnings from the iron-carbon alloy was 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 Schenck, with two modifications, namely, an indentation for the thermocouple and a quartz plug to displace the gases in the cold end of the tube. Finally, the reaction chamber and cap were connected with the remainder of the apparatus by a glass seal 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. The furnace was heated at such a rate as to reach 750° in an hour and a half. The pumping was continued and the temperature held at 750° for about 20 minutes to remove the strain caused by machining the alloy. In order to guard against formation of even traces of oxide the alloy was treated with pure carbon monoxide at this temperature for a few minutes and the reaction chamber again evacuated. 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°, the gas mixture was cautiously admitted through T and O, of Fig. 2, and the furnace was then allowed to cool to working temperature. The gases in storage bulb **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 a few centimeters the mercury reservoir in communication with storage bulb H. When equilibrium had been established, the stopcocks 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 barometric height by several centimeters. The gases were then collected in I by closing N and opening O. By closing P and raising the mercury reservoir, the gases were forced out through the lower U-tube where they were collected for analysis. The volume collected from one heating averaged about 24 cc.

The analysis of the gas was made by the Hempel method, using mercury as the trapping liquid in a small specially made gas buret. The carbon dioxide was absorbed by 40% potassium hydroxide solution and the carbon monoxide was determined by adsorption in cuprous chloride. The error in reading did not exceed 0.1 cc. which is well within 0.5%.

Experimental Results

The results obtained from the equilibrium studies are assembled in Table I.

TABLE I

RESULTS

The initial charge was 94% carbon monoxide and 6% carbon dioxide

No.	Alloy	Carbon %	Equilibrium gas mixture		Time Hrs.	Temp. °C.
			CO, %	CO_2, %		
I	I	1.05	64.04	35.96	32	650
II	I	1.05	64.64	35.35	34	650
III	II	1.55	64.8	35.2	17	650
IV	II	1.55	64.28	35.71	24	650
V	II	1.55	64.42	35.57	43	650
VI	I	1.05	76.27	23.73	10	700
VII	I	1.05	74.78	25.22	20	700
VIII	I	1.05	74.66	25.33	20	700
IX[a]	II	1.55	64.60	35.39	9	700
X[a]	II	1.55	66.66	33.33	9	700

[a] Alloys partially graphitized.

The gas equilibria were determined on two different alloys of iron and carbon. Alloy I contained 1.05% of carbon while Alloy II contained 1.55% of carbon. Determinations were made at 650° and 700° on Alloy I and at 650° on Alloy II. It will be noted that the agreement between the values for the gas equilibrium on Alloys I and II at 650° is quite satisfactory. Attempts to obtain equilibrium values for the high carbon alloy, No. II, at 700° resulted uniformly in graphitization. The appearance of the carbon phase was accompanied by a decrease of carbon monoxide in the equilibrium mixture. This lowering of the carbon monoxide content at equilibrium was as much as 10%, and served as a satisfactory index of graphitization. In all cases where a low percentage of carbon monoxide resulted, microscopic examination showed the presence of carbon. This leaves very little doubt that the equilibria obtained were those for the solid phases iron carbide and iron in contact with the gases carbon monoxide and dioxide.

The equilibrium values given in No. VI were not used in the calculations because a longer time than ten hours was found necessary to reach equilibrium.

In No. VIII the equilibrium was reached by holding the temperature at 675° for ten hours and then raising to 700° for the remainder of the reaction period. The purpose of this was to approach equilibrium from the carbon dioxide side without oxidation of iron. The good agreement between these values for 20 hours at 700° was taken as substantial evidence that equilibrium had been reached.

Interpretation and Calculation of Results

Consider the following free energy equations

$$3\ \mathrm{Fe}\ (\alpha) + 2\ \mathrm{CO(g)} = \mathrm{Fe_3C\ (s)} + \mathrm{CO_2\ (g)}.\quad \text{Free energy change} = \Delta F_1 \qquad (1)$$

$$2\ \mathrm{CO} = \mathrm{C\ (graphite)} + \mathrm{CO_2}.\quad \text{Free energy change} = \Delta F_2 \qquad (2)$$

$$3\ \mathrm{Fe}\ (\alpha) + \mathrm{C\ (graphite)} = \mathrm{Fe_3C}.\quad \text{Free energy change} = \Delta F_3 \qquad (3)$$

where the gases and solids are all considered at unit pressure and at the temperatures of 650° and 700°.

Subtraction of Equation 2 from Equation 1 gives

$$\Delta F_1 - \Delta F_2 = \Delta F_3 \qquad (4)$$

Assumption of the above pressures makes it possible to write

$$\Delta F_1 = -RT\ ln\ K_1 \qquad (5)$$

$$\Delta F_2 = -RT\ ln\ K_2, \text{ from which} \qquad (6)$$

$$\Delta F_3 = RT\ (ln\ K_2 - ln\ K_1) \qquad (7)$$

Assumption of the ideal gas laws gives,

$$\Delta F_3 = RT\left[ln\frac{P_{2\text{-CO}_2}}{P^2_{2\text{-CO}}} - ln\frac{P_{1\text{-CO}_2}}{P^2_{1\text{-CO}}}\right] \qquad (8)$$

Unfortunately, there are no reliable experimental data for the equilibrium constants of Reaction 2 at temperatures below 800°. Although the values of Boudouard[10] have been widely used in textbooks and elsewhere, they are probably considerably in error. Rhead and Wheeler[11] using an experimental scheme which brought approach to equilibrium at much slower rates than that used by Boudouard, questioned the results of the latter, because of the extremely low rates of approach to equilibrium at temperatures of 800° and below. Later,[12] using an experimental method very similar to that of Boudouard, they repeated their earlier work and obtained data at 800° as well as at higher temperatures.

The experimental values obtained on this later work do not agree well with their earlier work, and do not check that of Boudouard at 800°.

In checking over the data of the above-mentioned workers, it was noticed that the use of Boudouard's data at 650° and 800° in the equation

$$2.303 \log \frac{K_2}{K_1} = \frac{\Delta H}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \qquad (9)$$

gives a value for ΔH for Reaction 2 of —81,500 cal. A similar treatment of Rhead and Wheeler's earlier data gives values for ΔH which vary in an irregular manner from —58,000 to —33,000 cal. This treatment of the data of their more recent work gives values as follows: 800–900°, ΔH = —40,943 cal.; 900–1000°, ΔH = —41,952 cal.; and 1000–1100°, ΔH =

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[10] Boudouard, *Ann. chim. phys.*, **24**, 5 (1901).

[11] Rhead and Wheeler, *J. Chem. Soc.*, **97**, 2178 (1910).

[12] *J. Chem. Soc.*, **99**, 1140 (1911).

—41,979 cal. The best calorimetric value for ΔH at 18° according to Lewis and Randall[13] is —41,950 cal.

If the value —40,943 cal. for the temperature interval 800–900° in Rhead and Wheeler's later work be temporarily disregarded, the following conclusions may be drawn.

First, the value of ΔH for the reaction, $2\ CO = C + CO_2$, is practically constant over the temperature interval 18° to 1100°. Second, Boudouard's data at 650° and 800° as well as the earlier work of Rhead and Wheeler are in error.

In the calculations which follow, the value of ΔH = —40,943 cal. for the temperature interval 800–900° has been disregarded, since this value varies from the nearly constant value of —41,950 cal. in the direction which would result in case Rhead and Wheeler failed to get equilibrium between carbon monoxide and carbon at the lower temperature of 800°. They state that 72 hours were required and they approached equilibrium from only the one side.

For want of a better method, extrapolations for values of K at 650° and 700° for Reaction 2 were carried out. For this extrapolation, ΔH for this reaction was taken as —41,950 and $K = P_{CO_2}/P^2_{CO}$ was taken as being 3.573×10^{-2} which is the mean K from Rhead and Wheeler's values at 900°. Equation 9 was used.

Indicating the equilibrium constant for Reaction 2 by K_2, the values $K_{2-650} = 4.774$ and $K_{2-700} = 1.470$ are obtained.

The mean values for the gas composition for Equilibrium 1 at 650° are 35.58% of carbon dioxide and 64.42% of carbon monoxide. Those at 700° are 25.27% of carbon dioxide and 74.73% of carbon monoxide. Indicating values for the equilibrium constant of Reaction 1 by K_1, the values $K_{1-650} = 0.8574$ and $K_{1-700} = 0.4525$ are obtained. The use of the data at 650° for Reactions 2 and 1 in Equation 7 gives: $\Delta F_{3-650} = 2.303 \times 1.98 \times 923\ (\log 4.774 - \log 0.8574)$; $\Delta F_{3-700} = 3138$ cal.; and at 700°, $\Delta F_{3-700} = 2.303 \times 1.98 \times 973\ (\log 1.470 - \log 0.4525)$; $\Delta F_{3-700} = 2281$ cal.

Use of the equation

$$d(\Delta F)/dT = (\Delta F - \Delta H)/T \tag{10}$$

and of the assumption that $d\Delta F/dT$ is constant over the temperature interval 650–700° makes possible the calculation of ΔH for the reaction, $3\ Fe\ (\alpha) + C\ \text{(graphite)} = Fe_3C$, at both of these temperatures.

Thus $d(\Delta F)/dT$ = —17.36 calories per degree, from which $\Delta H_{650} = (3138 + 923) \times 17.36 = 19{,}163$ cal.; $\Delta H_{700} = (2281 + 973) \times 17.36 = 19{,}161$ cal.

In comparing these values with that of Ruff (15,300 cal. at 25°), it should be stated that if the difference is not due to the difference in temperature at which the determinations were made, it is in the direction which

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[13] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., **1923**, p. 574.

graphitization would produce in case it took place at 700° and did not in the determinations made at 650°. However, no indications of free graphite could be detected in the samples used, by microscopic methods or by solution in dilute acid.

A calorimetric determination of this quantity is now in progress in this Laboratory.

Summary[14]

1. Equilibrium values for carbon monoxide and dioxide with alpha iron and iron carbide, Fe_3C, at 650° and 700° and at a total pressure of one atmosphere have been determined.

2. ΔF for the reaction $3\ Fe\ (\alpha) + C\ (\text{graphite}) = Fe_3C$, is found to be 3,138 cal. (positive) at 650°, and 2,281 cal. (positive) at 700°.

3. Use of these data gives values of ΔH for this reaction of 19,163 cal. and 19,161 cal. at the temperatures 650° and 700°, respectively.

[Contribution from the Department of Physical Chemistry, University of Bristol]

AMALGAMS OF GOLD AND MERCURY

By George T. Britton[1] and James W. McBain

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In continuation of a systematic study of dental amalgams containing silver, tin and mercury,[2] preliminary experiments were carried out to determine the effect of gold, which is commonly added for its "benevolent influence."[3] It was found that the gold passes almost entirely into the solid phase, whether amalgams of pure tin or of pure silver or of both together are concerned.

The present work was therefore undertaken with a view to examining the nature of the binary system, gold-mercury, before proceeding further with the quaternary system. Published investigations of this system[4] show extraordinary discrepancies, and hence it was necessary to make new and careful determinations of the solubility of gold in mercury.

Method.—Parravano employed a fusion method, and Braley and Schneider used cooling curves in their research. In the present work a direct analysis of the liquid in contact with the solid phase has been made.

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[14] The work embodied in this paper is taken from a thesis submitted in partial fulfilment of the requirements for the degree Doctor of Philosophy at the Iowa State College.

[1] Experimental work by G. T. B.

[2] Joyner, *J. Chem. Soc.*, **99**, 195 (1911). McBain, *Dental Cosmos*, June, **1912**. Knight and Joyner, *J. Chem. Soc.*, **103**, 2247 (1913). Knight, *ibid.*, **105**, 639 (1914).

[3] McBain and Knight, *Rep. Sixth Internat. Congress Applied Chem.*, **1914**, Sect. IV, pp. 1–7; *Dental Cosmos*, **57**, 630 (1915).

[4] Parravano, *Gazz. chim. ital.*, [2] **48**, 123 (1918). Braley and Schneider, This Journal, **43**, 740 (1921).