1927

The preparation, acid hydrolysis and magnetic transformation of iron carbide

Waite Philip Fishel
Iowa State College

Recommended Citation

Fishel, Waite Philip, "The preparation, acid hydrolysis and magnetic transformation of iron carbide " (1927). *Retrospective Theses and Dissertations*. 13313.
https://lib.dr.iastate.edu/rtd/13313

THE PREPARATION, ACID HYDROLYSIS AND MAGNETIC TRANSFORMATION OF IRON CARBIDE

by

Waite Philip Fishel

A Thesis Submitted to the Graduate Faculty
for the Degree of

DOCTOR OF PHILOSOPHY

Major Subject: Physical Chemistry

Approved:

Signature was redacted for privacy.

In charge of Major work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State College
1927

ProQuest Information and Learning Company
300 North Zeeb Road
P.O. Box 1346
Ann Arbor, MI 48106-1346

TABLE OF CONTENTS

List of Figures

GENERAL INTRODUCTION

Cementite, a definite carbide of iron, having the formula Fe_3C, is found in all annealed carbon steels and in most cast irons. It may occur as discreet particles of free cementite or as a eutectoid mixture with alpha ferrite, which is known as pearlite. It is believed by many that it is this compound and not carbon which dissolves in gamma iron. All methods for the preparation of iron carbide depend upon its separation from iron-carbon alloys. Iron carbide has a specific gravity of approximately 7, is very hard, and is ferromagnetic at temperatures below 200° C., its Curie point. Since it decomposes at temperatures below its melting point, it has not been obtained in the massive state. When separated from iron-carbon alloys, its color varies with the size of the carbide particles, from a brownish black to a silvery grey. The quantity and metallographic distribution of cementite exert a very important influence upon the physical properties of iron-carbon alloys.

The content of this thesis is divided into three parts: the preparation of iron carbide, its acid hydrolysis, and its magnetic transformation. Concerning the preparation, a more convenient and rapid method is described. In principle it is similar to methods previously known. The hydrolysis was undertaken with the hope of obtaining some information which would augment the meager knowledge concerning the structure and reactions of carbides and which would explain some anomalies encountered in the analytical determination of combined and graphitic carbon. This work definitely connects the A_0 transformation found in high carbon steels and white cast irons with cementite and shows that it, like other magnetic changes, takes place over a temperature range.

PART I. THE PREPARATION OF IRON CARBIDE

Historical

The methods used for the preparation of iron carbide can be grouped into three classes:

(1) The separation of the carbide from iron-carbon alloys, by dissolving the more soluble ferrite in dilute acids, and leaving the carbide as a residue.

(2) Electrolytic solution using dilute acids as electrolytes and the iron-carbon alloy as anodes.

(3) Complete carburizing of pure iron by heating it with sodium cyanide, or other carburizing materials. The products thus obtained usually require a treatment with dilute acids to remove uncombined iron. This method is scarcely more than an extension of the first.

All methods require considerable time. In the first method either weak acids must be used or dilute solutions of stronger acids. This method depends upon finding a solvent which will dissolve the ferrite more rapidly than the cementite. No solvent is known which permits complete recovery of the carbide.

The first definite carbide of iron to be described was that prepared by Sir F. Abel and Mr. Deering (1) who isolated it by treating thin sheets of annealed steel with a mixture of dilute sulfuric acid and potassium dichromate. The residues were analyzed and the results obtained, while they did not agree very closely, led to the proposal of the formula Fe_3C as that of the carbide which existed in annealed steels.

Muller (2) by the action of dilute sulfuric acid upon annealed steel recovered about one half of the carbon present in the steel as a carbide whose composition agreed approximately with the formula Fe_3C.

Yermilov (3) prepared cementite from an annealed steel containing 1.94% carbon. The steel was dissolved slowly in 0.3% hydrochloric acid solution under an atmosphere of carbon dioxide. The residue consisted of a steel grey powder which was not spontaneously inflammable when exposed to air. Analyses showed the residue to contain from 6.66 to 6.67% carbon and from 93.25 to 93.40% iron. The theory for Fe_3C is 6.68% carbon and 93.32% iron.

Ruff and Gestern (4) prepared a quantity of carbide, by suddenly cooling molten iron which had been saturated with carbon and subjecting it to the following treatment. The high carbon alloy was broken up and treated for four weeks with a normal acetic acid solution. The spent acid was decanted and replenished frequently. At the end of this period the residue was ground and was treated for several weeks with a 0.2 normal acetic acid solution. The final residue was shaken with acetylene tetrabromide and the free carbon or graphite was decanted off. It was then washed with alcohol, then with ether, and dried in a vacuum. The composition of this residue agreed very closely with the theoretical composition of Fe_3C. It varied in color from a dark grey to a bronze yellow.

The electrolytic solution method of separating iron carbide from iron-carbon alloys has been used by the following workers:

Osmond and Worth (5) electrolyzed steel in a dilute hydrochloric acid solution. The steel was made the anode and a carbon rod served as the cathode. Thin metallic plates were obtained which they proved both microscopically and chemically to be identical with the carbide isolated by Abel.

In 1894 Arnold and Read (6) carried out rather extensive experiments upon the preparation of iron carbide. They electrolyzed steels in a hydrochloric acid solution of specific gravity 1.02. The cathode was a platinum plate placed within a porous cell. Two steels, one thoroughly annealed and the other normalized, were connected in series and electrolyzed under identical conditions. The anodes were periodically removed from the bath and the carbide was scraped off. After being washed and dried, the carbides were analyzed and were found to contain an excess of carbon. The carbide from the normalized steel contained the greater excess and was more finely divided. As will be brought out in the portion dealing with acid hydrolysis of Fe_3C, it will be shown that free carbon is one of the products formed by the action of hydrochloric acid on Fe_3C, and that an excess of carbon is always found in these residues unless it has been removed by washing or otherwise. It is also evident that the particle size of the carbide obtained in residues will depend upon the size of the carbide particles in the steel used. Arnold and Read found that quenched steels gave low yields of carbide which was contaminated with much free carbon. Their attempt to isolate a double iron manganese carbide, believed to exist in manganese steels, failed. This failure is due to the fact discovered by Fishel and Myers (7) that Mn_3C is readily hydrolyzed by water or by dilute acids.

Campbell (8) prepared a carbide of high purity by electrolyzing an annealed steel containing 1.29% carbon. The carbide was scraped off daily and the accumulated crude carbide was washed with sodium hydroxide solution and then repeatedly with distilled water. During the washing the material was thoroughly stirred up and the lighter portion, mainly graphite, was decanted off. Further purification by washing with alcohol and ether was applied.

Brodie, Jennings, and Hayes (9) prepared Fe_3C and determined its heat of combustion. They used the electrolytic method and were the first to recognize the desirability of using a well annealed steel of eutectoid composition (0.85% C) in order to decrease the formation of free carbon.

Moissan (10) recommended the use of fuming nitric acid to remove carbonaceous material and free carbon. After such a treatment, the carbide is dumped into a large volume of water.

Experimental

The carbide used in these experiments was separated from iron-carbon alloys of high purity. The alloys were made by melting, in an induction furnace, electrolytic iron in lined graphite crucibles and adding the required amount of carbon in the form of pure sugar charcoal. The crucibles were lined with a mixture consisting of previously fused and ground magnesium oxide and 10% aluminum oxide. This mixture was moistened with a magnesium chloride solution and was tamped about a cylindrical form within the crucible. The crucibles were dried and then fired at 1700° C. before being used.

Several ingots weighing about 200 grams and of approximately eutectoid composition (0.85% C) were prepared. They were held for 20 minutes well above the freezing temperature after the carbon had been added in order to insure homogeneity and separation of gases, and were allowed to cool in the furnace. They were held for two hours at 850° C., cooled slowly to 670° C., just below the Ar1 transformation, and held at this temperature for ten hours. Microscopic examination showed the cementite to be present in large spheroids. Large particles of cementite in the alloys insure large particles in the separated product and a purer product, since there is less decomposition of the cementite during the acid treatment and since the larger particles can be more easily washed by decantation.

The ingots were reduced to fine turnings in a lathe. The outer oxidized portions were discarded. The turnings were placed in flasks and were digested with 5 to 10% perchloric acid at room temperature. The spent acid was decanted and fresh acid added as needed. This treatment was continued until all the free ferrite had dissolved. During the solution a small amount of finely divided free carbon forms, most of which is decanted. A mass of steel turnings may be reduced to carbide by this method in two or three days. Dilute perchloric acid acts very slowly at room temperature on iron carbide, but dissolves the free ferrite fairly rapidly.

The residue, which is iron carbide plus a small amount of free carbon, was purified by shaking vigorously with water in a flask and decanting. During the decanting the flask was placed over a strong electromagnet. Iron carbide is strongly magnetic and is held in the flask while the carbon and other nonmagnetic materials are removed. This treatment was continued as long as any light material remained. The carbide was washed in the same manner with absolute alcohol and then with dry ether. The carbide was placed in a thick walled flask and evacuated until the ether was removed. The product prepared in this way, when dry, is stable in the air, but when moist with ether, will take fire if exposed to the air. The statement that iron carbide is spontaneously inflammable occurs many times in the literature. It is possible that the finely divided carbide catalyzes the oxidation of ether vapor, eventually resulting in combustion. Coarse particles of iron carbide have a grey metallic appearance while the finer particles are brown or black.

Some free carbon always results from the action of the acid upon the carbide during the solution of the ferrite. By repeated washing and decantation as described above, it is possible to almost completely remove this free carbon. However, graphite adheres very tenaciously to the carbide particles and is difficult to remove. A flotation treatment, proposed by Ruff and Gestern (4) for the separation of graphite, using tetrabromoethane as a floating agent, was tried. This method was found to be unsatisfactory since the floating agent was viscous and did not readily wet the graphite and carbide particles. Although the free carbon can be removed by repeated rubbing, washing, and decanting, it is best to regulate conditions so that very little free carbon is present. This can be done by using eutectoid steels well spheroidized. High carbon steels and white cast irons which have high carbide content, due to the form of the carbide particles, are not desirable starting materials since they yield residues with considerable free carbon.

About 50 grams of iron carbide was prepared by the perchloric acid method. This carbide was analyzed for carbon by combustion in oxygen and for iron by electrometric titration against a 0.1 N. dichromate solution. Blanks were run before and after each combustion. The following results were obtained:

	% Carbon	% Iron
	6.69	93.25
	6.67	93.37
	6.71	93.18
	6.66	
	6.72	
	6.59	
Av.	6.67	93.27

The theoretical composition of Fe_3C is 6.68% carbon and 93.32% iron. This carbide will be referred to hereafter as perchloric acid carbide. It was used in most of the hydrolysis experiments and in all the magnetic tests.

A small amount of iron carbide was prepared from similar pure iron carbon alloys, by the electrolytic process of Arnold and Read (6). It contained:

% Carbon	% Iron
6.64	93.31
6.61	93.28
6.64	93.29
6.63	

It was identical in appearance and behavior with the carbide prepared by the other methods.

About 80 grams of iron carbide was prepared by heating powdered electrolytic iron in an iron crucible with sodium cyanide at a temperature of 650° C. for twenty hours. The product when washed free from sodium cyanide contained about

5% carbon. It was then treated for a day with perchloric acid, washed and dried as described above. On analysis, it gave the following results for carbon:

% Carbon
6.68
6.60
6.69
6.71

Pierre Pingault (11) states that iron powder treated in the above manner will be completely carburized to Fe_3C.

Conclusion

Of the three methods used to prepare iron carbide the perchloric acid method is the most rapid and the least troublesome. This method was discovered in the search for an acid which would liberate, as gaseous hydrocarbons, all the combined carbon in cast iron without attacking the graphite. Among the various acids tried perchloric left the largest amount of a heavy residue which proved to be iron carbide.

PART II. THE ACID HYDROLYSIS OF IRON CARBIDE

Introduction

In this work an attempt has been made to determine the course of the reaction between iron carbide and hydrochloric acid of varying concentrations and under various conditions, by determining quantitatively the products formed. The total gases produced were oxidized and the carbon weighed as carbon dioxide. The carbon set free as amorphous or graphitic carbon was filtered off and burned to carbon dioxide. The evolved gases were analyzed to determine the compounds present and their amounts.

Historical

The action of acids upon carbon containing steels and irons has been investigated from an early date.

Joseph Priestly (12) mentioned the fetid odors arising when steel is dissolved in acids; and in 1786 L. Rinman (13) noted the relation between the carbon content of the steel and the carbon content of the gas evolved.

Hahn (1864) (14) states, that when cast iron is dissolved in dilute hydrochloric or sulfuric acids, a portion of the carbon passes off with free hydrogen as ethylene, propylene, butylene and dibutylene. He absorbed the gas in bromine water and fractionated the bromine derivatives. He found only unsaturated hydrocarbons.

S. Cloez (15) from similar experiments reported a predominance of methane.

H. Moissan (10) sealed iron carbide with dilute hydrochloric acid in a tube. The products reported are: 83.3% hydrogen, and 13.7% methane. Concentrated hydrochloric acid gave 73.5% hydrogen, and 26.5% methane.

Mylus and Foster (16) treated iron carbide with dilute hydrochloric acid. They report that the carbide is little affected by dilute acids, but that normal and concentrated acids dissolve it readily, leaving a minute residue which is insoluble in water but soluble in alcohol and ether. No amorphous carbon was reported. The gas evolved contained: 92.3% hydrogen, 6.3% hydrocarbons, and 1.4% nitrogen. They suggest pentane as the principal product.

In 1896 E. D. Campbell (8) prepared iron carbide by electrolysis. The product analyzed 6.64% carbon and 93.255% iron. "The carbide was practically completely soluble in moderately concentrated hydrochloric acid." The generating flask was connected directly to the gas burette and was swept out with carbon dioxide. About a half hour with heating was required to decompose a 0.6 gram sample. The total carbon in the gas was determined by combustion. A second sample of gas was absorbed in potassium hydroxide and bromine and the volume of the olefines noted. The remainder of the gas was then exploded for saturated hydrocarbons. The amount of carbon in the olefines was found by difference. A typical analysis follows: One gram of the carbide produced 250.5 cc. of gas, containing 208.1 cc. hydrogen. The total carbon amounted to 71.87 cc. The carbon dioxide from the paraffins was 35.68 cc., and the carbon dioxide from the olefines, by difference, was 9.32 cc. Campbell states that "The above would indicate only enough carbon to account for about 60% of the carbon in the carbide dissolved, thus showing that nearly 40% was present in the form of some hydrocarbon which was either condensed or remained in solution in the generating flask." From the volume of the CO_2 derived from the olefines, compared to the volume of the olefines, a predominance of C_4H_8 with some C_8H_{14} is indicated. From the odor of the liquid Campbell suspects butane and ethane as the principal saturated products liberated. Campbell's gas analysis and methods of identification of compounds are open to question. He failed to mention the formation of free carbon.

Much of the work described above is rather indefinite and conflicting. Most of the material found in Mellor's "Comprehensive Treatise on Inorganic Chemistry" is, however, taken from Campbell's article. Nothing of importance appeared in the literature until, in 1910, there appeared a thesis by Otto Werkmeister (17), entitled "The Formation of Iron Carbide and the Gaseous Products from its Decomposition with Mineral Acids." It was published in thesis form only and seems to have escaped the attention of the later writers.

Werkmeister decomposed iron carbide of high purity with 4 normal H_2SO_4, 2.617 normal HCl, and with one part concentrated H_2SO_4 to three parts H_2O. Approximately 10 gram samples were treated with 150 cc. of acid in a 600 cc. flask. The reactions were run at 60 to 80° C.

About one and three-fourths hours were required for decomposition. The generating flask was then swept out with 600 cc. of nitrogen. The gases produced were passed through a condenser cooled with liquid air or a mixture of solid carbon dioxide and ether, in which the heavier portion was condensed. The uncondensed gas, called "endgas", was collected over mercury. The condensed portion was vaporized and was analyzed separately, the analytical methods used are standard and the work is the most accurate and reliable of its kind up to date. The undecomposed residue and free carbon formed were not determined. Each portion of the gas was passed into bromine water to absorb olefines, which were then liberated and analyzed for total carbon and hydrogen. The volume of the paraffins equals the total volume minus the combined volumes of the olefines and free hydrogen. Table I gives the results combined from the condensed and uncondensed gas data.

Table I

The Composition of the Uncondensed Gases.

				Olefines absorbed in bromine water.			
Exp. No.	Acid used.	Gases cooled by.	Total Gas Vol. in cc.	Olefines in cc.	CO_2 from Olef.	H_2 from Olef.	Ratio CO_2/Vol.
1.	1 vol. H_2SO_4 to 3 H_2O	Solid CO_2	252.9	7.79	20.21	19.12	2.59
2.	4 N. H_2SO_4	"	252.5	7.17	20.20	21.26	2.81
5.	2.6 N. HCl	"	249.6	6.65	16.62	18.52	2.49
6.	2.6 N. HCl	"	251.8	6.25	18.18	20.04	2.90
5a.	2.6 N. HCl	un-cooled	256.4	11.24	47.1	48.4	4.18
6a.	2.6 N. HCl	"	258.7	12.44	51.0	52.4	4.1

Table I Continued.

	Paraffins						
Exp. No.	cc. para.	CO_2. cc. from	H_2. cc. from	Ratio CO_2/Vol.	Total CO_2 in cc.	% Tot. C in Fe_3C	cc. Free H_2
1.	--	22.8	--	--	43.05	34.52	---
2.	17.52	22.9	40.15	1.31	43.18	34.62	227.8
5.	18.98	28.4	47.67	1.49	45.02	36.10	224.0
6.	18.18	29.1	45.37	1.6	47.31	37.93	227.4
5a.	20.68	38.2	58.76	1.85	85.39	68.46	224.4
6a.	18.88	37.6	55.62	2.00	88.80	71.20	227.4

In experiment 5, 12 grams of carbide was treated with 300 cc. of 2.617 N. HCl at 80° C. for 2½ hours. About 3 liters of gas was collected, which is about 247 cc. per gram of carbide. The uncondensed portion analyzed 2.67% olefines, 89.73% hydrogen, and 7.60% paraffins. The 2.67% olefines on combustion gave 6.66% carbon dioxide and 7.42% hydrogen. Since one volume of ethylene plus oxygen yields two volumes of CO_2 and two volumes of H_2, and propylene yields three volumes of CO_2 and three volumes of H_2 per volume, these results would indicate a mixture of ethylene and propylene.

The condensed gas analyzed 6.00% olefines, which on combustion produced 31.93 volumes of CO_2 and 33.3 volumes of hydrogen with a ratio of CO_2/Vol. of gas equal to 5.332; and 2.65% paraffins, which produced 12.72 volumes of CO_2 and 15.96 volumes of hydrogen and a ratio of CO_2/Vol. of gas equal to 4.8. These ratios indicate higher molecular weight hydrocarbons up to at least pentylene and pentane.

Two determinations, 5a and 6a, were run without cooling the gas. In these determinations the ratios (CO_2/Vol. of gas) are higher for both the olefines and paraffins, which means that the higher molecular weight hydrocarbons had been condensed in the former experiments. The total per cent of the carbide carbon found in the gas also increased. In the experiments in which the gases were cooled, the average CO_2/Vol. ratio for the olefines is 2.62 and for the paraffins 1.37. This would indicate that the olefines were ethylene and propylene, and the paraffins methane and ethane. The ratios for the uncooled, and therefore total evolved gas are: olefines 4.14 and paraffins 1.92. These ratios would require olefines up to and including pentylene and paraffins principally ethane with some methane. Werkmeister (17) gives the calculated proximate composition of the total gases evolved in experiment 6:

87.88% Free H_2	3.04% CH_4	0.09% C_2H_4
	4.12% C_2H_6	2.42% C_3H_6
	0.89% C_5H_{12}	1.45% C_5H_{10}
		0.15% $(C_5H_{10})_2$
	8.05% Paraffins	4.11% Olefines

Experiment 5a:

87.55% Free H_2	0.108% $C_{10}H_{22}$	0.585% $(C_5H_{10})_2$
	0.537% C_5H_{12}	1.199% C_5H_{10}
	3.717% C_2H_6	1.533% C_3H_6
	3.698% CH_4	1.073% C_2H_4
	8.060% Paraffins	4.390% Olefines

Werkmeister's results fairly well establish the presence of paraffins and olefines containing as many as 5 carbon atoms. The ratios for the total uncooled gasses of experiments 5a and 6a, which are the averages for all compounds contained, can be expressed for the olefines by hydrocarbons up to 5 carbons and for the paraffins by methane and ethane. The gases in these two runs correspond to the gases which are reported in this thesis, except that the latter were generated at a higher temperature, which would be less favorable to the formation of high molecular weight hydrocarbons.

Schenck, Geisen, and Walter (18) treated high carbon steels, high manganese steels, and ferromanganese with acids.

The gases evolved were separated into fractions by various cooling agents. The fractions were analyzed separately. Pure iron carbide was not used; hence their results are not exactly comparable to this problem. From a 2.50% carbon steel, they report saturated hydrocarbons, principally methane with a small amount of ethane, and unsaturated hydrocarbons, ethylene, propylene, butylene and amylene, whose amounts decrease in the order named.

Later Schenck and Stenkhoff (19) decomposed iron carbide with sulfuric, benzenesulfonic, and acetic acids of various concentrations and in the presence of the corresponding ferrous salts. An excess of acid was allowed to act for three weeks upon weighed samples of the carbide at 60° C. The free carbon formed was determined by filtering, washing, and igniting the residues. The evolved carbon was determined by difference. Their results are included in table II.

Table II

Hydrolysis of Cementite to Free Carbon

Mol conc. H_2SO_4	2.5	2.5	2.5	0.017	0.017	0.017
Mol conc. Ferrous Sulfate	0.0	0.6	1.39	0.0	0.6	0.96
% Total C as Free C	15%	36%	73%	18%	55%	73%
Mol conc. benzenesulfonic acid	1.5	1.5	1.5	0.25	0.25	0.25
Mol conc. Ferrous benzenesulfonate	0.0	0.18	0.63	0.0	0.18	0.63
% Total C as Free C	33%	60%	87%	34%	60%	87%
Mol conc. Acetic acid	1.5	1.5	0.5	0.5		
Mol conc. Ferrous Acetate	0.0	0.385	0.0	0.385		
% Total C as Free C	41%	70%	68%	99%		

These workers failed to test the residue for undecomposed iron carbide. They assumed that this residue was free carbon only. The high results which they obtained for free carbon in all but the first experiment are undoubtedly in gross error due to the presence of undecomposed carbide in the residue. This conclusion is substantiated by the work reported here and by that of Ruff and Gestern (4), who purified their carbide by treating it for several weeks with 0.2 normal acetic acid. The value of 15% free carbon obtained with 2.5 molar H_2SO_4 agrees with the values recorded in tables III, IV, V, and VI, which the author obtained by using concentrated and dilute HCl.

Schenck and Stenkhoff built up quite a theory to account for the increase in free carbon with increasing pH and ferrous ion concentrations. Since their data is faulty, their theories accounting for their data are apt to be worthless.

Millner (20) attacks the above theory in a very satisfactory manner. He, however, does not question the data. Putnam and Kobe (21) in a review article entitled "Hydrocarbons from Carbides" seem to select Schenck's article as the outstanding one dealing with iron carbide.

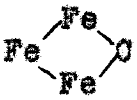
Several writers have attempted to explain the mechanism of the action of acids upon iron carbide. The following equations are frequently written:

$$Fe_3C + 6HCl = 3FeCl_2 + CH_4 + 2H$$

and

$$Fe_3C + 6HCl = 3FeCl_2 + C + 6H$$

These equations do not explain the formation of all compounds found.

Campbell (8) states that the formula is $(Fe_3C)_2$ and the free carbon is formed by the decomposition of methane. Werkmeister (17), in discussing Campbell's article, suggests that the structure may be represented by  or . The first structure when decomposed by acids should give, as the first product, a methylene free radical, CH_2, from which various other saturated and unsaturated compounds can result. He states that methane cannot be formed directly. The second structure is unlikely since it contains ferric iron.

Schenck (19) supposed that the free carbon resulted from the decomposition of methane at the temperature of the reaction. He suggests that an increase in pH lowers the reaction rate and consequently decreases the hydrogen overvoltage on the iron carbide. This would cause the hydrogen to be a less effective reducing agent and more free carbon to be formed. An increase of ferrous ions would decrease the tendency for iron to go into solution, resulting also in a decrease in polarization. As was mentioned previously, this data is questionable and Milner (20) disproves their theory.

Schmidt (22) states that CH_2 is first formed. The methylene radical may be hydrogenated to methane, or polymerized to ethylene, which in turn may be hydrogenated or form addition products with CH_2. In this manner a series of saturated, unsaturated, and cyclic products may result. He believes that free carbon results from the decomposition of CH_2, and that catalysts may influence the course of the reactions.

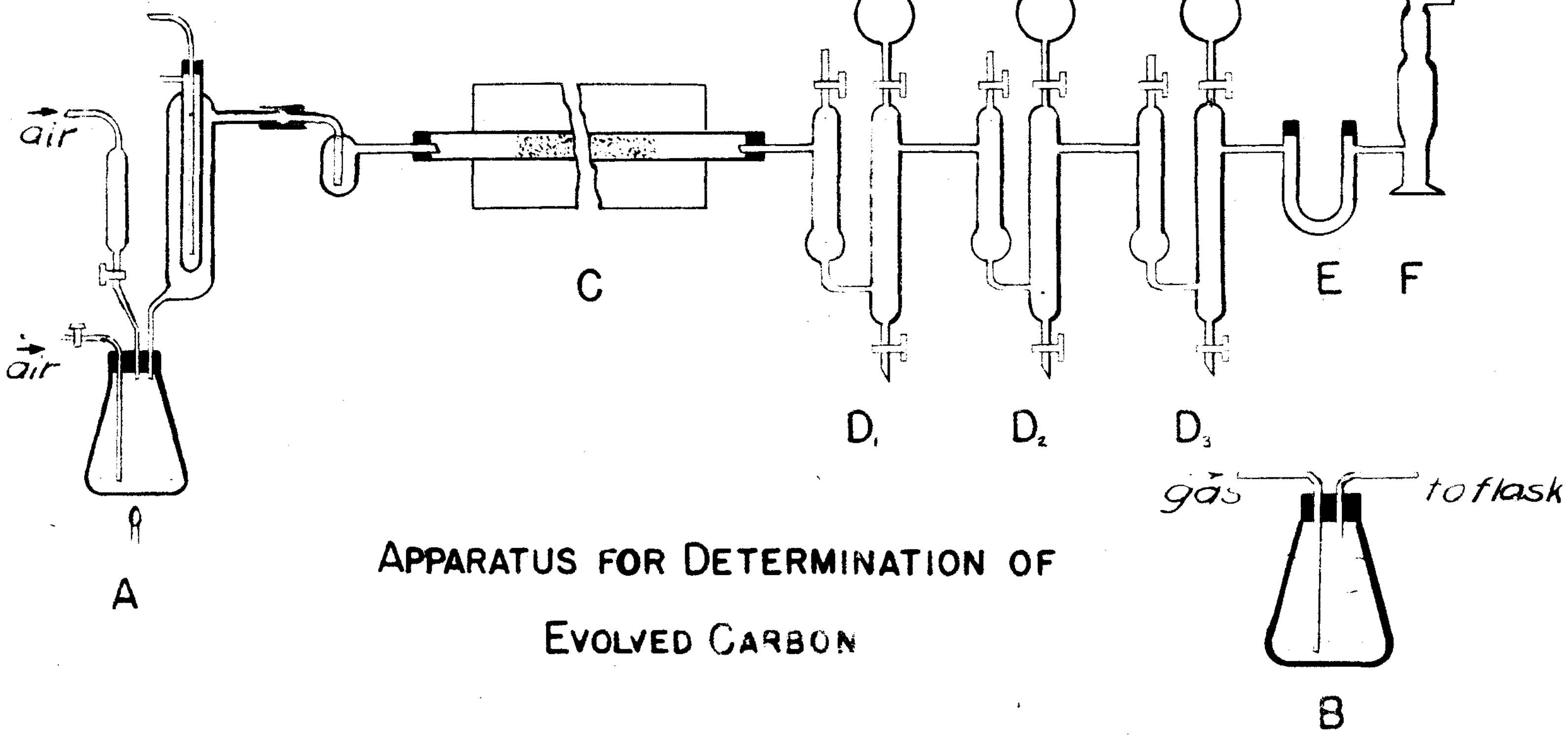
Travers and Diebold (23), in spite of the crystal structure evidence, propose that the ethylenic skeleton $>C = C<$ is present in the molecule; that the formula is $(Fe_3C)_n$; and that on solution in acids hydrogen first replaces the iron atoms without saturating the double bond. They state that in the presence of a catalyst, hydrogen adds to the double bond; that the activity of the hydrogen is a measure of the pH and decreases with increasing pH; and that in the presence of oxidizing agents the hydrogen is oxidized and the ethylenic skeleton is freed.

The methylene free radical theory satisfactorily explains the formation of all compounds found, but the initial formation of this radical is difficult to explain. It involves the assumption of divalent carbon as was proposed by Werkmeister (17) and is not in accord with crystal structure data. The existence of the methylene free radical has not been proved.

Experimental

The determination of the total carbon evolved

In order to determine the carbon liberated in the form of carbonaceous gases by the action of hydrochloric acid upon iron carbide, weighed samples of the carbide were placed in the evolution flask A of figure 1. Flask A is connected through a water-cooled reflux condenser to a quartz tube filled with copper oxide, and then to a purification train, or to three absorption flasks containing an ammoniacal solution of barium chloride. Flask A carries a dropping funnel for



APPARATUS FOR DETERMINATION OF EVOLVED CARBON

FIG. I

the introduction of acid and an air inlet which extends almost to the bottom of the flask. The quartz tube is heated to dull redness by means of an electric furnace. Carbon dioxide-free air under pressure is passed through the apparatus. All gases liberated are swept through the copper oxide tube, where they are oxidized. Two methods were used to absorb the carbon dioxide formed. The first is that proposed by McFarlane and Gregory (24) for the determination of small quantities of carbon dioxide. In this method the gas is passed into flasks B containing an ammoniacal solution of barium chloride. The carbon dioxide reacts with the cold solution to form soluble barium carbamate, which is decomposed by boiling into insoluble barium carbonate. The solution is heated during and after the absorption. The solution is then cooled in carbon dioxide-free air. When cold, it may be filtered in air without formation of more barium carbonate.

To begin a determination, the apparatus is swept out with air. The weighed sample of carbide is introduced into the evolution flask and a boiling solution, made up of 20 parts concentrated ammonium hydroxide and 100 parts of water, is filtered into flasks B. The acid is then run into flask A and a slow stream of air is bubbled through the apparatus. The generating flask is then heated on a water bath. The heating and introduction of acid is so regulated as to control the rate of gas evolution. About 30 minutes are required to decompose a 0.5 gram sample. When the sample has been almost completely decomposed, the water bath is removed and the evolution flask is heated to rapid boiling with a free flame. Meanwhile the air flow is increased and the heating is continued for about 30 minutes to completely sweep out all gases from the liquid and the combustion train. It was found necessary to continue the operation until a strong color of ferric chloride showed in the evolution flask. With the air still passing through the apparatus, flasks B are heated to decompose the barium carbamate. These flasks are then closed off by means of clamps and are cooled to about 10° C. When cool, the barium carbonate is filtered off and ignited. The amount of carbon evolved as carbonaceous gases is calculated from the weight of the barium carbonate. This method of determining carbon dioxide has the advantage that the gas does not require purification before being absorbed. It, however, necessitates a filtration and an ignition.

In the second method used to absorb carbon dioxide, the oxidized gases are passed through a Lundell scrubber filled with a solution of sodium arsenite, which removes HCl, Cl, and SO_2, and are then dried by passing through two Lundell scrubbers, containing sulfuric acid and potassium dichromate, and through a tube filled with dehydrite. The dried gases are then passed into a Fleming bulb. Both methods of determining carbon dioxide give concordant results if carefully used. In using the last method, it is necessary to reoxidize and dry out the combustion tube after each run and to frequently refill the sulfuric acid scrubbers. Considerable water is formed by the combustion of the hydrogen and some hydrochloric acid vapors escape the condenser and the copper oxide.

The general method of dissolving a sample in acid (HCl) and oxidizing all carbonaceous gases and absorbing the carbon dioxide formed was proposed and used by the author to determine the amount of combined or carbide carbon in cast iron. Several Bureau of Standards steels and irons were run by this method. Reproducible results, which were invariably low, were obtained upon all samples. The low results are due to the fact, shown in this work, that a portion of the combined (Fe_3C) carbon is not evolved but reacts to form free carbon. This discrepancy compares favorably with the 11.83% free carbon recorded in tables III, IV, and V.

At the completion of a determination, the liquid in the evolution flask A, which contains the free carbon, is filtered through a small quartz ignition thimble containing asbestos. These are dried at 100° C., and the free carbon is determined by combustion. The filtering of the finely divided free carbon is a very difficult process. It was found necessary to filter the solution twice through the same thimble in order to retain all the carbon. Some of the low results obtained for free carbon are traceable to this step.

Table III contains the percentages of evolved carbon and of free carbon obtained by treating 0.3 gram samples of iron carbide, prepared by the electrolytic process, with hydrochloric acid of sp. gr. 1.1, which is approximately 20% or 6 normal. The flasks were heated for 30 minutes on a boiling water bath and were then boiled with a free flame for 30 minutes more. The carbon dioxide, resulting from the oxidation of the evolved carbon, was absorbed in an ammoniacal barium chloride solution. The last column in the table is the sum of the evolved and free carbon and in most cases equals or approximates the total carbon present in the carbide. This fact excludes the possibility of liquid or solid hydrocarbons of high molecular weight and low volatility being formed during the acid hydrolysis of iron carbide. Such waxes and high boiling liquids were reported by Campbell (8). No traces of greasy materials were noticed on the inside of the evolution flasks, even though the same flask had been used repeatedly.

Table III

Hydrolysis of Fe_3C Prepared by Electrolysis with HCl, sp. gr. 1.1

g. Fe_3C	A % C Evolved	B % C Residue	Total A + B
.3	5.917	0.728	6.645
.3	5.900	0.782	6.682
.3	5.84		
.3	5.948	0.740	6.688
.3	5.938	0.746	6.684
.3	5.938	0.501	6.439
.3	5.88	0.461	6.343
.3	5.802	0.536	6.338
Average	5.89		

These results show that of the 6.68% carbon present in iron carbide an average of 5.89% is evolved as carbonaceous gases, and by difference 0.79% carbon should remain as free carbon; or 88.17% of the total carbon is evolved and 11.83% remains as free carbon. The last three results for residual or free carbon are considerably below the value 0.78%. These low results are probably due to loss during filtration. A large number of determinations will be described in the next section which do agree with this value.

After the results in table III had been obtained, an accident necessitated building a new condenser. Determinations were made on the perchloric acid carbide. The evolved carbon varied from about 4 to 5%. Then samples of the electrolytic carbide previously used were analyzed. They gave similarly low results. A search was then begun for the missing carbon. It was either evolved or left behind as free carbon or as liquid hydrocarbons. Some of the experiments used in this search will be described since they show the absence of liquid hydrocarbons of low volatility and the effect of nascent hydrogen upon the reaction.

In order to search for carbonaceous material other than filterable free carbon, the contents of the evolution flask, after being filtered, was returned to the evolution flask where it was treated with strong oxidizing agents such as ammonium persulfate, sulfuric chromic acid mixture, and concentrated nitric acid. All gases were oxidized and absorbed. No additional carbon was found.

In order to test the action of nascent hydrogen, which, if the equation $Fe_3C + 6HCl = 3FeCl_2 + 4H + CH_2$ is correct, should favor the formation of methane rather than long-chain hydrocarbons, iron carbide was mixed with finely divided tin, aluminum, or nickel and was compressed into pellets. These pellets were then treated as was the iron carbide. Such pellets were also made the cathode and were treated with hydrochloric acid in a specially designed evolution flask, while a direct current was passing and while the pellets were enveloped in a film of hydrogen. Under all these conditions the evolved carbon remained low and erratic. The free carbon in the residues, however, remained constant and about equal to the higher values recorded in table I. Several of these results are recorded in order to reinforce the data on free carbon. Per cents of free carbon obtained were: 0.88; 0.75; 0.93; 0.75; 0.76; 0.92; 0.96; 0.89; 0.90; 0.80. Average: 0.84% carbon.

The trouble was finally located in a small leak in the condenser which, under certain pressure conditions within the flask, allowed some of the gas to escape into the water line.

Samples of the carbide prepared by the perchloric acid method were then treated with hydrochloric acid of various concentrations. The results are given in tables IV, V, and VI. In table IV the perchloric acid-prepared carbide was treated for one hour with boiling HCl sp. gr. 1.1.

Table IV

Hydrolysis with HCl sp. gr. 1.1

	A	B	
g. Fe_3C	% C Evolved	% C Residue	Total A - B
.5	5.76	0.71	6.47
.5	5.66	1.01	6.67
.5	5.70	1.00	6.70

In the next series of experiments the carbide was treated with concentrated acid. When decomposed, water was added to dilute the acid and the solution was boiled and swept out for 30 minutes.

Table V

Hydrolysis with Concentrated HCl

	A		
g. Fe_3C	% C Evolved	% C Residue	Total A - B
.5	5.72	0.873	6.593
.5	5.803	0.715	6.518
.5	5.75	0.85	6.60
.5	5.79	0.80	6.59

In the third series of experiments dilute acid consisting of 1 part acid and 4 parts water was used.

Table VI

Hydrolysis with Dilute HCl

g. Fe_3C	A % C Evolved	B % C Residue	A - B Total	Total time-min.
.5	4.614	1.86	6.414	40
.5	5.48	1.00	6.48	40
.5	5.65	0.976	6.626	60
.5	5.53	0.640	6.17	60
.5	5.40	1.24	6.64	60
.5	5.997	.65	6.647	60
.5	5.456	----	----	60

The dilute acid gives slightly higher results for free carbon and lower results for evolved carbon. Part of this may be due to incomplete decomposition of the carbide. The first two determinations in table IV are low, due to incomplete decomposition and incomplete sweeping out of the gases. During the solution of Fe_3C in HCl, a peculiar odor is present. This odor remains until the liquid has been boiled and aerated until a distinct ferric chloride color develops, and suggests the presence of carbonaceous gases or of low boiling liquids of a reducing nature. In a determination, the results for evolved carbon will invariably be low, unless the solution has been heated and aerated for at least 30 minutes after decomposition of the carbide has been completed.

In substance these results show that the total carbon present in iron carbide, when decomposed by hydrochloric acid, can be accounted for as carbonaceous gases and as free carbon, and that the action cannot be represented by one simple equation. Some free carbon is always formed, the amount of which varies slightly with the concentration of the acid used. The mechanism of the reaction will be discussed after the presentation of the gas analysis results.

The composition of the gases resulting from the action of hydrochloric acid upon iron carbide

The gas was generated by the action of concentrated hydrochloric acid upon weighed samples of carbide, in a 50 cc. flask carrying an outlet tube connected directly to a two-way stopcock at the top of a gas storage burette filled with mercury. The stopper of the flask also carried a dropping funnel. The carbide was placed in the flask, and, with the two-way stopcock open to the air, acid was run in until the flask and tube running to the burette were filled. The stopcock was then closed and as the action began, some acid was forced into the dropping funnel, which was then closed off, and the gas was allowed to pass into the burette. At the completion of the reaction, the generating flask was again filled with acid. This eliminated most of the air and permitted all the gas to be collected. Concentrated acid was used in order to decrease the volume of liquid and the amount of gas which would remain dissolved in it. It is recognized that some gases, especially the heavier ones, remain dissolved and that the gas which is collected is not identical with or does not represent all the gases oxidized in the evolution experiments recorded in tables III to VI.

In order to obtain a rough measure of the amounts of carbonaceous gases held in solution, the contents of the generating flask was transferred to flask A of the evolution apparatus of figure 1, where it was boiled and swept out for 30 minutes and the evolved carbon measured. This amounted to about 20% of the total carbon.

About 80 cc. of air-free gas was collected from 0.3 g. of carbide, which represents about 50% of the total carbon.

The apparatus used for the analysis of the gas obtained by the acid hydrolysis of iron carbide was designed by the Bureau of Mines for the complete and partial analysis of gases. A description of the apparatus and directions for its operation are given in the Bureau of Mines Bulletin No. 197. A photostat of the apparatus is shown in figure 2. The gas was analyzed for carbon dioxide, illuminants, oxygen, hydrogen, carbon monoxide and saturated hydrocarbons. A data sheet follows, which shows the method of calculation.

Vol. of sample	74.9 cc.	
Vol. after KOH	74.0	
	.9 cc.	CO_2 and HCl. Other tests show no CO_2; therefore, HCl.
Vol. after fuming H_2SO_4	71.0	
	2.1 cc.	Illuminants
Vol. after pyrogallic acid	62.6 cc.	
	8.3 cc.	Oxygen 37.2 cc. Nitrogen
Vol. after CuO	27.0 cc.	
	35.6 cc.	Hydrogen
Vol. after KOH	27.0 cc.	
	0.0 cc.	Carbon Monoxide
Vol. oxygen added	64.2 cc.	
Total volume before combustion	91.2 cc.	
Vol. after combustion	81.6 cc.	
Vol. of contraction	9.6 cc.	
Vol. after KOH	76.8 cc.	
Vol. of carbon dioxide	4.8 cc.	equivalent to 4.8 cc. CH_4
	22.2 cc.	Nitrogen by difference

The only saturated hydrocarbon present is methane since the contraction is just twice the amount of carbon dioxide formed by combustion. The results on the air-free basis are: 4.94%

APPARATUS for GAS ANALYSIS

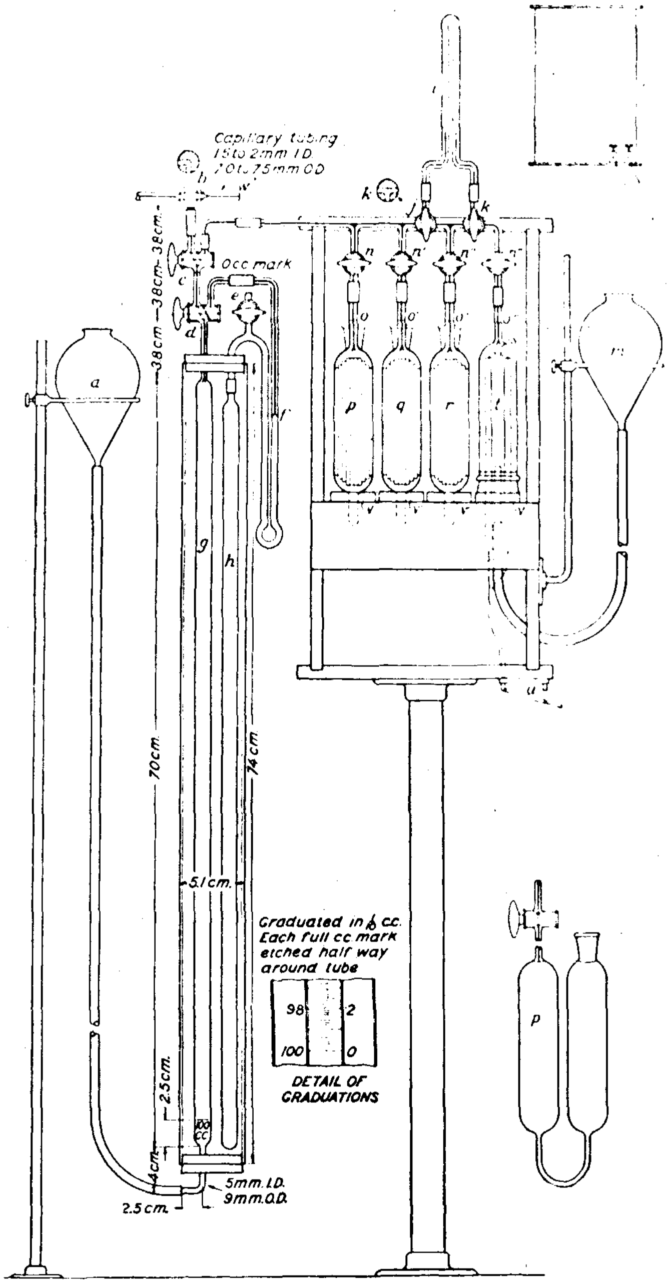


FIGURE 1.--Details of apparatus. Front view: *a*, Leveling bulb; *b*, three-way L bore cock; *c* and *d*, three-way parallel bore cocks; *e*, two-way cock; *f*, mercury or oil mark; *g*, burette; *h*, Pettersson compensating tube; *i*, copper oxide tube; *j* and *k*, stopcocks; *l*, electric furnace for copper oxide tube; *m*, mercury bulb; *n*, *n'*, *n''*, and *n'''*, cocks; *o*, *o'*, and *o''*, reagent marks; *o'''*, mercury mark; *p*, pipette to remove CO_2; *q*, pipette to remove illuminants; *r*, pipette to remove O_2; *s*, ends of platinum coil; *t*, pipette to determine CH_4 and C_2H_6; *u*, switch; *v*, *v'*, *v''*, and *v'''*, supports for pipettes

Fig.2

illuminants, 83.76% hydrogen, and 11.3% methane. The results from several determinations are recorded in table VII.

Table VII

Results of Gas Analysis

cc. gas Sample	cc. CO_2 and HCl	cc. Ill.	cc. O_2	cc. N_2 Calc.	N_2 by Diff.	H_2	cc. Contr.	cc. CO_2
No. 1 79.5	1.0	1.9	5.4	21.6	17.7	47.7	--	--
No. 2 65.6	0.1	1.3	4.8	19.2	20.5	31.4	11.3	4.8
No. 3 74.2	0.5	2.1	4.9	19.6	17.5	43.9	11.6	5.3
No. 4 74.9	0.9	2.1	9.3	37.2	22.2	35.6	9.6	4.8
No. 5 74.7	0.5	2.3	7.3	29.2	23.7	36.3	12.8	4.6
No. 6 86.2	0.0	1.9	9.8	39.2	35.9	33.6	9.0	5.0
No. 7 83.0	0.0	1.8	--	--	--	29.1	10.0	5.0
No. 8 73.2	0.6	2.6	5.5	22.0	21.5	37.1	19.9	5.9

The composition of the gases evolved, calculated on the air-free basis are presented in table VIII.

Table VIII

Composition of Gases
(Per cent by volume)

Number	Illuminants	Free Hydrogen	Methane
2	3.23	85.0	11.9
3	4.09	85.5	10.3
4	4.94	83.7	11.3
5	5.30	83.0	10.5
6	4.7	82.9	12.3
8	5.7	81.3	12.9
Average	4.62	83.4	11.5

In these results the assumption is made that methane is the only saturated hydrocarbon present. This assumption is substantiated by the ratio between the contraction and the volume of the carbon dioxide formed during the combustion. The equations for calculating percentages of ethane and methane in mixtures, from combustion data are:

$$\text{Ethane} = \frac{2\ (\text{Vol. } CO_2) - \text{Contraction}}{1.5}$$

$$\text{Methane} = \text{Vol. } CO_2 - 2(\text{Vol. ethane})$$

Sample No. 6 alone gives a positive value for ethane. According to these equations sample 6 is composed of 1.6% ethane and 8.09% methane. Separate tests on samples of the gas were made for carbon dioxide and acetylene. No traces of these gases were found. Carbon monoxide was also absent. The above results show that hydrogen, methane and most probably ethylene are the principal constituents. From the crystal structure of iron carbide, one would not expect to find acetylenic compounds; and long-chain hydrocarbons could result only from secondary reactions. No carbides are known which evolve carbon monoxide.

Discussion of Results

By the evolution experiments it has been shown that, by the reaction of dilute and concentrated hydrochloric acid, iron carbide is decomposed to produce 12.5% of the total combined carbon as free carbon and the remainder as carbonaceous substances which are volatilized under the conditions of the experiment. The complete volatility and the absence of any traces of oily films, such as are present in a similar hydrolysis of manganese carbide, eliminate the possible existence of solid and liquid hydrocarbons, which have been reported by previous writers. Also the spent acids have been extracted with ether and have been treated with oxidizing agents in an attempt to find such compounds.

The fact, that in order to obtain complete evolution of of carbon, it is necessary to pass air through the solution until the iron has been oxidized after the carbide has been decomposed, suggests the possibility of the existence of an unstable complex between carbonaceous gases and ferrous iron. A similar complex is formed when iron carbide dissolves in nitric acid and is the basis for the colorimetric determination of combined carbon in steel and cast iron. Whitely (25) has shown that nitric acid liberates about 50% of the combined carbon as carbonaceous gas during the first half hour of heating and that all the carbon cannot be evolved even after several hours heating. No free carbon is produced. It might be well to mention that the free carbon formed by the action of hydrochloric acid is very finely divided and dissolves in nitric acid when heated. The resulting solution, however, contains no iron.

The gases evolved and analyzed in table VIII represent about 50% of the total carbon present in the carbide. In collecting these gas samples the acid in the generating flask was heated to boiling for a short time only, and the liquid was not swept out with an inert gas. Some gas was lost during collection and during transfer to the gas pipette. If the 12.7% free carbon be subtracted, there remains about 37.3% of the carbon left in the liquid or lost. This carbon is in some form which can be volatilized by continued heating as is shown by the evolution experiments. The carbon found in this liquid amounts to about 33% of the total. The question naturally arises, is this carbon not included in the gas samples of the same nature as that analyzed? If it be assumed that it is, a rough calculation can be made showing that the reaction between hydrochloric acid and iron carbide produces 12.7% of the total carbon as free carbon, 39% as illuninants, and 48% as methane.

The free hydrogen content of the evolved gas is related to the reactions in the following way: The reaction $Fe_3C + 6HCl = 3FeCl_2 + C + 3H_2$ produces a gas which is 100% H_2; $Fe_3C + 6HCl = 3FeCl_2 + CH_4 + 2H_2$ produces a gas which is 50% H_2; $2Fe_3C + 12HCl = 6FeCl_2 + C_2H_6 + 3H_2$ with 75% H_2; and for the production of ethylene 80% H_2; for propylene 83.3%; and for propane 85.6%. Using the percentages of hydrogen in the above reactions, and according to the above distribution or division, the hydrogen content of the total gas calculates about 70%. It is by analysis 83.4%. This disagreement is not surprising when one considers the nature of the calculation and the relative solubilities of the gaseous substances.

There is to a certain extent a parallelism between the hydrolysis of iron carbide and manganese carbide (Mn_3C). As shown by Myers (7) manganese carbide reacts with warm water, all the combined carbon being liberated as carbonaceous gases. The gas produced by water hydrolysis contains 3.39% illuminants, 75% free hydrogen, 0.3% carbon monoxide, 12.13% methane, and 7.07% ethane. If the same carbide is hydrolyzed with 10% hydrochloric acid, the hydrogen content of the gas is 95%. Acid hydrolysis produces considerable free carbon, some liquid hydrocarbons, with a corresponding decrease in the amount of volatile hydrocarbons. The results of acid hydrolysis have been summarized by Myers as follows: dilute hydrochloric acid converts 43.35% of the total combined carbon to free carbon; 17.9% to liquid hydrocarbons; and 38.78% is evolved as carbonaceous gases. The presence of liquid hydrocarbons is shown by the appearance of an oily film on the inside of the generating flask. This film is absent if water is the hydrolyzing agent. These two related carbides cannot be compared as to their reaction with water, since iron carbide is not attacked by water.

Theoretical Discussion

The chemical properties of a substance are fundamentally related to its molecular formula and to the arrangements of the atoms in the molecule with respect to one another. In certain carbides and other binary compounds we are confronted by the problem of anomolous valence. Iron in iron carbide is certainly divalent, since it forms ferrous salts when dissolved in nonoxidizing acids. According to the older ideas of valence, carbon in a single molecule of Fe_3C would have a valence of six. The covalency maximum for elements of the first short period of the periodic table is four. There are no known examples where this is exceeded. A structural formula for $(Fe_3C)_n$ can be written, in which each carbon is attached to four iron atoms and each iron atom except the end ones are attached to two carbons. This structure satisfies the valence requirements but does not agree with crystal structure data and does not account for the products formed by the reaction of the carbide with acids.

Iron carbide crystallizes in the orthorhombic system, the unit cell containing four molecules of Fe_3C. The lattice parameters as determined by Westgren and Phragmen (26) on cementite crystals obtained from spiegeleisen, are $a_o = 4.53$; $b_o = 5.11$; and $c_o = 6.77$ A. U. The crystals were not pure cementite. The positions of the iron and carbon atoms in the cementite lattice were determined by Hendricks (27) from Westgren and Phragmen's data and from measurements which he made on pure iron carbide by the powder method. Hendrick's arrangement has been accepted by Westgren (28) and is the accepted structure at present. Hendricks places a carbon atom at each corner of the rhombohedron, one at the center of each end face, one at the center of each long or Y edge and one at the center of the rhombohedron. With this arrangement each carbon is surrounded by six almost equally distant iron atoms, which form the corners of an octahedron with the carbon at the center. Each iron atom is shared between two carbons and each iron forms a corner of two octahedra. This means that the C to C bond does not exist, but that a carbon is attached to an iron which is in turn attached to a second carbon. The radius of the carbon atom is about 0.55 A. U.; the iron to carbon distance about 1.9 A. U.; and the iron to iron distance about 2.4 to 2.7 A. U. The crystal structure is not considered completely solved. Hendricks states that there is some uncertainty in the location of the carbon atoms. The arrangement according to Hendricks is shown in figure 3.

One can scarcely refrain from proposing a simple cubic arrangement of the carbons with six equidistant iron atoms forming the corners of a regular octahedron with a carbon at the center and with each iron shared between two carbons. This structure agrees with the arrangement of the atoms in a solid solution of carbon in gamma iron. Carbon is practically insoluble in body-centered alpha iron, but is soluble in face-centered gamma iron. The carbon atom probably occupies the large open space at the cube center, since this is the only cavity large enough to accommodate a carbon atom. In this position each carbon is surrounded by the six equidistant face iron atoms and is identical with the simple cubic arrangement suggested above except for the eight corner atoms. By such a structure the separation of iron carbide from solid solution during cooling and

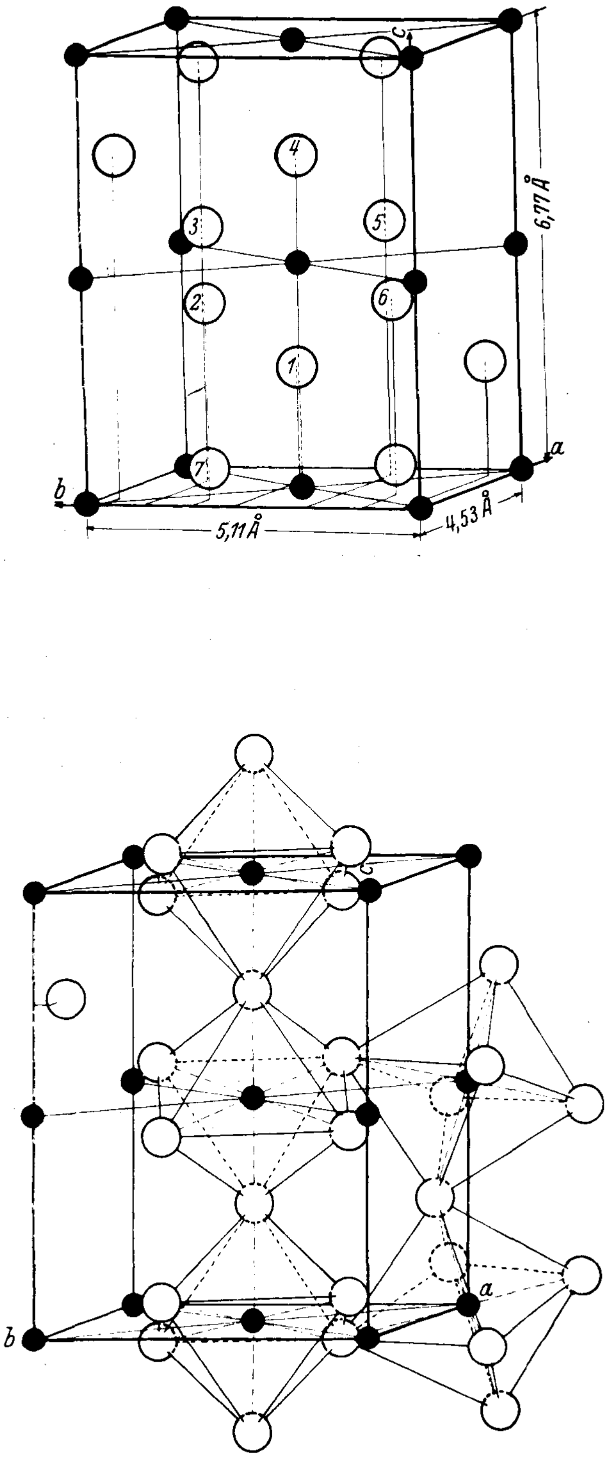


Fig. 3. Crystal Structure of Iron Carbide
According to S. B. Hendricks
Z. Krist. 74, 542.

at the gamma to alpha transformation can be readily explained. Thus cementite, or potential cementite, could exist in solid solution. The existence of cementite in solid solution is a much debated question. Some chemical evidence applying to this question was produced by Fishel and Myers (29) who showed that carbon or iron carbide in a state of solid solution, austenite, reacts with hydrochloric acid in the same manner and to give the same products as does iron carbide.

The determination of a structural formula for iron carbide is rendered difficult by the fact that it takes part in few reactions. Iron carbide can be decomposed by heating, burned, converted to free carbon and ferric chloride by the action of chlorine, and oxidized by nitric acid in which a variable amount of the carbon is slowly liberated as carbonaceous gases and the remainder forms an unstable colored compound with iron and nitric acid. These reactions give no evidence concerning its structure. Its reaction with nonoxidizing acids furnishes little evidence. The products formed, free carbon, methane, and unsaturated hydrocarbons, indicate that it is not a simple reaction, but a series of consecutive reactions. Since the C to C linkage is not present in the lattice, compounds containing more than one carbon must result from secondary addition reactions. No satisfactory structural formula for iron carbide has been proposed. It is probably what Sidgwick (30) would call a giant molecule or a lattice compound which does not exist as single molecules but only as a lattice aggregate. Hagg (31) states that carbides of the transition elements are not true compounds but are metallic in nature. Iron which has a 2, 8, 14, 2 arrangement of electrons has such a strong tendency to complete its M shell that it does not furnish any electrons to the lattice structure. According to Hume-Rothery (32), "Fe, Co, and Ni act as if they had zero valence and contribute no electrons to the lattice. In intermetallic compounds formulae corresponding to the normal valencies of the elements are comparatively rare." Intermetallic compounds or interstitial structures often result in the face-centered lattice, by the insertion of an atom at the center of such cubes. It is in this way that iron carbide forms when carbon dissolves in gamma iron. The iron carbide lattice is considered to be nonionic.

It is quite likely that iron carbide cannot be represented by a structural formula of the usual type employing the normal valencies of iron and carbon, and the usual types of valence bonds. It is pictured as atoms of carbon each surrounded by six iron atoms. Its lattice bonds are certainly not of the ionic type. Part may be covalent and part metallic. A lattice in which four of the iron atoms are attached to carbon by covalent bonds and the remaining two iron atoms form metallic links comes nearest to fitting the conditions. Such a structure would not account for the formation of CH_2 and free carbon on hydrolysis. There is no reason to assume that part of the carbon is differently constituted or attached than the rest.

PART III. THE CURIE OR MAGNETIC TRANSFORMATION IN IRON CARBIDE. THE A_0 POINT

Introduction

This work was undertaken because of the disagreement in the existing data concerning the position of this transformation and concerning its exact nature. The consensus of opinion is that this transformation occurs at a definite temperature which is difficult to locate accurately, due to a lag or slowness in the transformation rate. The modern theories of magnetic changes and the fundamental causes of magnetism indicate that such changes should take place over a temperature range.

In this work the loss of magnetism on heating and the gain on cooling were measured by two methods, one of which is essentially new and has not been previously applied to the measurement of the magnetic properties of carbides.

Historical

The so called A_0 transformation has been recognized in high carbon steels and white cast irons for a long time. Since its intensity increases with increasing carbon, it was assumed that it was connected with iron carbide. It was discovered in 1909 by Wologdine (33) who placed it at 180° C. This transformation has been detected in steels by thermal, magnetic, and dilatation methods.

Smith (34) studied the thermomagnetic properties of a steel containing 0.85% carbon and found that the magnetization reaches a maximum at 213° C. He remarked that this phenomenon might be due to a magnetic transformation in iron carbide.

Honda and Takagi (35) studied twelve steels, ranging in carbon content from 0.14 to 1.50%, by a magnetometric method. A change in magnetization was observed between room temperature and 220° C. The maximum magnetization was reached at 170° C. The amount of magnetization increased with increasing carbon up to 0.85% and then decreased gradually. No change in magnetization was noted in carbon-free iron within this range. The change was therefore attributed to Fe_3C. These authors (36) later studied steels containing 2.90 to 3.49% carbon and a cast iron containing 4.15% carbon. They found that the magnetization remains constant up to 160° C. and then rapidly diminishes. From 215° C. upward the magnetization decreases but little. The lower temperature at which magnetization begins to decrease on heating and to increase on cooling was found to depend upon the magnetic field. They state that "The upper point, 215° C. was found to be perfectly definite." Their curves, however, show a loss in magnetization on heating beginning at about 180° and extending to 215°. One cannot see their justification for selecting 215° as the temperature of the transformation. They failed to correct their former statement concerning the decrease in magnetization with carbon above the eutectoid composition.

Tamman and Ewig (37) made temperature magnetization curves on a series of steels. The loss in magnetization in the neighborhood of the A_0 (210°) was shown to be proportional to the carbon and therefore to the iron carbide present.

Chevenard (38) detected this point in steels at 210° C. by a dilatation method.

Honda and Murakami (39) were the first to use separated iron carbide in their experiments. The carbide used contained 6.08% carbon and 93.5% iron. They measured the intensity of magnetization in magnetic fields of various strengths. The carbide powder was contained in a copper tube. From their curves, which are very similar to those shown in Honda's (36) former paper, they estimate the critical point to be at 215° C. They state that "We have thus obtained a direct proof that in the magnetization curve, the transformation, beginning at about 210° C. by cooling and ending at the same temperature by heating, is really due to the magnetic transformation in iron cementite." Again as in the former curves, the break begins at about 160° and ends at 215° C.

Ishiwara (40), using a sensitive torsion magnetometer, finds that the magnetic susceptibility of iron carbide increases rapidly on heating and reaches a maximum at about 170° C. It then decreases very rapidly, reaching its minimum at about 250° C. He is the only writer who suggests that the transformation occurs over a temperature range.

Lehrer (41) by magnetometric measurements upon steel places the transformation at 215° C. Likewise Mittasch and Kuss (42) by the same methods found a similar value. Travers and Diebold (43) find the Curie point at 210° C., while Mehl and Wells (44) state that, in a very pure iron-carbon alloy containing 1.35% carbon, it occurs at 200° C. and that it does not occur over a temperature range, but at a constant temperature.

In a summary of existing data, Epstein (45) states that "The exact nature of A_0 is in doubt; as the magnetic measurements show a large temperature interval between the beginning and the end of the transformation, it is difficult to assign a definite value to the point."

Experimental

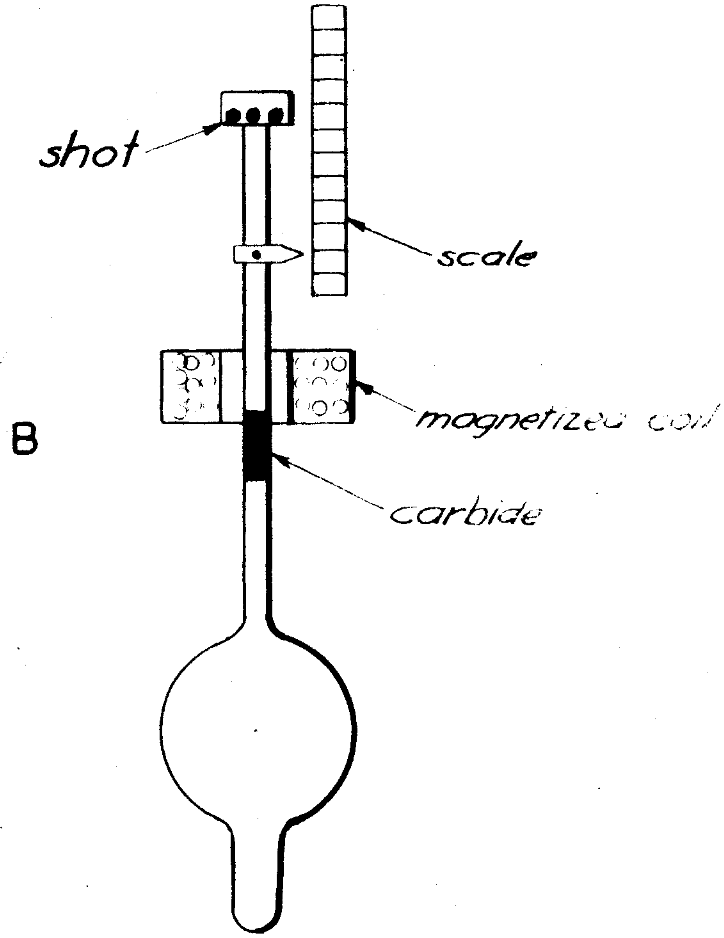
Preliminary experiments

In the preliminary experiments, about 2 grams of iron carbide was sealed in a short glass tube, forming a plummet. This, with a perforated glass tube about it to hold it upright, was heated in an oil bath. An electromagnet was placed about an inch above the plummet and when a current was passed through the coil of the magnet, the plummet would be attracted to the magnet as long as the carbide was magnetic. On heating, no change in the behavior of the plummet was noticed until a temperature of about 200° was reached. The response of the plummet then decreased rapidly until at about 218° C. it refused to be moved. Although this experiment proved that iron carbide underwent a magnetic transformation and located its temperature approximately, it was evident that a more sensitive apparatus was necessary.

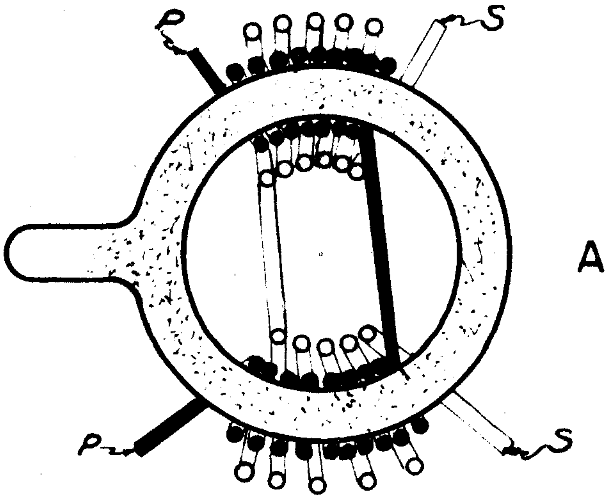
The magnetic transformation by the transformer method

A magnetometer was then constructed which consisted of a ring made of thin glass tubing, filled with iron carbide and wound with a primary and a secondary of about 100 turns of fine enameled copper wire. The primary was connected through a tapping key to a source of direct current, which was controlled by a rheostat and was kept constant during a determination. The secondary was attached to a sensitive wall type galvanometer. This assembly is essentially an alternating current transformer in which the iron carbide acts as the core material. The current induced in the secondary should be proportional to the permeability and the magnetization of the core material. The ring and coils are shown full size in A, figure 4. When the key is closed a current passes through the primary and a current is induced in the secondary. The magnitude of the induced current is measured by the maximum deflection of the galvanometer.

This assembly was placed in a well insulated oil-filled thermostat, equipped with a stirrer, two immersion heaters, and an automatic temperature regulator. The bath could be



HYDROMETER



RING AND COILS

FIG. 4

heated or cooled slowly; or it could be held at any desired temperature. Temperatures were measured by a calibrated thermometer attached to the coil. The continuous type of heating and cooling experiments was run at the rate of 2 degrees per minute and readings were taken at 30-second intervals.

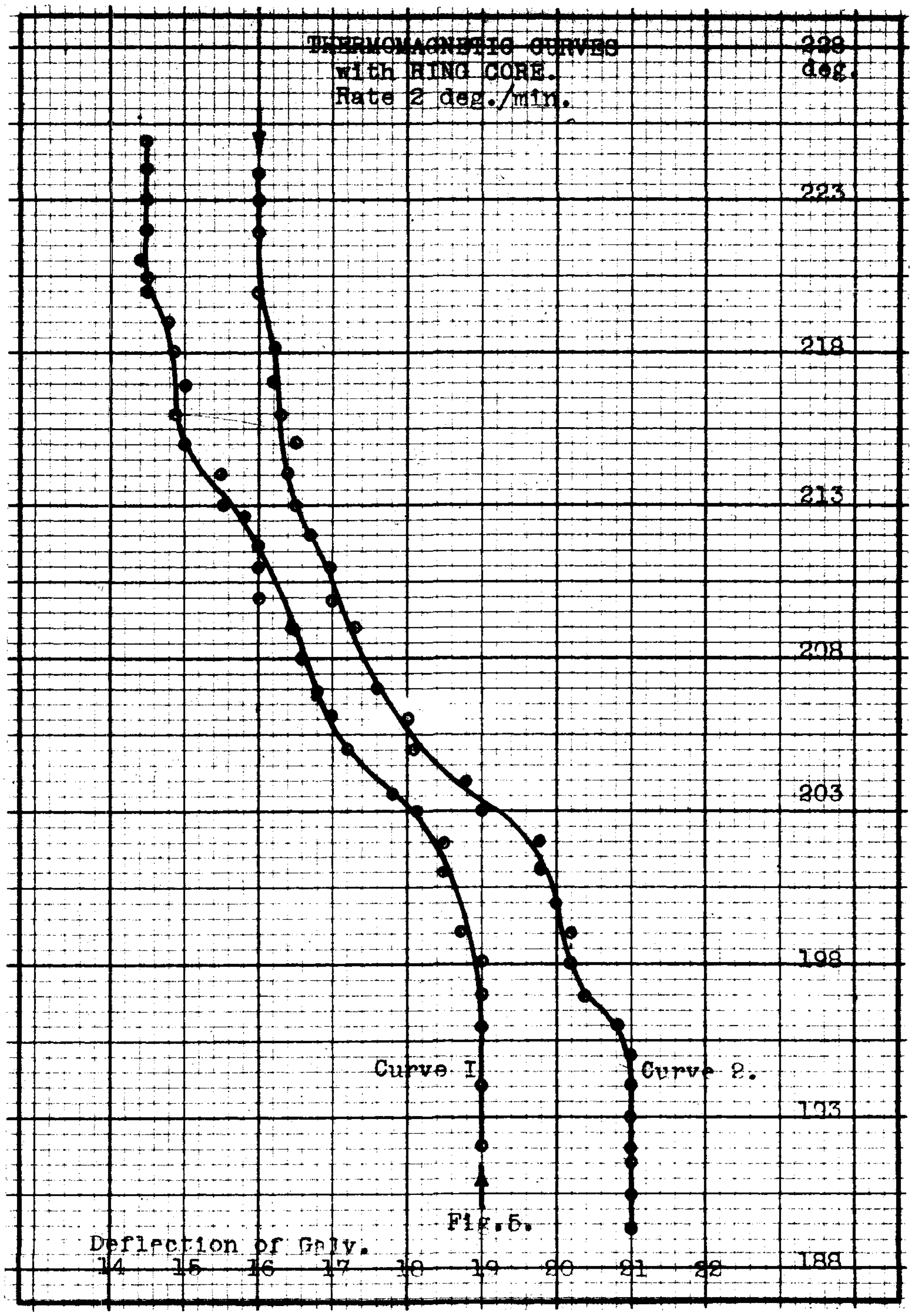
The experimental results are presented in the form of curves, figures 5 and 6, in which temperature is plotted against galvanometer deflections in scale divisions. The maximum galvanometer deflection was about 20 scale divisions while the carbide was magnetic and about 15 when nonmagnetic. This decrease occurred between 198 and 215° C. The maximum deflection of the galvanometer is influenced somewhat by the manner of closing the key. There is also some lag in temperature between the thermometer and the carbide.

The information gained from the experiments described above is summarized in table IX.

Table IX

Summary of Data

Heating	Initial break-	Practically completed at-	Second break at-	No change above-
Curve 1	198° C.	214° C.	216° C.	220° C.
Curve 3	200.5	211	216	223
Curve 5	198	——	——	222
Curve 6	198	211	215	——
Cooling				
Curve 2	195	214	218	220
Curve 4	197	210	214	217



THERMOMAGNETIC CURVES
with RING CORE.
Rate 2 deg./min.

Fig.5.

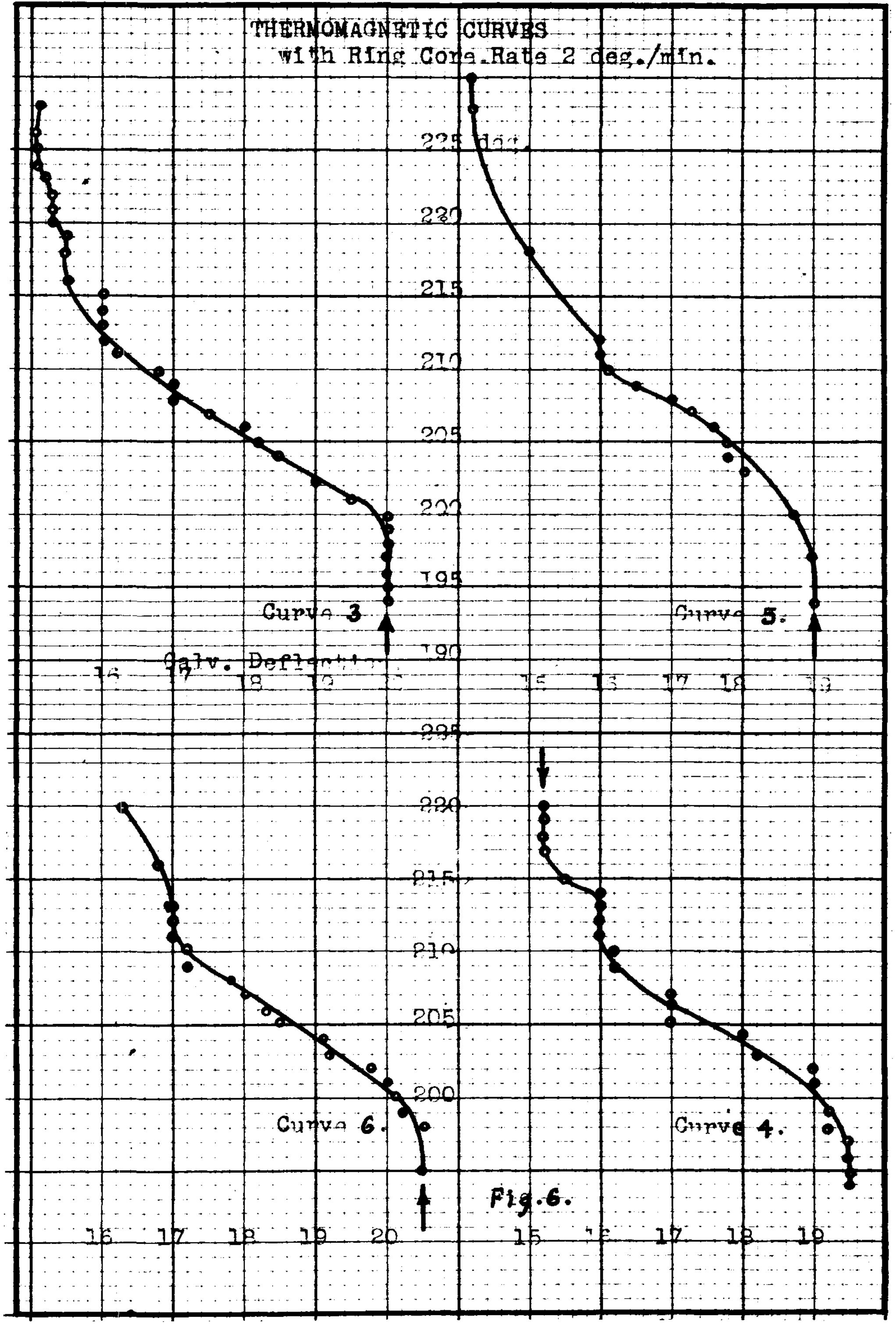

THERMOMAGNETIC CURVES
with Ring Core. Rate 2 deg./min.
225 deg.
220
215
210
205
200
195
190
Curve 3
Curve 5.
Galv. Deflection
16
17
18
19
20
15
16
17
18
19
225
220
215
210
205
200
Curve 6.
Curve 4.
16
17
18
19
20
15
16
17
18
19

Fig. 6.

The data for curve 6 were obtained in a different manner. The regulator was set for each temperature and the temperature of the bath was kept constant until a series of readings had been made at that temperature. After the coil had reached constant temperature, readings were taken after 5, 10, 15, and 20 minutes. The purpose was to determine the effect of time upon the transformation. There was no change in the readings at any temperature even after 20 minutes. This fact shows that the transformation is not a slow change which would be completed, if sufficient time were given, at some temperature below the maximum 215° C., but that regardless of time only a certain part of the magnetism is lost at each temperature. The reversibility of the transformation will be shown in a more conclusive manner in the next series of experiments to be presented.

The transformer experiments show that the magnetic transformation in iron carbide on heating begins at about 198° C. and is practically complete at 211° C., that a slight loss in magnetism occurs up to about 216° C. and that practically no change occurs above 220° C. Some of the curves indicate a hysteresis of 2 or 3 degrees. This lag is believed, from later evidence, to be due to experimental error, and not to represent a true hysteresis between the points on heating and cooling. We are unable to explain the break in the curves at 215° C. unless it is simply the end of the transformation.

The magnetic transformation by the hydrometer method

In order to measure the magnetic change in iron carbide more accurately and more directly, an apparatus was designed in which the force of attraction of a magnetic field of unknown but constant strength upon the carbide could be measured. This apparatus is shown in B, figure 4. It consists of a hydrometer bulb designed so that it will float perpendicularly in the oil bath, and a coil which produces the magnetic field. The carbide to be tested was sealed up in the hydrometer stem a little distance above the bulb. It was packed in tightly in order that any magnetic pull would be transmitted to the hydrometer. The exposed end of the hydrometer carried a pointer and a small cup for the addition of shot to compensate for the changes in specific gravity of the oil. The magnetizing coil was wound around a glass spool which was firmly held in place by a glass rod sealed to the spool and held in a clamp at the top of the thermostat. The spool carrying the coil was placed around the hydrometer stem just above the carbide and was large enough to permit it to move freely up and down. The exact position of the coil with respect to the carbide was so adjusted as to give the maximum rise of the hydrometer when it was weighted to the zero point on the scale. A millimeter scale was mounted just behind the pointer, by which the rise of the hydrometer could be measured. The thermostat was the same as that used in the former experiments. It was necessary to stop the stirrer during the adjusting of the hydrometer so that the pointer stood on the zero point and during the taking of readings. In this apparatus the attraction of the magnetic field upon the carbide is balanced by the force of gravity acting upon the hydrometer. The changes in viscosity and specific gravity of the oil, with temperature, are factors which influence the rise of the hydrometer. The change in specific gravity is compensated for by the addition or removal of weights, so that the same net weight is in operation during the run. The decrease in viscosity of the oil during heating operates to increase the rise of the hydrometer and therefore to minimize the effect due to the loss of magnetism. It was not found necessary to run blank determinations, using, in place of the carbide, a magnetic substance which has no transformation in the temperature range, in order to determine the effect of these two factors.

Heating and cooling data are obtained in the following manner. The regulator is set for the desired temperature. The heaters and stirrer are turned on, and after the bath has reached the desired temperature and is remaining constant, the stirrer is stopped. The hydrometer is quickly weighted so that the pointer is on zero. The key is tapped, and the rise of the hydrometer is noted. During a run, the current through the magnetizing coil is kept constant. About four hours are required to complete a heating or a cooling run, which should insure equilibrium conditions in the carbide at each temperature.

The data from the hydrometer experiments are presented in the form of curves in figures 7, 8, and 9. In these experiments, two hydrometers were made. Hydrometer number I contained the iron carbide prepared by hydrolysis and hydrometer number II that prepared by the perchloric acid method. The data for curve 10 were obtained by allowing the thermostat to cool with the heaters off. Some lag in temperature between the carbide and the bath may be involved in this experiment. All other experiments were made by setting the regulator for each temperature. In some of the experiments both the maximum rise of the hydrometer and the rest position were taken. The rest position is obtained by holding the key closed until the hydrometer comes approximately to rest. In all curves except those indicated, the maximum rise in millimeters is plotted against temperature. The rest positions, as shown by curves 11a and 11b, give similar curves.

The complete data for curve 9 are presented in table X in order to show the precautions taken to determine the effect of time and previous treatment upon the magnetic properties and upon the rate at which magnetic equilibrium is reached in the carbide.

Table X

Data for Curve 9. Hydrometer No. II

Temp.	Max. Rise	Rest Point	Temp.	Max. Rise	Rest Point
166° C.	7.0 mm.	5.0 mm.	203° C.	5.5 mm.	3.5 mm.
168	7.5	5.0	204	5.5	3.5
171	7.0	5.0	Held one hour at 204.		
173	7.5	5.0	Cooled to 200. The reading:		
176	7.5	5.0	200	6.5	——
178	7.5	5.0	205	5.25	3.0
183	7.5	5.0	207	4.0	2.25
188	7.5	5.0	210	3.0	3.0
193	7.5	5.0	212	3.0	2.0
196	7.5	5.0	213	2.25	1.25
198	7.0	4.5	214	2.25	1.25
After			215	2.0	1.25
20 min.	7.0	4.5	217	2.0	1.2
200	6.5	4.0	219	1.75	0.75
After			222	1.5	0.5
20 min.	6.5	4.0	229	1.5	0.5
201	6.5	4.0	231	1.5	0.5
202	6.0	3.5			

The procedure illustrated in the data for curve 9 was frequently practiced. A measurement would be made near the initial break, 197° C. The temperature would be held constant for some time and other readings would be taken. In other instances the run would be continued to some higher or lower temperature and would then be returned to the former temperature. The readings at a given temperature always agreed, regardless of the previous treatment or the direction of approach. This agreement definitely proves that magnetic equilibrium is rapidly reached in the carbide and that there is no hysteresis lag in the transformation.

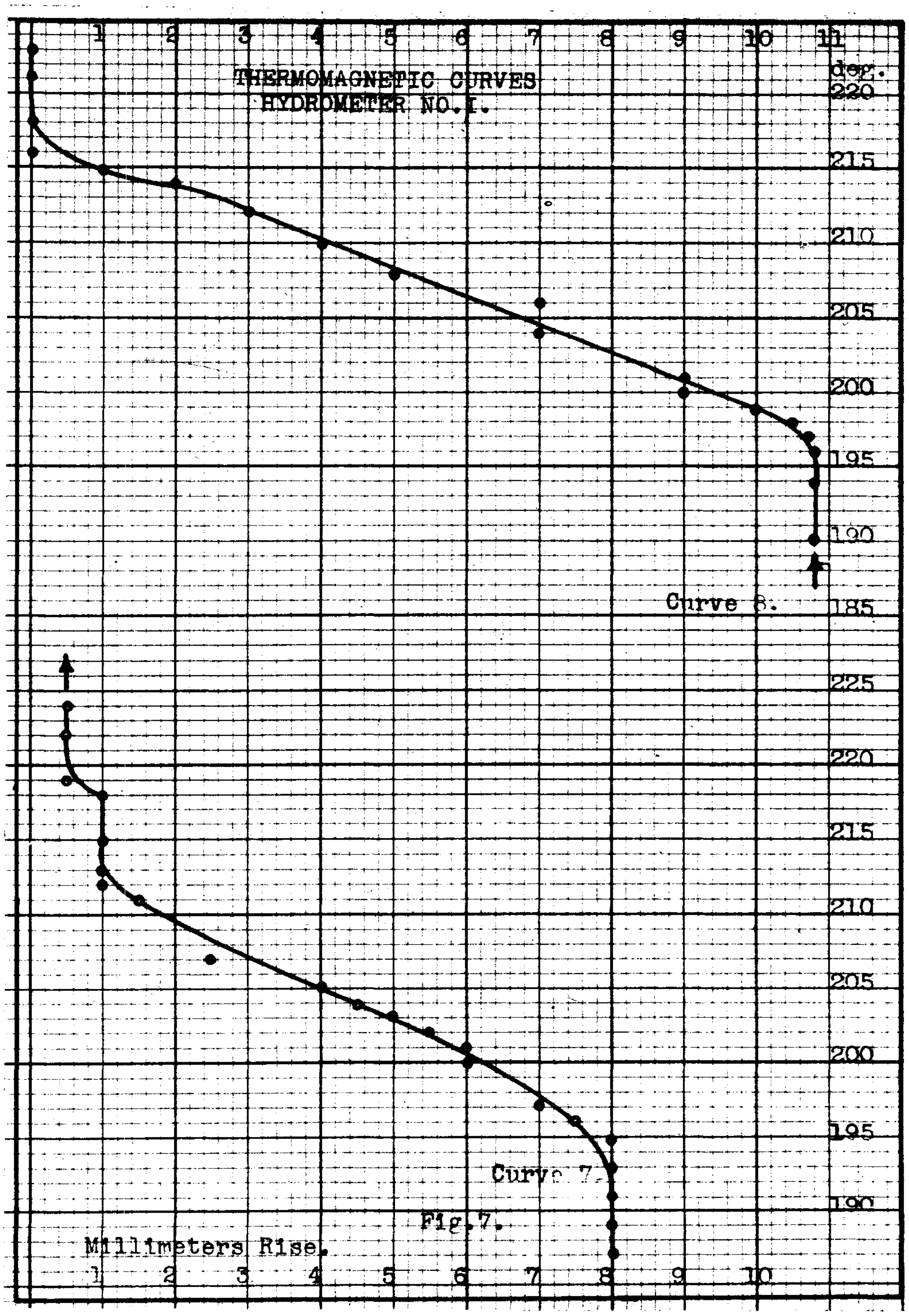

THERMOMAGNETIC CURVES
HYDROMETER NO. I.
1 2 3 4 5 6 7 8 9 10 11
deg.
220
215
210
205
200
195
190
185
Curve 8.
225
220
215
210
205
200
195
190
Curve 7.
Millimeters Rise.
1 2 3 4 5 6 7 8 9 10

Fig. 7.

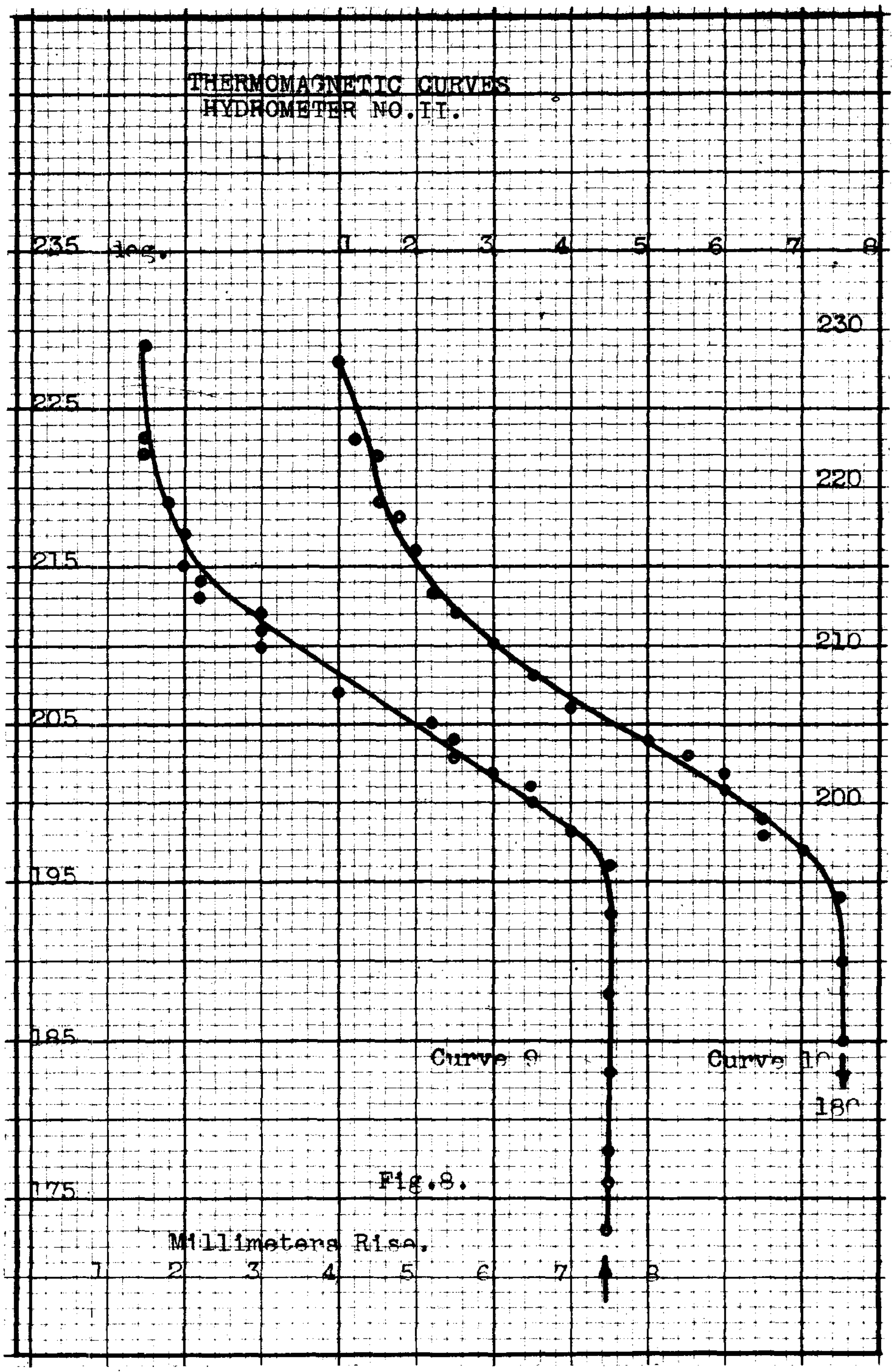
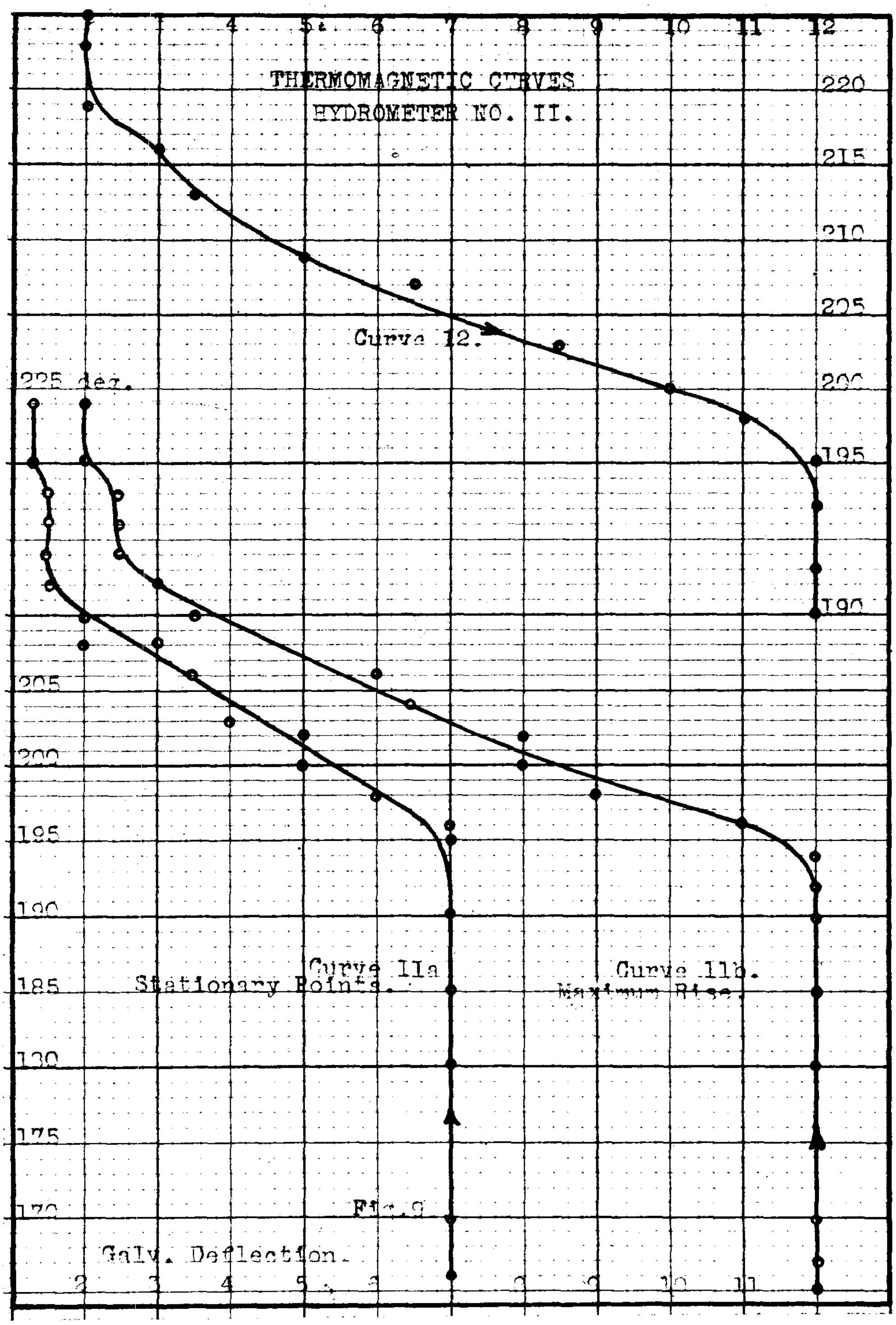


Fig.8.

THERMOMAGNETIC CURVES
HYDROMETER NO.II.
235 deg.
225
215
205
195
185
175
1
2
3
4
5
6
7
8
230
220
210
200
180
Curve 9
Curve 10
Millimeters Rise.
1
2
3
4
5
6
7
8



THERMOMAGNETIC CURVES
HYDROMETER NO. II.

Fig. 9

Discussion of Results of Magnetic Analysis

According to the magnetic analysis experiments there is a loss of magnetism on heating, beginning at about 197° C. and extending to about 210° C., at which temperature the carbide is practically nonmagnetic. The magnetism then remains practically constant to about 216° C., above which there is a small loss. On cooling, the magnetism is regained at the same temperatures at which it was lost on heating. The heating and cooling curves are superimposible, with no temperature variation. The small break in the neighborhood of 215° C. appeared also in the former set of curves. The curves in figures 5-9 show that the magnetic transformation in iron carbide occurs over a temperature range, and not at a definite temperature, and that the transformation is completely reversible.

Theoretical Discussion

Ferromagnetism is an atomic property and results from the unbalanced magnetic fields produced by electrons rotating about the nucleus of an atom and spinning on their axes. In many atoms these magnetic fields are so oriented as to neutralize each other. The resulting atom is nonmagnetic. It is only in the transition elements of the first long period, Fe, Co, and Ni, in which strongly unbalanced fields are found. In Fe the M or third shell contains a 2, 6, 6 arrangement of its electrons and the shell is incomplete. The two lower shells are completely filled, and the outer one contains two electrons. The direction of the spins is such that they are all balanced except the last six in the M shell. Five of these are believed to have positive spins and one negative. The iron atom is therefore ferromagnetic. In order for a substance to be ferromagnetic in the aggregate, the magnetic fields of the atoms within small portions of the substance, called "domains", must be parallel. A force operates between neighboring atoms to keep their spins parallel. This is known as the "exchange" force and is determined by the ratio between the diameter of the atom and the diameter of the electron shell in which the electron spins are uncompensated. The allignment is also influenced by the arrangement of the atoms in the crystal lattice. The exchange forces which operate to keep the spins parallel are opposed by thermal agitation. When the thermal agitation prevails, the Curie point is reached and the substance ceases to be ferromagnetic. It seems reasonable therefore that all magnetic transformations should take place over a temperature range; and that thermal agitation at one temperature would be sufficient to disallign certain domains, and that a higher temperature would be required to disallign others. This is similar to the "Barkhausen" effect, which is shown by the increasing magnetic field required to orient the various domains and thus to completely magnetize the material. A magnetic substance is not magnetized as long as the domains have random orientation.

In order to be magnetized a specimen must be acted on by a magnetic field of sufficient strength to orient all domains parallel.

The fact that iron carbide is strongly ferromagnetic, and that it loses its magnetism at A_o, a temperature much lower than A_2, the magnetic transformation of free iron, is proof that iron carbide is a compound.

GENERAL SUMMARY

In Part I, a new and simple method has been described for the separation of iron carbide from iron-carbon alloys.

In Part II, it has been shown that the carbon evolved by acid hydrolysis of iron carbide, plus the free carbon formed, equals the total carbon present in the carbide. This proves that the carbon-containing products formed are either gases or volatile liquids. The reaction between hydrochloric acid and iron carbide produces about 12.5% of the total carbon as free carbon and the remaining 87.5% as volatile hydrocarbons.

The gases evolved were found to be composed of 83.4% free hydrogen, 11.5% methane, and 4.62% unsaturated hydrocarbons.

In Part III, the Curie point or magnetic transformation in iron carbide was found to take place over a temperature range, whose lower temperature is about 197° C. and whose upper one is about 215° C. The main part of the transformation was found to occur between 198 and 210° C. A small change in magnetism was found at 215° C. The magnetic transformation was found to be completely reversible.

LITERATURE CITED

1. Abel, F. and W. H. Deering. Notes on the condition in which carbon exists in steel. J. Chem. Soc. (London) 43, 303-308 (1883).

2. Muller, C. G. Neue Experimental- Untersuchungen über den Gasgehalt von Eisen und Stahl. Stahl und Eisen, 443-454 (1883).

3. Yermilov, Y. The heat formation of iron-carbon alloys. J. Russ. Met. Soc. 4, 357-365. Original not seen. Chem. Abst. 6, 2387 (1912).

4. Ruff, Otto, and E. Gestern. Über das Triferro-carbid. Ber. 45, 63-72 (1912).

5. Osmond and Werth. Théorie cellulaire des propriétés de l'aciér. Ann. Mines. 8, 6-10 (1885).

6. Arnold, J. O., and A. A. Read. Chemical relations of iron and carbon. J. Am. Chem. Soc. 65, 788-792 (1894).

7. Myers, W. R. The preparation and hydrolysis of manganese carbide. Unpublished thesis. Library, Vanderbilt University, Nashville, Tenn. (1937).

8. Campbell, E. D. A pure carbide of iron. Am. Chem. J. 18, 836-847 (1896).

9. Brodie, G. H., W. H. Jennings, and Anson Hayes. Heat of formation of cementite as electrolyzed from a pure iron-carbon alloy. Trans. Am. Soc. Steel Treating. 10, 615-629 (1926).

10. Moissan, Henri. Action de l'acétylène sur les meteaux-ammoniums. Compt. rend. 187, 554-556 (1928).

11. Pingault, Pierre. Sur les conditions de formation de le cémentite. Compt. rend. 187, 554-556 (1928).

12. Priestley, Joseph. Experiments and observations relating to air and water. Phil. Trans., Royal Soc. London. 75, 279-309. (1785).

13. Rinmann, L. Über den Stickstoffgehalt in Stahl und Roheisen. J. prakt. Chem. (1) 100, 33-37 (1867).

14. Hahn, H. Chemische Untersuchung der beim Lösen des Roheisens entstehenden Producte. Ann. (Liebig) 129, 57-77 (1864).

15. Cloez, S. Nature des hydrocarbures produits par l'cation des acides sur la fonte blanche miroitante manganésifère. Compt. rend. 85, 1003-13 (1877). Ber. 7, 823 (1874).

16. Mylus, F., F. Foster, and G. Schoene. Das Carbid des gegluhten Stahls. Z. anorg. allgem. Chem. 13, 34-48 (1897).

17. Werkmeister, Otto. Über Bildung und Zerfall von Eisenkarbid und die gasförmigen Produkte der Einwirkung von Mineralsäuren. Published thesis. Tech. Hochschule "Fridericiana" zu Karlsruhe (1910).

18. Schenck, R., J. Giesen, and Fr. Walter. Über die Saurezerlegung metallographisch definierter Eisen- und Mangancarbidlegierungen. Z. anorg. allgem. Chem. 127, 101-136 (1923).

19. Schenck, R., and R. Stenkhoff. Über die Säurezerlegung des Eisencarbides. Z. anorg. allgem. Chem. 161, 287-303 (1927).

20. Millner, Theodore. Bemerkung zur Arbeit der Herren R. Schenck und R. Stenkhoff. Z. anorg. allgem. Chem. 164, 186-188 (1927)

21. Putnam, G. L., and K. A. Kobe. Hydrocarbons from carbides. Chem. Rev. 20, 131-141 (1937).

22. Schmidt, J. Über die Zersetzung von Carbiden durch Wasser oder verdunnte Sauren. Z. Elektrochem. 40, 170-185 (1934).

23. Travers, A., and R. Diebold. Sur le mécanisme de décomposition de la cementite pure par les acides. Compt. rend. 205, 916-918 (1937).

24. McFarlane and Gregory. The determination of carbon dioxide. Chem. News 94, 133-140 (1906).

25. Whitely, J. H. The Eggertz test for combined carbon in steel. J. Iron Steel Inst. Carnegie Scholarship Memoirs, 8, 1-101 (1917).

26. Westgren, A., and G. Phragmen. X-ray studies on the crystal structure of steel. J. Iron Steel Inst. 105, 241-273 (1922).

27. Hendricks, S. B. The crystal structure of cementite. Z. Krist. 74, 534-545 (1930).

28. Westgren, A. Cementitens Kristalstruktur. Jernk. Ann. 116, 457-468 (1932).

29. Myers, W. R. Some chemical evidence concerning the condition of carbon in austenite. Unpublished thesis, Library, Vanderbilt University, Nashville, Tenn. (1934).

30. Sidgwick, N. V. The electronic theory of valence. p. 90, Oxford University Press. (1927).

31. Hägg, G. Eigenschaftender Phasen von Übergangselementen in binären Systemen mit Bor, Kohlenstoff und Stickstoff. Z. physik. Chem. Abt. B. 6, 221-232 (1930).

32. Hume-Rothery, Wm. The structure of metals and alloys. Inst. of Metals Monograph and Report Series 1, 90-100 (1936).

33. Wologdine, M. Sur les propriétés magnétique de quelques composés du fer. Compt. rend. 148, 776-777 (1903).

34. Smith, S. W. J. The thermomagnetic study of steels. Proc. Phys. Soc. 25, 77-81 (1912).

35. Honda, K., and H. Tagei. On the magnetic transformation of cementite. Science Repts. Tôhoku Imp. Univ. First ser. 2, 203-207 (1913).

36. Honda, K., and H. Takagi. On the magnetic transformation of cementite. Science Repts. Tôhoku Imp. Univ. First ser. 4, 161-168 (1915).

37. Tamman, G., and K. Ewig. Zur Kenntnis des Eisencarbid (Fe_3C). Z. anorg. Chem. 167, 385-400 (1927).

38. Chevenard, P. Cementite in annealed, tempered and semi-tempered steels. Compt. rend. 164, 1005-1008 (1917).

39. Honda, K., and T. Murakami. On the thermomagnetic properties of carbides found in steels. Science Repts. Tôhoku Imp. Univ. First ser. 6, 23-29 (1917).

40. Ishawara, T. On the magnetic analysis of carbides found in different kinds of steels. Science Repts. Tôhoku Imp. Univ. First ser. 6, 285-294 (1917).

41. Lehrer, E. Über ein registrierendes Magnetometer für technische Messungen an stark gestörten Orten. Z. techn. Phys., 9, 136-143 (1928).

42. Mittasch and Kuss. Über die Ammoniaksynthese mit katalysatoren, die aus komplexin Cyaniden des Eisens entstehen. Z. Elaktro. Chem. 34, 159-170 (1928).

43. Travers and Diebold. Sur l'isolement de la cementite pure par attaque acide des matériaux ferreux et sur quelques propriétés physique de ce corps. Compt. rend. 34, 797-799 (1937).

44. Mehl, R. F., and C. R. Wells. The constitution of high purity iron-carbon alloys. Am. Inst. Mining Met. Eng. Tech. Pub. No. 798, 41-65 (1937).

45. Epstein, Samuel. Alloys of iron and carbon v. I, 34-40, McGraw-Hill Book Company. New York. (1936).

VITA

On the ninth of December, 1890, near the village of Pleasant City, Ohio, there was born to Anna May Bugher Fishel and John B. Fishel a son who was named Waite Philip. He attended the local public schools, and, by teaching and attending college intermittently, obtained a Bachelor of Arts degree from Ohio University at Athens, Ohio, June, 1918.

During the last portion of his college career, he served as assistant in the Department of Chemistry. The year following graduation he was an instructor in the same Department. In 1919 he came to Iowa State College as a graduate assistant in chemistry, in which position he served for three years. He received a Master of Science degree from Iowa State in the summer of 1921. Since that time he has held the position of Assistant Professor in Metallurgy at Vanderbilt University, Nashville, Tennessee.

In the course of his scientific efforts, he has endeavored to specialize in Physical Metallurgy, and has directed and conducted some work in the field of metallic carbides.

He wishes at this time to express his appreciation to all the inspiring teachers with whom he has come in contact at Iowa State, and especially to Dr. H. Wilhelm who so generously gave his time to the criticism of this thesis.