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# The heat of formation of cementite as electrolyzed from a pure iron-carbon alloy of eutectoid structure and composition

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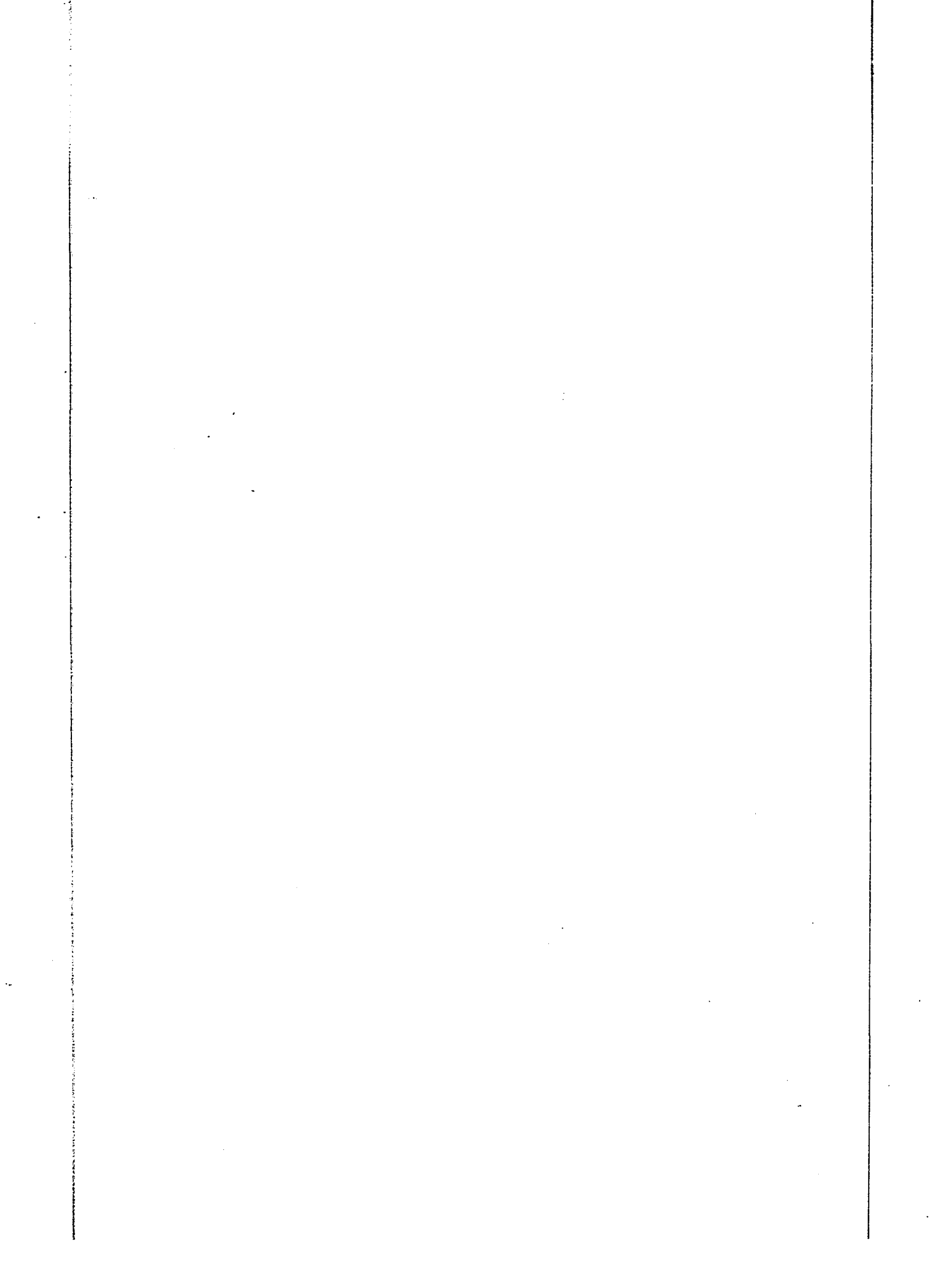
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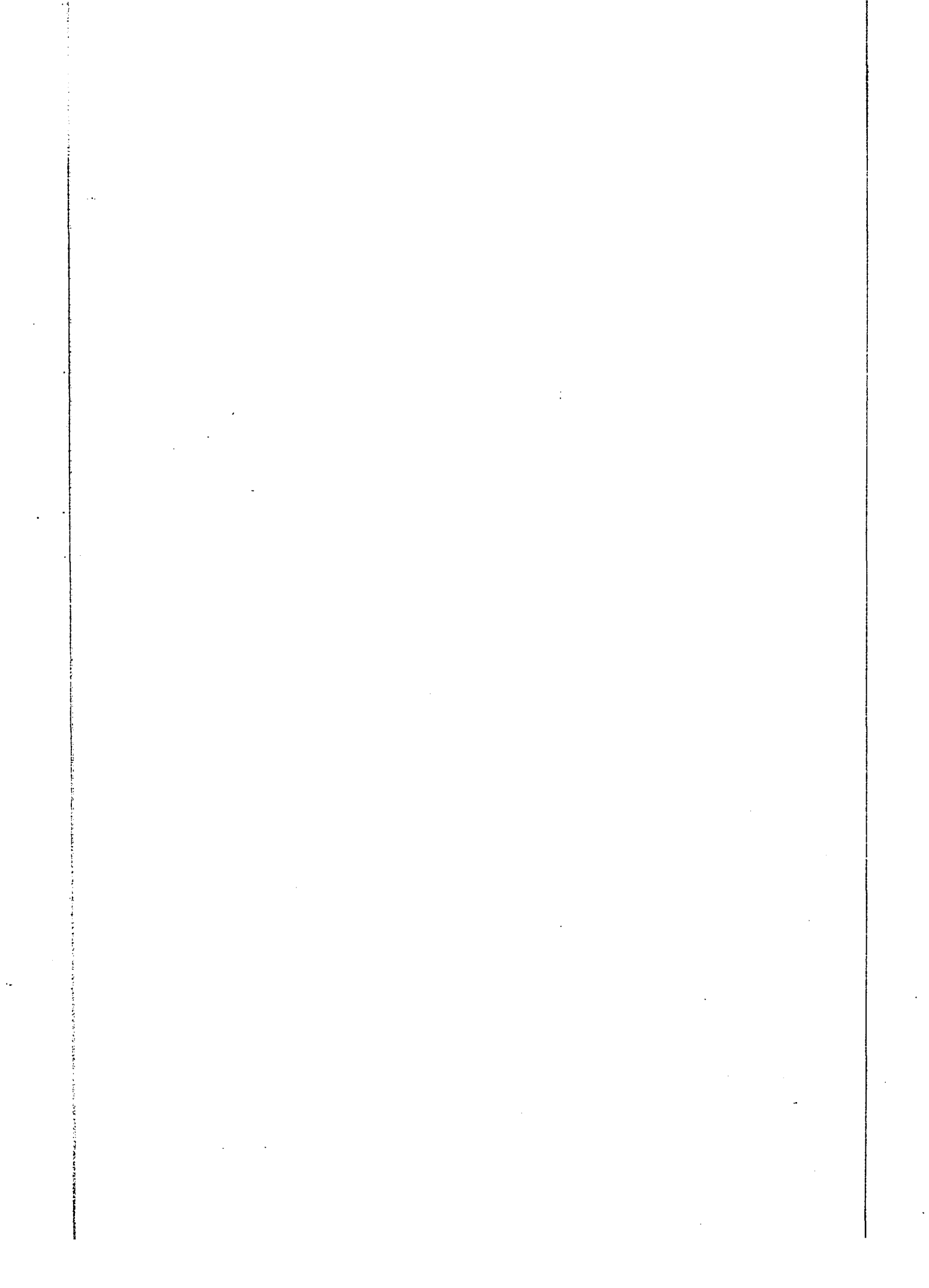
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THE HEAT OF FORMATION OF CEMENTITE AS ELECTROLYZED FROM  
A PURE IRON-CARBON ALLOY OF EUTECTOID STRUCTURE AND COMPOSITION

A Thesis  
Submitted to the Graduate  
Faculty in Candidacy for the  
Degree of

DOCTOR OF PHILOSOPHY

BY

George Hendrie Brodie and William Harney Jennings

Major Subject: Physical Chemistry

Approved:

Signature was redacted for privacy.

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In charge of Major Work

Signature was redacted for privacy.

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Head of Major Department

Signature was redacted for privacy.

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Dean of Graduate College

Iowa State College

1926

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## HISTORICAL AND THEORETICAL CONSIDERATIONS

The formation of Cementite from the elements iron and carbon, or the reverse reaction whereby the carbide is decomposed into these elements, presents for study a problem which is highly interesting from a theoretical standpoint and, at the same time, of major importance to further development of the iron and steel industry. Particularly is it desirable to know whether heat is evolved or absorbed when this compound, which has the composition  $Fe_3C$ , is formed from its elements.

Campbell and his associates<sup>1</sup> were probably the first to prepare this carbide in a state of sufficient purity to warrant its use in a determination of the heat of formation. He obtained this carbide by electrolyzing samples of well annealed steel, having a carbon content of 1.29%, in a dilute solution of hydrochloric acid. Campbell dissolved his carbide in slightly acid potassium cupric chloride solution, filtered off the carbonaceous residue, and determined the carbon content by the combustion of this residue in oxygen. In this way he found his carbide to contain 6.64% of carbon. Gravitric and volumetric determinations of iron showed the iron content to be very nearly 93.3%. Analyses for phosphorus and manganese were also made. Traces of the former, but none of the latter, were reported.

1. Am. Chem. J., 18, 836 (1896)

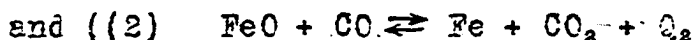
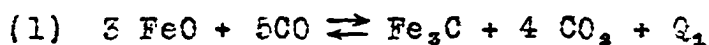
Using this fairly pure carbide Campbell undertook to determine its heat of formation by a rather ingenious calorimetric method<sup>2</sup>. He dissolved pure iron in slightly acid ammonium cupric chloride (or the corresponding potassium salt) and measured the heat effect. By dissolving cementite under the same conditions, and noticing the difference in the quantities of heat evolved by corresponding amounts of iron in each case, Campbell expected to obtain the heat of formation of the carbide. If, as Campbell assumed, the carbon was all precipitated in the free state, this method should give very accurately the value sought. Jeromin<sup>3</sup> objected to Campbell's work on the ground that hydro-carbons would be evolved by the small amount of acid present. Ruff<sup>4</sup> emphasizes this point but does not appear to have tested its validity. Each of these men raised this objection because the molecular heat of formation of cementite as determined by Campbell was a positive quantity (8494 cal.), while they believed, from theoretical considerations, that the heat of formation should be negative.

Experimental work in this laboratory has shown that with the concentration of acid used by Campbell there is no detect-

2. J. Iron Steel Inst. (London), No. 1, 211 (1901)
3. Z. für Electrochem 17, 93 (1911)
4. Metallurgie (Ferrum), 8, 459 (1911)

able evolution of hydro-carbons. Apparently Jeriomin's objection is without foundation in fact. The writers have found, however, that the precipitate obtained, when the carbide is dissolved under these conditions, is heavier than the carbon in the carbide and consequently cannot be simply free carbon as Campbell assumed. If the carbon has combined in some manner with one or more of the substances present, and such combination is accompanied by a heat effect of appreciable magnitude, Campbell's results must be in error. This precipitate appears to be insoluble in concentrated hydrochloric acid and dries to constant weight at 110°C. It is our intention to make a further investigation of this precipitate in the near future.

A few years later Schenck, Semiller, and Falcke<sup>E</sup>, made equilibrium studies of the following reactions:



By attaining equilibrium at two different temperatures in each case, and analyzing the gaseous phase to obtain the equilibrium pressures of CO and CO<sub>2</sub>, they were able, by means of the van't Hoff equation, to calculate Q<sub>1</sub> and Q<sub>2</sub>. By multiplying equation (2) by 3, and subtracting from equation (1), they obtained the equation: (3)  $2 \text{CO} + 3 \text{Fe} \rightleftharpoons \text{Fe}_3\text{C} + \text{CO}_2 + Q_1 - 3Q_2$ .

E. Ber. 40, 1704 (1907)

Knowing  $Q_1$  and  $Q_2$ , and also the heats of formation of CO and  $CO_2$ , the heat of formation of  $Fe_3C$  was readily obtained. In this manner they calculated the value 8940 cal. for the molecular heat of formation of cementite. The agreement of their value with that of Campbell was considered proof of the validity of their results. Terres and Pongracz<sup>6</sup> have shown quite conclusively, however, that when iron is acted upon by carbon dioxide not only ferrous oxide (as shown in equation 2) but higher oxides as well are formed, and probably solid solutions. This makes it extremely difficult, if not impossible, to correctly identify the solid phases present. Consequently it would seem that Schenck's results must also be considered untrustworthy, and that the seemingly close agreement with Campbell is merely the result of chance.

About 1911 Yermilov<sup>7</sup> carried out what seems to have been a complete and thorough calorimetric determination of the heat of formation of cementite. Unfortunately his original article is not available in America but the essential information is largely available in abstract form. This investigator prepared cementite from an annealed steel containing 1.94% carbon and only a few hundredths of a percent of impurities, most of

6. Z. fur Elektrochem 25, 386 (1919)

7. J. Russ. Met. Soc. (1911) (Original not seen); Stahl u Eisen, 32, 65 (abstract) (1911); C. A. 6, 2, 2387 (1912)

which was silica. The iron was slowly dissolved in 0.3-0.4% HCl solution in an atmosphere of carbon dioxide. The carbide, which remained as a residue, consisted of a steel grey powder which was not spontaneously combustible. A series of analyses showed the carbide to contain from 6.66-6.70% carbon, and from 93.25-93.40% iron. Apparently the degree of purity was very satisfactory, as would be expected from the fact that this cementite was prepared from a practically pure iron-carbon alloy.

Yermilov burned this carbide in a Berthelot Bomb which he had previously calibrated by using naphthalene as a standard. Correcting for radiation, and analyzing the oxides of iron formed, he was able to calculate the heat of formation of the carbide by taking the difference in the heat effect obtained and that which would have been obtained if the iron and carbon had been in the free state. Using the value 274,600 cal. as the molecular heat of formation of magnetite, Yermilov found that in each case the heat evolved was a trifle less than would have been evolved by the elements in the free state, provided the values used for the heats of formation of the oxides were correct. The average difference in the heat effects, calculated on this basis, gave, as the heat of formation of cementite, the value 2270 cal. per mol. Yermilov concluded that this value might be zero, since the result differed from zero by not more than the maximum experimental error.

It should be noted that Yermilov used a value for the heat of formation of magnetite which is about 7000 cal. greater than values more commonly accepted. Assuming that three-fourths of the iron in his carbide burned to magnetite (which was doubtless nearly true), his value for the heat of formation of cementite would be lowered more than five thousand calories by using the lower value for the heat of formation of magnetite. This would make his results show about -3000, or less, for the molecular heat of formation of cementite. The fact that he used an annealed, almost pure iron-carbon alloy should also be emphasized. The carbide was of very nearly theoretical composition. Since no objection to his work is known, it would seem that his results are probably correct, within experimental error, for the carbide with which he was working.

About one year later, but apparently without knowledge of Yermilov's work, Ruff and Gestern<sup>8</sup> also carried out a calorimetric determination of the heat of formation of iron carbide. They prepared their carbide in a manner entirely different from any employed by previous investigators. A crude iron containing 4.13% C, 0.2% P, 0.15% Mn, 0.074% Si, 0.006% S, and 0.005% Cu, was melted in contact with excess carbon so

8. Ber. 45, 1 (1912)

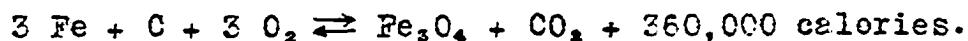
that the molten iron was completely saturated with carbon at the temperature of the melt. This melt was suddenly quenched by pouring upon a cold iron plate. The fragments were then further broken up and treated for four weeks with normal acetic acid solution. At the end of this period the residue was further broken up and then treated for several weeks with 0.2 normal HCl solution. The final residue was shaken with acetylene tetrabromide to free from graphite, washed with alcohol and ether, and dried in a vacuum. Analysis showed a carbon content of about 6.69%, and an iron content of about 93.28%. The carbide particles varied in color from a dark grey to a bronze yellow.

Ruff burned this carbide in an enamel-lined Berthelot Bomb, in 25 atmospheres of oxygen. The sample was contained in a small quartz crucible which does not seem to have been provided with a cover. In light of our experience in burning cementite in an oxygen bomb, the writers do not clearly understand how Ruff could use a quartz container without the formation of iron silicate or solid solutions. Nor is it clear how particles of the unburned carbide were kept from blowing out of the container if it was not enclosed. However, it is very probable that Ruff devised ways of overcoming such difficulties, if they were encountered in burning his coarser particles of carbide. The oxides of iron, resulting from the



combustion, were dissolved in strong boiling sulphuric acid, in a stream of  $\text{CO}_2$ . The solution was then titrated directly with permanganate to obtain the value for the  $\text{FeO}$ . After reducing with zinc the solution was again titrated with the same solution to obtain the value of the total iron. In this way

Ruff found that the iron had burned to a mixture of  $\text{Fe}_3\text{O}_4$  and  $\text{FeO}$ . In this laboratory it has been found that the iron in our finely divided cementite always burns to a mixture of  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_2\text{O}_3$ . But here it is very probable that the larger particles of the carbide, with which Ruff was carrying out combustions, may have been responsible for the lower state of oxidation. By correcting the heat effect obtained for the excess  $\text{FeO}$  which did not burn to  $\text{Fe}_3\text{O}_4$ , according to the equation:  
$$3\text{FeO} + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{Fe}_3\text{O}_4 + 77010 \text{ cal.}$$
 Ruff obtained the equation:  
$$\text{Fe}_3\text{C} + 3 \text{O}_2 \rightleftharpoons \text{Fe}_3\text{O}_4 + \text{CO}_2 + 375,100 \text{ cal.}$$
 Taking as the heat of formation of magnetite the value 265,200 calories he then obtained the equation:



The difference in the two quantities of heat evolved, if the quantities are correct, must represent the molecular heat of formation of cementite. Since more heat is evolved by the burning of cementite than by the burning of corresponding amounts of free iron and carbon the heat of formation must be negative. Ruff's figures show this value to be -15,100 calories per mol.

Two years later Ruff and Gestern<sup>9</sup>, using their own value for the heat of combustion of FeO to Fe<sub>3</sub>O<sub>4</sub>, which they determined to be 85,800 calories per mol of magnetite formed, recalculated both their value for the heat of formation of magnetite and their value for the heat of formation of cementite. They obtained 267,100 calories as the molecular heat of formation of magnetite, and -15,300 calories as the molecular heat of formation of cementite.

The work done by these investigators seems to have been carried out carefully and thoroughly. At present there is no definitely known objection to their work or calculations, and until such objections are known it must be assumed that their results are very nearly correct for the carbide with which they worked. A repetition of Ruff's work in the immediate future is planned for this laboratory.

Very recently an investigation was made in this laboratory<sup>10</sup> of the system Fe<sub>3</sub>C, Fe, (alpha) CO, and CO<sub>2</sub>. From the equilibrium values of the gases present at 650°C the free energy change accompanying the reaction:



was determined. Knowing the free energy change accompanying

9. J. Iron Steel Inst., 87, 1, (1913)

10. Maxwell and Hayes, J. Am. Chem. Soc., 48, 3, 584 (1926)

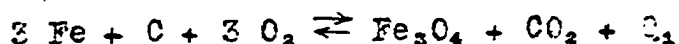
the reaction (2)  $2 \text{CO} \rightleftharpoons \text{C (graphite)} + \text{CO}_2$ , and subtracting (2) from (1) we obtain the equation:  $3\text{Fe (a)} + \text{C (graphite)} \rightleftharpoons \text{Fe}_3\text{C}$ . The free energy change for this last equation must be the difference between the free energy change of (1) and that of (2). This gave a value for  $\Delta F$  of 3138 cal. at 650°C, and 2281 at 700°C. Making use of the equation  $d(\Delta F)/dT = (\Delta F - \Delta H)/T$ , and assuming that  $d(\Delta F)/dT$  is constant over the temperature interval used and equal to -17.36 cal. per degree, it was possible to calculate  $\Delta H$ .  $\Delta H$  was found to be 19,163 cal., and 19,161 cal. at the temperatures 650° and 700°, respectively. In other words the heat of formation was found to be -19,162 cal. per gram mol over this temperature interval.

The value for the heat of formation of cementite thus obtained may be said to be a qualitative check of Ruff's work, although the agreement is not very close. To obtain further information on this subject, and clear up, if possible, the uncertainty regarding this heat effect, the writers determined to make a precision calorimetric determination, using eutectoid cementite of the highest possible purity. It is with this calorimetric determination that the following paper deals.

The theory underlying a direct combustion calorimetric determination of the heat of formation of a substance is very simple. Briefly, it may be stated as follows: "The change in heat content of a substance (or substances), in passing reversibly from state A to state B, is independent of the path

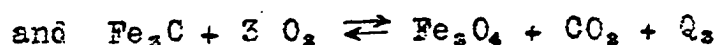
taken." This necessarily follows from the Conservation of Energy Principle, for otherwise a system could be set up from which unlimited amounts of heat could be obtained.

Let us assume that we have three mols of iron and one mol of carbon in the free, or elementary, state which we will call state A. Let these substances pass reversibly into  $\text{Fe}_3\text{O}_4$  and  $\text{CO}_2$ , according to the reaction



This direct oxidation we may call route one, and the final state in which the iron and carbon are found we will call state B.

On the other hand we may let the iron and carbon unite reversibly to form iron carbide, and then let the carbide be oxidized reversibly according to the following reactions:



In each case  $Q$  represents the number of calories of heat evolved by the reaction. It is seen that once more the final state B, in which the iron and carbon are found at the end of this two-step process, which we may call route two, is the same as before. Consequently the change in heat contents, or the amounts of heat evolved, must have been the same by either route. This means that  $Q_1 = Q_2 + Q_3$ , or  $Q_2 = Q_1 - Q_3$ . But  $Q_2$  is the heat of formation of  $\text{Fe}_3\text{C}$  from 3 Fe and C. Then if  $Q_1$  is known, and  $Q_3$  is measured, we have a very simple and direct means of cal-

culating  $O_2$ . This is essentially what we have done, except that the calculations have been extended to allow for the  $Fe_2O_3$ , which was found to be formed along with the  $Fe_3O_4$ .

It must be conceded at the outset that any determination of the heat of formation of cementite, which involves a knowledge of the heats of formation of the oxides of iron, must be uncertain to the extent of three to four thousand calories per gram-molecule, since the heats of formation of these oxides, as determined by different investigators, vary by corresponding amounts. The value of the calorimetric data, however, is not greatly impaired by this uncertainty, for results may be recalculated at any time when more accurate determinations of the heats of formation of the oxides become available. Aside from this objection the direct combustion calorimetric method is advantageous in that it offers little possibility of large errors when the work is carefully carried out. Hence the method is very reliable within the range of experimental error.

The values which we have chosen to use in the following determinations are as follows: For the molecular heat of formation of magnetite, 267,400 cal., or 1595.6 cal./gram Fe; For the molecular heat of formation of ferric oxide, 195,700 cal., or 1753 cal./gram Fe; And for the molecular heat of formation of carbon dioxide, 94,200 cal., or 7850 cal./gram C. The value for magnetite is that recorded by Berthelot<sup>11</sup> and is es-

11. Thermochemie II, 284 (1881)

essentially the same as the final value of Ruff<sup>12</sup>. The value for ferric oxide is almost identical with that recorded by Le Chatelier<sup>13</sup>, and is the mean of the four most likely values recorded in the literature. If we had chosen to employ the most recent values for the heats of formation of these oxides, as calculated by Tigerschield<sup>14</sup>, (271,000 for  $\text{Fe}_3\text{O}_4$ , and 197,500 for  $\text{Fe}_2\text{O}_3$ ) our data would give a value for the heat of formation of cementite which would be about 3000 cal. per mol greater than the value which we have recorded. The heat of formation of  $\text{CO}_2$  from graphite and oxygen is fairly well established at 94,2000 cal. per mol<sup>15</sup>, or 7850 cal. per gram of C.

The maximum experimental errors in the following calorimetric determinations are estimated to be as follows: In the weight of the water used, an uncertainty of one gram. In the water equivalent, an uncertainty of one unit. In the temperature rise, an uncertainty of  $0.002^\circ\text{C}$ ., corresponding to about 5 cal. In the heat which would have been evolved by the combustion had the elements been in the free state, an uncertainty due to errors in analysis, of 3 to 4 calories. This gives a total possible uncertainty of about 11 cal. in each combustion. Since the samples used averaged about 1.15 grams, this amounts to a possible error of about 9.57 cal./gram. And since the formula weight of iron carbide is 179.5, the maximum possible

12. Loc. cit. p. 9.

13. Compt. rend. 120, 625 (1895)

14. C. A., 19, 1085 (1925)

15. Roth and Wallasch, Z. fur Elektrochem 21, 1, (1915)  
Also Ber. 46, 896 (1913)

uncertainty in the determined heat of formation per mol, due to experimental errors, is  $9.57 \times 179.5$ , or about 1720 cal. Under favorable conditions the amount of uncertainty can be materially reduced, particularly in the temperature rise. Furthermore, the chances of making all maximum errors in the same direction during any one determination are vanishingly small. Consequently we may place the experimental uncertainty at less than 1000 cal. per mol.

## PREPARATION AND ANALYSIS OF THE CARBIDE

The carbide with which the combustions were to be carried out was prepared in the following manner: Sheet Armco Iron was cut into strips about 9 cm. wide and sufficiently long to give a mass of about 150 grams when freed from all traces of surface impurities by grinding and buffing. These strips were then rolled into a tight roll having a circular opening down the center about 0.5 cm. in diameter. Into this opening was packed 1 gram of 200 mesh graphite for each 10<sup>0</sup> grams of iron. The slug thus prepared was fitted into a magnesia-lined graphite crucible and the whole placed in the induction furnace. The temperature was raised fairly rapidly until the contents of the crucible not only melted but became a thoroughly mobile fluid. At this point the temperature was kept constant for about 30 minutes, since previous experience had shown that holding at this temperature for such a period is necessary if uniform distribution of the carbon is to be secured. At the end of this period the current was shut off and the melt allowed to cool. When four such melts had been made the resulting alloys were placed in the control furnace, heated to 850°C, held at that temperature for three hours, and allowed to cool at the rate of six degrees per hour until well below the critical range.



The iron-carbon alloys thus prepared showed 100% pearlitic structure. No traces of excess cementite, excess ferrite, or graphite, could be detected under the microscope. Although nearly one percent of graphite had been added some had been lost as gaseous oxides. Previous experience had shown that it is necessary to add excess graphite in about this ratio, on account of the loss due to oxidation.

These alloys were electrolyzed in a solution made up of boiled distilled water 95%, and concentrated HCl solution 5% by volume. A round platinum electrode served as the cathode, while the alloys, distributed around the platinum electrode, served as anodes. A layer of paraffin oil, floating on top of this solution, served to exclude air and thus prevent oxidation of the alloys at the point of contact with both air and solution. A current density of from 0.005 to 0.01 amperes per square cm. was used to bring about the solution of the iron. The apparatus was so arranged that a considerable volume of the solution was beneath the electrodes. Since the solution of ferrous sulphate formed had a density considerably greater than that of the dilute HCl solution it sank rapidly to the bottom of the container. On this account it was necessary to renew the solution only about once every twelve hours. In some cases this period was extended to twenty-four hours without harmful results.

Once each day, during the electrolysis period, the layer of carbide was scraped from the alloys with the dull smooth

edge of a knife. The first layer, which might have contained surface impurities, was rejected, but all subsequent yields were quickly washed several times with previously boiled distilled water, then with absolute alcohol, and finally with anhydrous ether. The last traces of ether were removed by evacuation. The carbide was then placed in small tightly stoppered bottles to be kept until needed.

Two series of analyses for carbon and iron were made; one before and one after the period during which the combustions were being carried out. No change in composition could be detected. In each case the carbon content was determined by direct combustion in the regulation manner. Every precaution was taken to prevent possible errors. The first series of iron determinations were made by dissolving the cementite in sulphuric acid solution (25% by volume), reducing with zinc, boiling out the hydrogen, cooling in a stream of  $\text{CO}_2$ , and titrating with 0.08255 N  $\text{KMnO}_4$  solution. Such an amount of sample was taken as would require from 80 to 100 c.c. The first 50 c.c. were added from a pipette calibrated to deliver exactly this volume. The titration was then completed in the usual manner, using a 50 c.c. burette. Repeating all operations, without adding carbide, two blank determinations were made. The values 0.32 and 0.35 c.c. were thus obtained. The value 0.33 was used in calculating the iron content of the carbide. A typical analysis follows: Weight of sample 0.4457 grams,  $\text{KMnO}_4$  sol. required

for blank 0.33 c.c., difference required for iron in carbide 90.26 c.c. Then

$$\frac{90.26 \times 0.08255 \times 0.01584 \times 100}{0.4457} = \% \text{ Fe} = 93.36$$

In the same manner the values 93.27, 93.40, and 93.31% were obtained.

The second series of iron determinations were made by the Dichromate Method, as given in "Quantitative Chemical Analysis" by Talbot, using double the amounts suggested, and with the added precaution of filling the titrating flask with  $\text{CO}_2$  after reducing the iron but before the excess stannous chloride was removed. The potassium dichromate solution was of such strength that one c.c. was equivalent to 0.006571 grams of iron. A typical analysis follows: Weight of sample 0.5362 grams, dichromate solution required 76.15 c.c. Then

$$\frac{0.006571 \times 76.15 \times 100}{0.5362} = \% \text{ Fe} = 93.32$$

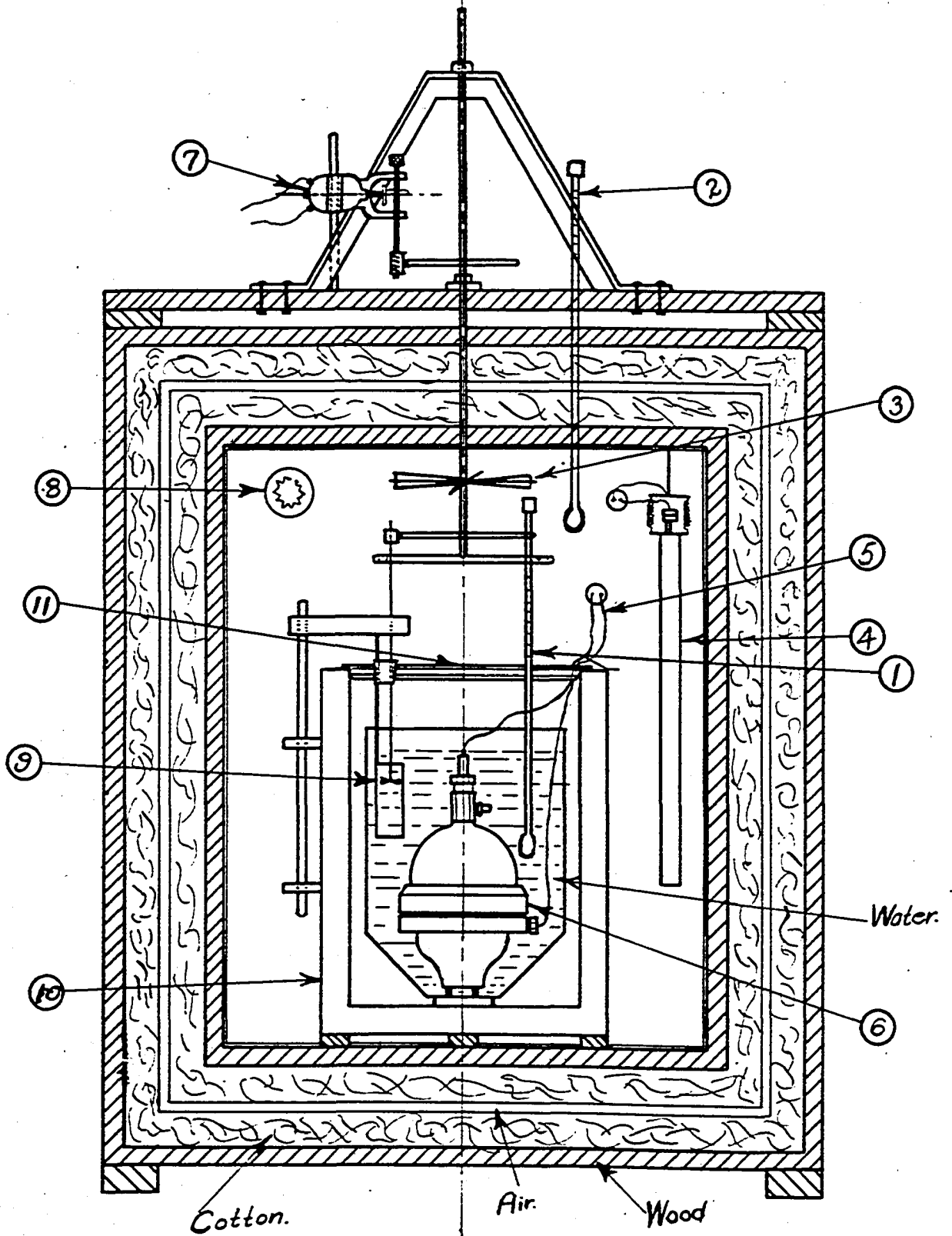
In the same manner the values 93.40, and 93.23 were obtained. The dichromate solution had previously been standardized against pure iron wire by the same method and under the same conditions as to size of sample and volume of solution. The permanganate solution had been standardized against Bureau of Standards sodium oxalate. As a mean of all the values obtained for iron we have the figure 93.33. While this exact check of the theoretical value is, of course, due largely to chance, these results

do show a very satisfactory degree of purity when considered with the mean value for all the carbon determinations, which value is 6.66% C. Obviously all impurities present could not have totaled more than a few hundredths of a percent.

In all, fourteen carbon determinations were made. The first series gave the following values: 6.64, 6.65, 6.69, 6.66, 6.66, 6.67, 6.67, 6.66, 6.65, and 6.66% C. A typical analysis follows: Weight of sample 0.2625 grams, gain in weight of KOH absorption bulb 0.0641 grams. Then

$$\frac{0.0641 \times 12 \times 100}{44 \times 0.2625} = \% C = 6.66$$

The last series gave the values 6.69, 6.66, 6.65 and 6.64% C. As already stated, the mean value of fourteen closely agreeing determinations gives 6.66% as the carbon content of the cementite as compared with the theoretical value 6.67%.



FRONT SECTIONAL VIEW OF SPECIALLY CONSTRUCTED  
CONSTANT TEMPERATURE BOX, WITH CALORIMETER AND BOMB IN PLACE

FRONT SECTIONAL VIEW OF SPECIALLY CONSTRUCTED  
CONSTANT TEMPERATURE BOX, WITH CALORIMETER AND BOMB IN PLACE

Explanation of Figure

- (1) Calibrated Beckmann Thermometer, read through a window in front side of box by means of a cathetometer, with an error of less than  $0.001^{\circ}\text{C}$ .
- (2) Beckmann Thermometer, showing Box Temperature
- (3) Air Circulating Fan
- (4) De Khotinsky Mercury Temperature Regulator
- (5) Fuse Wire Leads
- (6) The Emerson Bomb
- (7) 110 Volt Motor
- (8) 50 Watt Heating Lamp
- (9) Stirring Mechanism
- (10) Calorimeter Jacket
- (11) Calorimeter Cover

## THE CALORIMETRIC DETERMINATIONS

The Emerson Oxygen Bomb Calorimeter, mounted inside of a constant temperature box, was used to determine the heat evolved when the sample of carbide was burned. A motor, mounted above and outside of the box, actuated the stirrer of the calorimeter and also a device to keep the air inside of the box in uniform circulation. The temperature inside of the box was held constant, at a temperature of 30°C., by means of a De Khotinsky mercury expansion element which operated a relay. This relay, in turn, opened or closed the circuit to a fifty watt lamp mounted inside of the box. A temperature of 30°C. was selected to overcome the difficulty encountered when the room temperature rose above 25°, as it usually did in warm weather.

A platinum resistance thermometer was first used to measure the rise in temperature. This instrument, although capable of very high accuracy under the most favorable conditions, was later abandoned in favor of a calibrated Beckmann thermometer. This thermometer, which was read through a glass window in the constant temperature box by means of a cathetometer, was more stable, more convenient, and of about the same precision.

Bureau of Standards benzoic acid was used as a standard to determine the water equivalent of the calorimeter. Consider-

able difficulty was at first experienced in getting checks on this value. The trouble was finally traced to the presence of impurities in the commercial oxygen being used. Other and supposedly much better grades of oxygen were tried, but all seemed to contain enough nitrogen, or hydrogen to vitiate the results. A tank of special calorimetric oxygen was finally obtained from the Air Reduction Sales Company of Cleveland, Ohio. This oxygen was free from nitrogen and hydrogen and proved satisfactory in every respect. All of our recorded calorimetric data were obtained when using this oxygen.

The method of procedure in the determination of the water equivalent was as follows: The sample of benzoic acid was compressed into a pellet in which the iron fuse wire was imbedded. The sample taken usually weighed in the neighborhood of 0.7 grams, while the weight of the fuse wire usually amounted to about 0.0075 grams. The sample thus prepared was suspended over a nichrome dish inside of the bomb by connecting the ends of the fuse wire to the terminals provided. By suspending the sample in this manner it was found that complete combustion was obtained in nearly every case. On the other hand, if the sample was allowed to lie in contact with the cold dish, it was very difficult to secure complete combustion.

The bomb was then assembled, evacuated to a pressure of 2-3 mm., filled with oxygen at one atmosphere, evacuated again, and finally filled with oxygen at a pressure of 250 pounds.



The double evacuation served to remove the nitrogen, from the air which was inside of the bomb. The needle valve was then closed, the bomb disconnected from the filling apparatus, tested in water to detect any leaks, wiped dry and placed in the calorimeter. Two weighed flasks, containing distilled water at different temperatures, were at hand, and from them water was added in such proportions that the desired temperature was secured. The temperature was adjusted to be from one half to one degree below the temperature of the box. The amount of water used was something over 2000 grams in every case.

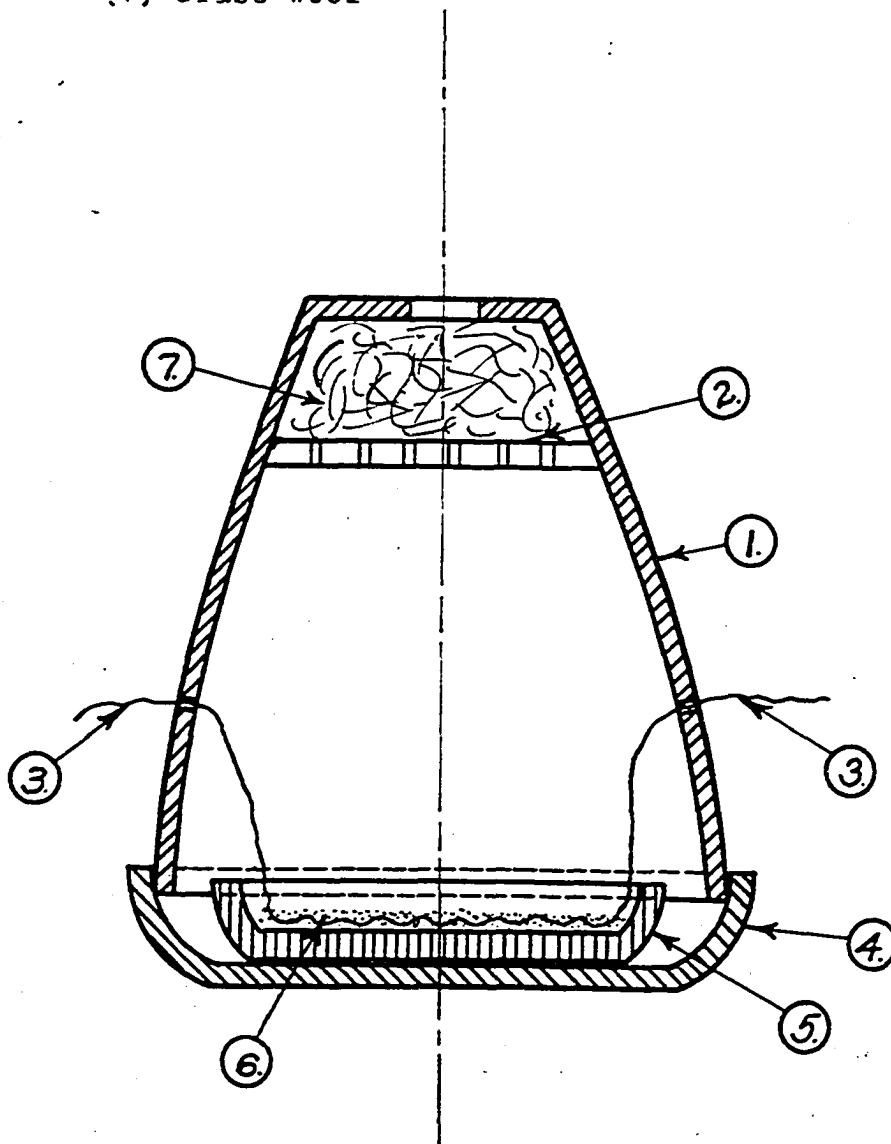
The correct amount of water at the desired temperature having been added, the cover was placed on the calorimeter, the Beckmann thermometer fitted into place, the constant temperature box closed and the motor allowed to run until the temperature remained constant or showed a regular rate of change from reading to reading. Readings were then taken for an interval of ten minutes. In every case one reading was taken each minute. At the end of this preliminary period the sample was fired by closing the proper circuit. After firing, readings were taken until the rate of change of temperature again became constant, and for a five to ten minute interval after this constant rate was obtained. It usually required six or seven minutes to complete the absorption of the heat produced. When all necessary readings had been taken, the bomb was removed from the

calorimeter, opened, and examined for incomplete combustion.

A typical set of data and calculations are as follows: Weight of sample of benzoic acid 0.7880, weight of iron fuse wire 0.0068, weight of unburned fuse wire 0.0026, weight of fuse wire actually burned 0.0042, heat evolved by burning fuse wire 6.6 cal., weight of water 2036.3, observed temperature rise 1.963° C., radiation correction (as calculated by the Regnault-Pfaundler formula) 0.027, corrected temperature rise 1.990, heat of combustion of the benzoic acid 6320 cal/gram. Then  $(0.7880 \times 6320) - 6.6 =$  heat given up to the calorimeter = 4986.76 cal. And  $2036.3 \times 1.990 =$  heat absorbed by the water = 4052.24 cal. Hence  $4986.76 - 4052.24 =$  heat absorbed by bomb and container = 934.52 cal. Therefore  $934.52/1.990 =$  water equivalent of calorimeter = 470. In similar manner the values 469, 473, 470 and 471, were obtained. An average of these five values is very nearly 471, which is the value used in subsequent calculations.

When the attempt was made to burn our cementite in an open dish, or crucible, serious difficulties were encountered. Particles were blown out and remained partially unburned, while the hot oxides attacked the container. Nichrome, platinum and alundum were all found to alloy or unite chemically with the hot oxides. Obviously this gave rise to a heat effect which would probably vitiate any results obtained under such conditions. This difficulty was overcome by using a dish of MgO,

- (1) Alundum Crucible
- (2) Perforated Porcelain Plate
- (3) Fuse Wire
- (4) Alundum Dish
- (5) Magnesia Dish
- (6) Sample of the Carbide
- (7) Glass Wool



SECTION OF CONTAINER IN WHICH THE SAMPLES OF  
CARBIDE WERE BURNED

and enclosing this dish in an aluminum container of the largest size that could be placed inside of the bomb. Of course the addition of these comparatively heavy refractories changed the heat capacity of the calorimeter, but this has been allowed for in the calculations. The magnesia dish was made shallow and of the greatest possible area so that the sample of the carbide could be spread in a thin layer. This was found to materially decrease the chance of incomplete combustion. To further insure that the sample all burned the pressure of the oxygen was increased to 370 pounds, or about 25 atmospheres. The slight increase in the heat capacity of the bomb due to the extra oxygen it now contained was very nearly equalized by the removal of the small nichrome dish which was used with the benzoic acid samples.

When satisfactory conditions for the combustion of the carbide had been determined, several samples were burned. The procedure was essentially the same as that employed in determining the water equivalent, but the presence of the refractories caused a less rapid transfer of heat to the calorimeter and, consequently, a longer period during which heat was being absorbed. Since loss of heat, due to radiation and evaporation, was continually taking place, the correction to be added to the observed rise was much greater than when the combustion period was of shorter duration.

When the products of the combustion were examined they were found to consist of a fine red powder, which was practically pure ferric oxide, and a dark colored magnetic mass which was essentially of the composition of magnetite. Very great care was taken to remove all of the oxides for analysis. The larger particles were crushed in a mortar, after which the mixture was put into a flask containing sulphuric acid solution (two and one half volumes of water to one volume of concentrated acid) and in which the air had been replaced by carbon dioxide. The flask was then heated in a stream of carbon dioxide until solution of the oxides was complete. This usually required several hours. When cooled the resulting solution was titrated with  $\text{KMnO}_4$  solution and the value of the  $\text{FeO}$ , expressed in c.c. of  $\text{KMnO}_4$ , thus obtained. The iron was reduced with zinc, the hydrogen boiled off, the solution quickly cooled in a stream of carbon dioxide, and again titrated with more of the same permanganate solution. The value for a blank on the zinc, although this value was too small to have much significance, was subtracted from the number of c.c. required for this second titration. This gave the value of the total iron, expressed in c.c. of  $\text{KMnO}_4$ .

From the two values obtained as above it is easy to calculate the fraction of the total iron present which burned to magnetite, and the fraction which burned to ferric oxide, without knowing the strength of the permanganate solution. If we assume

that all the FeO present came from the magnetite, which may be represented by the formula  $FeCFe_2O_3$ , then three times the number of c.c. required for the FeO, divided by the number of c.c. required for the total iron, must represent the fraction of the total iron which burned to magnetite. Likewise, the number of c.c. required for total iron, minus the number of c.c. required for magnetite, divided by the number of c.c. required for total iron, must represent the fraction of the iron which burned to ferric oxide. A specific example will make this more clear.

In a certain determination the titration for FeO required 21.12 c.c. The titration for total iron required 73.25 c.c. Then

$\frac{3 \times 21.12}{73.25}$  = fraction of the iron which burned to magnetite.

And  $\frac{73.25 - (3 \times 21.12)}{73.25}$  = fraction of the iron which burned to

ferric oxide. Knowing the weight of the sample used, and the amount of iron which it contained, we have all the data necessary to calculate how much heat should have been evolved if the iron and carbon had been present as the elements instead of combined in the compound  $Fe_3C$ .

The method of analyzing the oxides and making the calculations is essentially the same as that used by Ruff and Gestern, with the exception that we were dealing with magnetite and ferric oxide, while they were concerned with magnetite and ferrous oxide. A more elaborate electrometric titration, which we first attempted to use, was found to be no more accurate and much more troublesome than the simpler method just described. A prelimi-

nary test of this method, using samples of natural magnetite, gave very satisfactory results. It is to be noted that slight inaccuracies in the analyses do not very materially affect the final result, since the error is not absolute but represents only the difference between the heats of combustion of iron to magnetite and to ferric oxide.

In the following table are given the results of the final determinations. While most of the data are self-explanatory as tabulated, the following explanations will serve to make clear any tabulations which may not be self-evident. By "Total heat capacity of the calorimeter" is meant the number of grams of water used, plus the water equivalent of the calorimeter, plus the heat capacities of the refractories used. By "Corrected temperature rise" is meant the final temperature of the heat absorption period, minus the firing temperature, plus the radiation correction. By "Total iron burned" is meant the iron in the sample of carbide plus the weight of the fuse wire which was burned. This quantity is equal to the weight of the sample times 93.33%, plus the weight of fuse wire burned. By "Heat evolved by iron burning to magnetite" is meant the total iron burned times the fraction which burned to magnetite, times the value 1595.6 (which is the number of calories evolved when one gram of iron burns to magnetite). Similarly "Heat evolved by iron burning to ferric oxide" means the total iron burned, times

the fraction burned to ferric oxide, times the value 1753 (which is the number of calories evolved when one gram of iron burns to ferric oxide). "Heat evolved by carbon burned" is the weight of the carbon in the sample times 7850 (which is the number of calories evolved by one gram of carbon on burning to carbon dioxide). "Total heat which free elements would have evolved" is the sum of these three heat effects. "Heat evolved by combustion of the sample" is given by multiplying the total heat capacity of the calorimeter by the corrected temperature rise.



	I.	II.	III.
Weight of sample	1.1582	1.1383	1.1466
Weight of fuse wire burned	0.0090	0.0094	0.0084
Weight of water used	2034.0	2037.1	2033.8
Total heat capacity of calorimeter	2516.0	2517.1	2533.8
Corrected temperature rise	0.9499	0.9387	0.9429
c.c. of $KMnO_4$ solution for ferrous iron	21.12	19.56	18.50
c.c. of $KMnO_4$ solution for total iron	73.25	71.84	73.51
Fraction of iron burned to magnetite	$\frac{62.36}{73.25}$	$\frac{58.68}{71.84}$	$\frac{55.50}{73.51}$
Fraction of iron burned to ferric oxide	$\frac{9.87}{73.25}$	$\frac{13.16}{71.84}$	$\frac{18.01}{73.51}$
Total iron burned	1.0900	1.0718	1.0786
Heat evolved by iron burning to magnetite	1503.3	1397.2	1299.1
Heat evolved by iron burning to ferric oxide	258.1	344.2	363.2
Weight of carbon burned	0.0772	0.0759	0.0765
Heat evolved by carbon burned	606.5	596.1	600.4
Total heat which free elements would have evolved	2369.9	2337.5	2362.7
Heat evolved by combustion of sample	2389.95	2362.7	2389.3
Difference, or heat of formation of sample	-20.05	-25.2	-26.6
Heat of formation per gram of the carbide	-17.33	-22.15	-23.20
Mean heat of formation per gram		-20.9	
Heat of formation per Gram-Molecular weight			-3,752 cal.

Thus, using the values selected for the heats of formation of magnetite and ferric oxide, we have obtained -3,752 cal. per mol as the heat of formation of the cementite electrolyzed from a pure iron-carbon alloy of eutectoid structure and composition.

A comparison of the results obtained by various investigators in this field, considered with the history of the carbide with which each one worked, leads to the conclusion that cementite may exist in two allotropic forms having the same chemical composition but differing in heat content.

If we disregard the work of Campbell, and of Schenck, on the grounds of definitely known objections to their work, we have left for consideration the value of Yermilov (2270 cal.), that of Ruff (-12,300 cal.), that of Maxwell and Hayes (-19162 cal.), and the value obtained by the writers (-3752 cal.). We have already mentioned the fact that Yermilov's value, if recalculated on the same basis as our value, or that of Ruff, would give about -3000 cal. instead of 2270. Thus our work checks that of Yermilov very closely, while Maxwell's value qualitatively checks that of Ruff.

It seems highly improbable that such discrepancies in results could be caused by experimental errors, or by the very small amounts of impurities in the carbide used. What is much more likely is that all of these results are at least approximately true, and that the carbides on which the widely divergent

results were obtained were themselves different. While definite proof is still lacking, the writers advance the following possible explanation: Cementite, as formed at a high temperature in an iron-carbon alloy, has a certain definite heat content. On cooling it tends to undergo transition, with evolution of heat, to an allotropic form of lower heat content. However, owing to the pressure and rigidity of the steel, the transition is prevented and the cementite retains its modification which is stable at the higher temperature. In the process of preparing cementite from an annealed steel, by any solution method, the very thin plates of cementite undergo transition when the iron is dissolved away and the pressure and rigidity consequently removed. Therefore, the heat of formation, as determined on a sample of carbide prepared in this way, would appear greater than the value determined on a sample which had not undergone transition, since the heat content would be less.

Maxwell's data give the heat of formation for the carbide as it exists in the alloy. Consequently we would expect his value to be the lowest possible, which it apparently is. Since Ruff worked with solid fragments of massive cementite, as distinguished from the very thin plates of eutectoid cementite, and since these fragments possessed considerable hardness and rigidity, it seems reasonable to suppose that most of his car-

bide had not undergone transition, although that on the surface of the fragments probably had. Consequently we would expect Ruff's value for the heat of formation to be low but not as low as Maxwell's value; which again is in accordance with the facts. Yermilov prepared his carbide, as did the writers, by solution of the iron from an annealed steel. Then we would expect that his carbide, and our own, had undergone transition when recovered, and that the heat of formation, as determined on this carbide, would be considerably greater than the value obtained by Ruff, or by Maxwell. Our results, in close agreement with those of Yermilov, seem to bear this out. Thus, we see that the available facts are in support of this explanation. Work is now being carried on to add to the evidence for or against this hypothesis.

### SUMMARY AND CONCLUSIONS

We have determined the heat of formation of cementite, as electrolyzed from a pure iron-carbon alloy of eutectoid structure and composition, and have obtained the value -3752 cal. per mol. From a consideration of the results recorded by other workers on this problem, and the results which we have obtained, we have concluded that the heat content of cementite, as prepared from an annealed steel by a solution method, is different from that of cementite as it exists in the alloy. To account for this difference we have advanced the hypothesis that a transition takes place in the cementite when it is freed from the pressure and rigidity of the steel. The heat evolved during this transition accounts for the wide discrepancy in the recorded results for the heat of formation of this compound.