titative basis because neither the strengths of the acids nor the activities of hydrogen ion in solutions so concentrated in phosphorous acid are known.

For the exchange of the phosphorus bonded hydrogen in phosphorous acid a mechanism consistent with the results is

$$L_2(HPO_3) + L^+ \rightleftharpoons L_3(HPO_3)^+ \qquad (8)$$

$$L_3(HPO_3)^+ \rightleftharpoons L_3(:PO_3) + H^+ \qquad (9)$$

$$L_3(:PO_3) + D^+ \rightleftharpoons L_3(DPO_3)^+ \qquad (10)$$

$$L_3(DPO_3)^+ \rightleftharpoons L_2(DPO_3) + L^+ \qquad (11)$$

where L is D when read in the forward direction for H_3PO_3 in D_2O and L is H when read in the reverse direction for D_3PO_3 in H_2O. This statement is an oversimplification because in each case all L will not be exclusively either D or H, due to the exchange reaction 1 and also to reactions 3 or 6 respectively, as they proceed producing the species opposite to that originally present in the solvent.

The complete steady-state solution of equations 8–11 is derived easily, but the resulting expression is complex. Reactions 8 and 11 may be considered to be rapid as compared with (9) and (10) which are rate determining. The mechanism accounts for the increase of reaction rate as the solution becomes more acid, and for the lack of any appreciable exchange for the salts of phosphorous acid. A similar mechanism has been proposed for the exchange in hypophosphorous acid.[6]

It is not possible to calculate an isotope effect from the experimentally determined rate constants, since several of the species postulated in the mechanism contribute to the over-all reaction to an unknown extent in each solvent mixture. Considering only the stretching frequency of the P–H and P–D bonds, the maximum isotope effect at 25° may be calculated[12] to be $k_H/k_D = 5.1$. The results and interpretation are consistent with the idea that exchange takes place *via* a free electron pair on the element bonding hydrogen, *e.g.*, $L_3(:PO_3)$.

Acknowledgment.—The author wishes to express his appreciation to Professor John T. Edsall for his encouragement and interest in this work.

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Cambridge 38, Mass.

[Contribution from the Central Experiment Station, Bureau of Mines, U. S. Department of the Interior]

Saturation Magnetizations of Iron Carbides[1]

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Received August 21, 1958

Magnetic characteristics of iron carbides were obtained to permit their quantitative determination in Fischer–Tropsch catalysts and in steels at various stages of tempering. Iron carbides were prepared by reducing iron oxide powder with hydrogen at 208°, carburizing to ϵ-iron carbide with carbon monoxide at 170° and then tempering *in vacuo* to χ-iron carbide and subsequently to cementite. Specific magnetizations were measured between about 2 and 10 kilo-oersteds from 50° to about 200–350°. The data were corrected for contributions due to impurities and extrapolated to infinite field and 0°K. to obtain the magnetic moments of the carbides: 1.70–1.72 (ϵ-carbide), 1.72–1.75 (χ-carbide) and 1.72–1.79 (cementite) Bohr magnetons per iron atom. The paramagnetic moments of χ-iron carbide and cementite were 5.55 and 3.89 Bohr magnetons, respectively.

Introduction

Quantitative thermomagnetic determination of crystalline phases involved in solid-phase reactions of steel and of iron Fischer–Tropsch catalysts is possible only with data obtained at or near magnetic saturation, or with saturation data obtained by extrapolation to infinite field strength.[2] Consequently, the saturation magnetizations of the pure phases must be known. Such data are available for α-iron[3] and cementite.[4] They have not been available for the ϵ- and χ-iron carbides, although their specific magnetizations at room temperature are known to be roughly equal to that of cementite.[5]

Previous preparations of carbides of iron especially those of χ-iron carbide and ϵ-iron carbide have been relatively impure. Even specimens containing only 50% of the desired compound have been considered reasonably satisfactory.[5] The specimens described here represent an order of magnitude of increased purity with respect to the amount of iron in the desired form. The amount of promoters, copper and sodium oxide, which are present in these preparations are less then 2% and do not dissolve in the carbide phase to any detectable extent according to the known solubility relationships. The methods of synthesis here described should therefore be regarded as the best now available for χ- and ϵ-iron carbide. Similarly, the magnetic properties reported here are believed to have general significance.

Experimental

Preparation of Carbides.—Direct determination of the specific magnetization of the iron carbides requires specimens in which the carbide in question is the major phase, and the amount of iron present in any paramagnetic form should be as small as possible. Extraction of χ-iron carbide and ϵ-iron carbide from tempered steels is an uncertain procedure[6] and specimens so obtained are likely to contain

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[1] This investigation was supported in part by the Aeronautical Research Laboratory, Contract 33(616)-52-12, project 52-670-270.

[2] J. Crangle and W. Sucksmith, *J. Iron Steel Inst.* (*London*), **168**, 141 (1951).

[3] R. Becker and J. Döring, "Ferromagnetismus," Julius Springer, Berlin, 1939, p. 39; L. F. Bates, "Modern Magnetism," Cambridge, London, 1951.

[4] P. Weiss and R. Forrer, *Ann. Phys.*, **12**, 279 (1929).

[5] L. J. E. Hofer, E. M. Cohn and W. C. Peebles, This Journal, **71**, 189 (1949).

[6] M. Okada and Y. Arata, *Tech. Reports Osaka University*, **3**, 311 (1953); *J. Japan Inst. Metals* (*Sendai*), **19**, 186 (1955).

paramagnetic iron salts. A preferred method of preparation is by direct carburization of reduced iron having a large surface area.

A precipitated, doubly promoted iron oxide (Bureau of Mines catalyst P-3002, Fe:Cu:Na = 58.99:0.43:1.25) was used, which contained a minimum of promoters and permitted higher iron carbides to be produced in a reasonable time.[6] The material was reduced at 208° for 1164 hours in hydrogen that was purified with palladized asbestos at 300° and dried with magnesium perchlorate. When reduced to metallic iron, metallic copper and sodium carbonate, the mass of the powder should have been 62.3% of the unreduced mass; the observed value was 62.5%. This result, and the fact that the mass did not change during the last 10 of the 48 days of reduction, were considered proof of essentially complete reduction (see Fig. 1).

The iron was carburized with carbon monoxide at 170° for 464 hours until the carbon:iron mass ratio as determined by mass increase had become 0.1033; the theoretical ratio for Fe_2C is 0.1075 (see Fig. 1). The carbide produced by this procedure is the ϵ-phase. However, not all of the carbon in the catalyst need be carbidic; some may be present as free carbon. Furthermore, a minor portion of the increase in mass probably is caused by incorporation of some oxygen from carbon monoxide.[7] When the product was subjected to X-ray powder diffraction analysis,[8] the only identifiable reflection obtained besides those of ϵ-iron carbide was the strongest one of α-iron.

Previous studies had shown that the transitions from ϵ- to χ- and from χ-iron carbide to cementite proceed by nucleation and growth and furthermore that, with suitable temperatures and reaction periods, the first transformation can be completed before cementite is formed.[9,10] This was used to advantage in preparing relatively pure specimens of χ-iron carbide and cementite, comparable with ϵ-iron carbide in particle size and promoter content. Conversion of ϵ- to χ-iron carbide was complete, as determined by thermomagnetic analysis, in 70 minutes at 343°. Similarly, conversion of χ-carbide to cementite was accomplished at 550° in 345 minutes.

Magnetic Measurements.—A modified Mathieu-type magnetic balance[11] was used for this study. It permitted[11] measurements of the absolute values of magnetic moments.

The ϵ-iron carbide was analyzed by heating slowly from room temperature to 200° in a series of magnetic fields ranging in strength from 1.86 to 9.73 kilo-oersteds. These measurements could not be extended up to the Curie point, because ϵ-iron carbide decomposes at an appreciable rate even at 245° as kinetic studies had shown. For the final analysis, the sample was heated rapidly to 383°. A Curie point seemed to occur at about 350°, but this low value[6] may be attributed to incipient decomposition.

The product of the conversion ϵ- to χ-iron carbide was analyzed at the same series of field strengths noted above from room temperature through its Curie point (247 ± 3°) to 356.5°. Finally, χ-iron carbide was converted to cementite. Similarly, the cementite was analyzed at these field strengths from room temperature up to 554°.

Thermomagnetic data for cementite (Curie point 212 ± 3°) and the higher carbides are given in Table I. Whereas cementite is known to be Fe_3C,[12] the compositions of the higher carbides are uncertain and may vary with the method of preparation.[7,13–15] Because of this uncertainty, specific magnetizations are reported here per gram of iron, not per gram of iron carbide, unless stated otherwise.

A single sample was used to obtain all the data of Table I and subsequent chemical analysis showed it to contain 0.0951 g. of iron.

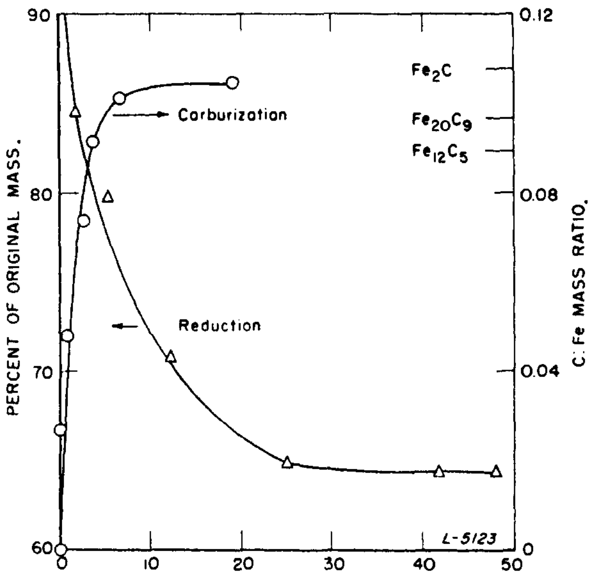

Fig. 1.—Reduction at 208° and carburization at 170° of iron powder.

Glossary

A	constant
a	over-all coefficient of magnetic hardness
b	coefficient of magnetic hardness for the ferromagnetic impurity
B	constant
c	coefficient of magnetic hardness for iron carbide
f	fraction of total iron in the carbide phase
H	field strength
k	Boltzmann constant
M	atomic weight of iron
N	Avogadro number
n	magnetic moment in Bohr magnetons
s_H	apparent total magnetization per gram of iron at field H and temp. T
s_T	apparent total saturation magnetization per gram of iron at temp. T
T	temperature (°K.)
β	numerical value of Bohr magneton
θ	Curie point (°K.)
σ_H	specific magnetization of iron carbide at field H and temp. T
σ_T	saturation specific magnetization of iron carbide at temp. T
σ'_H	specific magnetization of ferromagnetic impurity at field H and temp. T
σ'_T	saturation specific magnetization of ferromagnetic impurity at temp. T
σ_0	saturation specific magnetization of iron carbide at 0°K.
σ_α	magnetization of α-iron
σ_θ	magnetization of cementite
σ_χ	magnetization of χ-iron carbide
χ	specific magnetic susceptibility
χ_e	specific magnetic susceptibility of carbide

Note: Specific magnetizations and magnetic susceptibilities are expressed per gram of iron unless otherwise indicated.

Evaluation of Data

The amounts of ferromagnetic impurities were determined by interpretation from the amounts of the residual magnetism above the Curie point. The apparent total saturation magnetizations, s_T, at specific temperatures were obtained by extrapolating to infinite field the apparent total magnetizations, s_H, at these temperatures as measured at different fields. These were corrected for contributions from ferromagnetic impurities, then extrapolated to 0°K. and finally converted

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(14) K. H. Jack, *Proc. Roy. Soc.* (*London*), **195A**, 34 (1948).

(15) H. Pichler and H. Merkel, U. S. Bur. Mines Tech. Paper 718, pp. 28–42, 1949.

TABLE I

APPARENT TOTAL MAGNETIZATIONS OF IRON CARBIDES, EXPRESSED AS ERGS/GAUSS-GRAM Fe

Field strength, kilo-oersteds Temp., °C.	9.73	9.44	8.61	6.49	4.51	1.86
			ε-Iron carbide			
...	(27°)138.0	(38°)136.2	(31°)134.1	(34°)124.8	(34.5°)112.5	(26.5°)75.5
50.0	136.4	135.2	132.9	123.6	111.8	74.8
66.5	...	134.1	132.0	122.4	111.1	74.4
83.0	134.1	133.3	130.4	121.4	110.4	74.2
99.0	...	131.6	129.2	120.3	109.5	73.7
114.5	131.4	130.4	127.6	119.1	108.6	73.4
129.5	...	128.7	126.6	117.7	107.6	72.9
144.5	127.9	127.0	125.1	116.1	106.5	72.7
160.0	...	125.6	123.4	114.8	105.2	72.1
174.5	124.4	123.4	121.4	113.1	...	71.4
189.0	...	121.4	119.6	111.4	...	70.6
203.5	120.0	119.2	117.4	109.3	100.5	69.8
232.0	113.7					
260.0	106.1					
287.5	97.2					
316.0	80.6					
343.0	48.7					
370.0	24.3					
383.0	13.4					
			χ-Iron carbide			
...	(36.5°)121.4	(30°)121.6	(35°)118.7	(26°)110.8	...	(26°)72.6
50.0	120.0	119.3	116.9	108.3	103.2	71.5
83.0	115.1	114.4	112.3	104.0	99.8	69.6
114.5	109.2	108.8	107.0	...	95.1	67.9
144.5	102.3	101.9	100.1	93.3	89.7	65.4
174.5	93.9	93.3	91.4	85.8	82.8	61.8
203.5	82.5	81.9	80.0	75.3	73.2	55.9
217.5	75.0	74.3	72.6	68.1	66.2	51.4
232.0	65.3	64.9	63.3	58.8	56.7	44.4
246.0	52.9	51.7	50.3	...	42.1	31.1
260.0	38.1	36.6	35.1	29.1	25.1	15.2
274.0	25.9	24.7	23.4	18.5	15.5	8.9
287.5	19.0	17.9	16.8	13.2	11.0	6.8
302.0	15.1	14.1	13.4	10.7	9.0	6.2
316.0	12.9	12.0	11.4	9.2	8.1	5.6
329.5	11.4	10.4	10.1	8.3	7.2	5.5
343.0	10.4	9.5	9.2	7.6	6.8	4.9
356.5	9.6	8.7	8.4	6.9	6.3	4.6

(*Continued on next page*)

to magnetic moments in Bohr magnetons per atom of iron. The moments for two of the carbides also were determined from paramagnetic susceptibility measurements above but near the Curie point.

Interpretation of Residual Magnetization.—The high magnetizations above the Curie points can have resulted only from ferromagnetic impurities. For cementite, the residual magnetization was about 8 ergs/gauss-g. Fe at 9.73 kilo-oersteds and 400°.[16] The residual magnetization of χ-iron carbide was lower; that of ε-iron carbide could not be estimated because of the carbide's instability.

Only metallic iron, magnetite or a ferrite could have caused such appreciable residual magnetization. Metallic iron might have remained in the sample because of incomplete carburization, or it might have been formed by thermal decomposition of carbide. Oxygen, probably incorporated to a small extent during carburization, may have oxidized metallic and/or carbidic iron upon subsequent heating. Furthermore, some of the promoter may have been dissolved in the newly formed magnetite, further changing its magnetic moment.

In the absence of definite information on these phases and the changes in them during repeated heating and cooling, one may assume two extremes —that all residual magnetization was caused by iron or that it was all caused by magnetite. Although the possibility of formation of alkali and/or copper ferrite instead of magnetite is recognized, too little is known about their magnetic properties to correct for them. In the absence of data, a further assumption is that the residual magneti-

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(16) The units of specific magnetization and magnetic susceptibility were derived by E. M. Cohn and M. Mentser, *Am. J. Phys.*, **21**, 681 (1953).

TABLE I (*Continued*)

Field strength, kilo-oersteds Temp., °C.	9.73	9.44	8.61	6.49	4.51	1.86
Cementite						
...	(34°)131.6	(29°)131.4	(32.5°)127.8	(36°)119.4	(28°)105.8	(26°)59.6
50.0	128.9	128.4	125.6	118.5	104.2	60.4
83.0	...	...	119.7	113.1	101.0	59.8
114.5	...	...	111.6	106.5	96.1	59.1
144.5	103.4	102.5	101.8	97.5	89.0	57.5
174.5	89.2	...	88.3	84.5	78.6	55.2
189.0	...	80.0	78.8	74.9	70.3	51.8
203.5	66.7	67.0	66.2	62.0	57.6	44.8
217.5	49.5	50.2	47.5	42.7	37.0	22.5
232.0	33.1	32.8	31.4	27.0	22.5	14.0
246.0	23.6	24.4	22.8	19.8	16.8	10.8
260.0	18.3	19.2	18.1	15.8	13.4	8.8
274.0	...	16.4	15.4	13.4	11.9	8.0
287.5	13.4	14.5	...	12.4	11.0	7.5
302.0	12.4	13.4	12.8	11.5	10.5	7.2
316.0	11.7					
329.5	11.2					
343.0	10.7					
370.0	9.9					
396.0	9.38					
422.0	8.75					
448.5	8.26					
475.0	7.63					
501.0	6.88					
527.0	5.92					
554.0	4.45					

zation of the ε-iron carbide specimen was the same as that for the χ-iron carbide specimen.

The residual magnetization, σ'_T $(1 - f)$, may be evaluated quantitatively by the Honda–Owens equation

$$\chi = \chi_0 f + \sigma'_T(1 - f')/H \qquad (1)$$

Plots of χ as a function of H^{-1} yielded straight lines for χ-iron carbide and cementite (Fig. 2). Near the Curie points, the contributions from the carbides were considerable, because ferromagnetism did not disappear sharply. However, at temperatures well beyond the Curie point, the slopes became constant and represented true residual magnetizations. These were 3.00 and 8.75 ergs/gauss-g. Fe for χ-iron carbide at 356° and cementite at 302°, respectively.

The amount of carbided iron in each of two of the carbides then was estimated from the known saturation magnetizations of α-iron[8] and magnetite.[3] The results are shown in Table II.

TABLE II

CALCULATION OF IRON IN CARBIDES

Carbide	Assumed impurity	σ'_T	$\sigma'_T \times (1 - f)$	
χ (356°)	α-Fe	200	3.00	0.985
	Fe_3O_4	106	3.00	.972
Cementite (302°)	α-Fe	203	8.75	.957
	Fe_3O_4	116	8.75	.925

The greater residual magnetization of cementite, as compared with χ-iron carbide, might be due to some decomposition of carbide into metallic iron plus free carbon or recrystallization of magnetic impurities from subdomain size to ferromagnetic particles or perhaps be simply an indication of the precision of measurement.

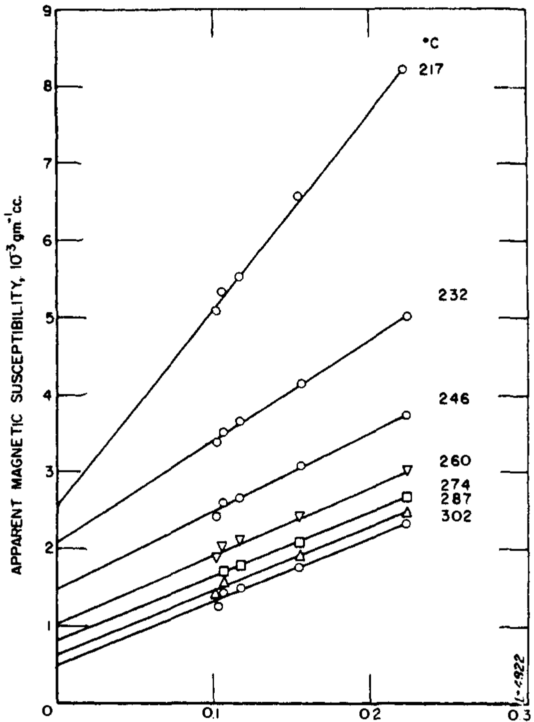

Fig. 2.—Variation with field strength of apparent magnetic susceptibility of cementite.

Apparent Total Saturation Magnetization of Carbides.—Since the carbides consisted of finely divided particles that were not compacted, one may expect them to exhibit a high degree of magnetic hardness. The equation

$$s_H = s_T(1 - a/H) \qquad (2)$$

was used to obtain the total magnetization at saturation, s_T, as well as the coefficient of magnetic hardness, a, which is a function of packing, crystallite size, crystal orientation, crystal imperfection and habit, etc.[17] Plots of s_H as a function of H^{-1} (Fig. 3) yielded values of "a" ranging from 1000 to 1600 oersteds. Values of "a" are not characteristic but differ from one specimen to another. Intercepts of s_H with the ordinate are s_T. Table III shows these values for the three preparations.

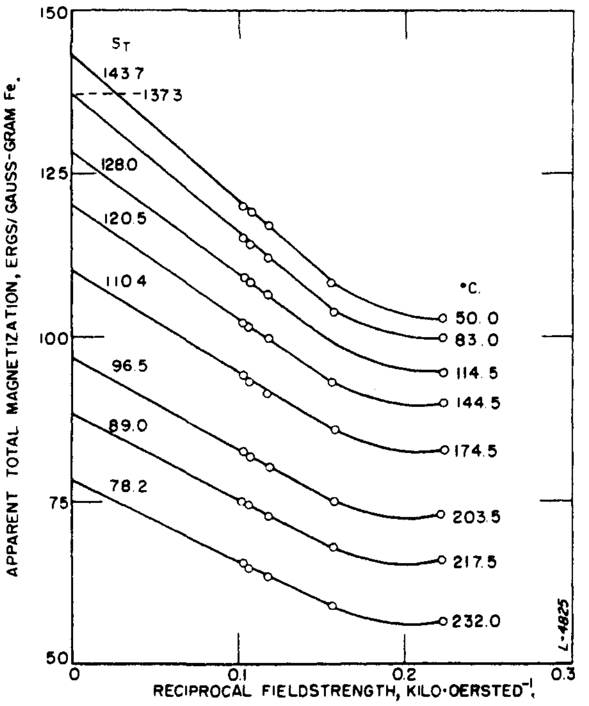

Fig. 3.—Approach to saturation magnetization of χ-iron carbide.

The apparent total magnetization at saturation will have the form indicated in equation 2 even if it is the sum of magnetizations of two or more ferromagnetic substances. In this case the field dependence law of the specific magnetization of the pure carbide may be written

$$\sigma_H = \sigma_T(1 - c/H) \qquad (3)$$

and the corresponding equation for the ferromagnetic impurity is

$$\sigma'_H = \sigma'_T(1 - b/H) \qquad (4)$$

The coefficients of magnetic hardness of the carbide, c, and the impurity, b, are of course unknown and undeterminable. The magnetizations of both constituents are additive, hence

$$s_H = f\sigma_H + (1 - f)\sigma'_H \qquad (5)$$

By substituting equations 3 and 4 into equation 5, expanding and combining terms, the equation results

$$s_H = \{f\sigma_T + (1 - f)\sigma'_T\}\{1 - [fc\sigma_T + (1 - f)b\sigma'_T]/[f\sigma_T + (1 - f)\sigma'_T]H\} \qquad (6)$$

With

$$s_T \equiv f\sigma_T + (1 - f)\sigma'_T \qquad (7)$$

and

$$a \equiv [fc\sigma_T + (1 - f)b\sigma'_T]/[f\sigma_T + (1 - f)\sigma'_T] \qquad (8)$$

equations 5 and 6 are identical in form with equation 2.

Correction for Ferromagnetic Impurity.—To estimate the effect of ferromagnetic impurities and to determine by difference the saturation specific magnetization of the carbide proper, one rearranges equation 7 to

$$\sigma_T = [s_T - \sigma'_T(1 - f)]/f \qquad (9)$$

Since σ'_T in Table II is not measured at the same temperature as s_T, it must be corrected to the temperature at which s_T was measured. The magnitude of the correction depends upon the identity assumed for the impurity and can be made with thermomagnetic data given by Weiss and Forrer.[4] Table IV was calculated assuming the impurities to be either α-Fe or magnetite as shown.

Table III

Apparent Total Magnetization at Saturation, (Ergs/gauss-g. Fe)

Temp., °C.	ε-Iron carbide	χ-Iron carbide	Cementite
50.0	161.3	143.7	150.2
83.0	159.2	137.3	140.5
114.5	155.2	128.0	129.2
144.0	151.4	120.5	116.0
174.5	147.3	110.5	95.7
189.0	...	...	89.3
203.5	142.2	96.5	75.0
217.5	...	89.0	...
232.0	...	78.2	...

Table IV

Saturation Magnetizations of the Iron Carbides (Ergs/gauss-g. Fe)

Temp., °C.	ε-Iron carbide		χ-Iron carbide		Cementite	
	a	b	a	b	a	b
50.0	162.1	160.4	144.0	142.5	151.4	147.3
83.0	159.9	158.3	137.3	135.9	140.8	137.1
114.5	155.9	154.2	127.8	126.6	128.6	125.4
144.0	152.0	150.4	120.2	119.0	114.4	111.6
174.5	147.9	146.2	109.9	108.7	96.2	93.7
189.0	...	...	...	...	86.1	83.8
203.5	142.6	141..2	95.6	94.8	70.7	68.9
217.5	...	...	88.0	87.2	...	...
232.0	...	...	76.9	76.2	...	...

[a] Assumed impurity is Fe_3O_4, [b] Assumed impurity is α-Fe.

The two values shown at each temperature for a given carbide are within 4% of each other and most lie within 2% of each other. As the data of Table I indicate some inflection near the Curie point of magnetite, at least part of the impurity is magnetite.

The ratio of the magnetic moment of χ-iron carbide and cementite at 50° and infinite field (Table IV)

$$\sigma_\chi/\sigma_\theta = 0.950(Fe_3O_4) \text{ or } 0.967(\alpha\text{-Fe})$$

may be compared with the data of Crangle and Sucksmith[2] at 20° and 17 kilo-oersteds

$$\sigma_\chi/\sigma_\theta = 0.976$$

Similarly the ratio of the magnetic moment of χ-iron carbide to that of α-iron at 83° and infinite field, (Table IV).

$$\sigma_\chi/\sigma_\alpha = 0.618(Fe_3O_4) \text{ or } 0.613(\alpha\text{-Fe})$$

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(17) L. Néel, *J. phys. radium*, [8] 9, 12 (1948).

may be compared with a value at 80° and 10 kilo-oersteds computed from data obtained by Eisler, Newton and Adcock.[18]

$$\sigma_\chi/\sigma_\alpha = 0.610$$

Since the published values are not saturation values, the agreement is quite satisfactory.

Discussion

Saturation Magnetic Moment at Absolute Zero.—Saturation specific magnetizations were obtained at absolute zero by employing the method of least squares in conjunction with the equation[4]

$$\sigma_T = \sigma_0(1 - AT^2 - BT^4) \qquad (10)$$

The constants, A and B, thus calculated for equation 10 are given in Table V. The low values are obtained assuming α-Fe is the impurity and the high assuming magnetite. In making the least square extrapolations, the five lowest temperature data points were taken in every case.

TABLE V

CONSTANTS OF EQUATION

$$\sigma_T = \sigma_0(1 - AT^2 - BT^4)$$

(As determined by method of least squares)

	ϵ-Iron carbide		χ-Iron carbide		Cementite	
	a	*b*	*a*	*b*	*a*	*b*
σ_0	172.1	170.0	175.4	172.4	178.5	172.1
$A \times 10^6$	0.36	0.32	1.53	1.44	0.54	0.41
$B \times 10^{12}$	1.72	1.89	1.70	2.04	8.84	9.35

[a] Assumed impurity is Fe_3O_4. [b] Assumed impurity is α-Fe.

Magnetization data of Tables IV and V may be recalculated in terms of ergs/gauss-g. Fe_3C. Selected values so recalculated are compared with some published data in Table VI. The agreement is good.

TABLE VI

SPECIFIC MAGNETIZATION OF CEMENTITE

	Specific magnetization ($T > 0$°K.)			Saturation specific magnetization ($T = 0$° K.)
Source	σ_H, ergs/gauss-g. Fe_3C	H, kilo-oersteds	T, °K.	σ_0, ergs/gauss-g. Fe_3C
Blum and Pauthenet[19]	159.4	19.5	0	...
Esser and Osterman[20]	136.8	..	..	...
Guillaud[21]	...	..	..	169.3
Lange and Mathieu[22]	139.3	9	273	...
Saito[23]	135	10	298	167.2
Stäblein and Schroeter[24]	127.8	..	..	...
Weiss and Forrer[4]	139.2	∞	293	166.3
This study	137–141	∞	323	160.6–166.5

An additional check may be made as follows. The ratio of the saturation magnetization at 0° and at 293°K. is known from Weiss and Forrer's work and is 1.195. The ratio of the saturation magnetizations at 293° and at 323°K. can be calculated from equation 10 and the constants of Table V and is 1.012. The ratio of the saturation magnetization at 0° and 323°K. is therefore 1.012 × 1.195 = 1.210. From this ratio and the experimental value of saturation magnetization obtained in the present study at 323°K.—137.5 to 141.3 ergs/gauss-g. Fe_3C—the value at 0°K. can be calculated. The value thus obtained, 166.5 to 170.7 ergs/gauss-g. Fe_3C, is again satisfactory.

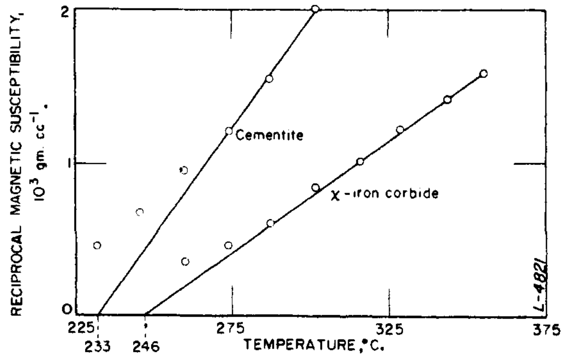

Fig. 4.—Determination of paramagnetic Curie points of iron carbides.

The over-all error in the σ_0 values may be estimated by comparing the present value with the published values for cementite. This is of the order of ±3%. Since comparable methods were used in determining σ_0 for both ϵ- and χ-iron carbide, the error in these cases may be presumed to be about the same.

Atomic Ferromagnetic Moment.—The saturation magnetization at 0°K. can be converted to the magnetic moment in Bohr magnetons per iron atom by the factor $M/N\beta$, equal to 0.01000 for iron; the values are shown in Table VII. The moments of all three carbides are within 4% of each other.

TABLE VII

MAGNETIC MOMENT PER IRON ATOM

Phase	Magnetic moment, Bohr magnetons
ϵ-Iron carbide	1.70–1.72
χ-Iron carbide	1.72–1.75
Cementite	1.72–1.78
α-Iron	2.218

The magnetic moment of all these carbides is identical within experimental error. This value coincides closely with the magnetic moment of cobalt metal, 1.715 Bohr magnetons. It is therefore probable that these carbides have an electronic structure similar to cobalt. This would result from the donation of one electron into the "d" shell of every iron atom. In the carbide FeC and the various forms of Fe_2C the valence state of the carbon must differ from that in Fe_3C, since these binary compounds have different formulas. Either the contribution of each carbon atom is less than that in Fe_3C or only a part of the carbon has the same valence as in Fe_3C and the rest has a different value. In this connection the carbide FeC[25]

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according to Louw, VanDenBerg, Ferreira and Pienaar[26] contains two chemically distinct forms of carbon. This suggests the simple hypothesis that the carbon atoms in excess of the ratio of one carbon atom to three iron atoms donate no electrons at all. This would mean, for FeC, that $^2/_3$ of the carbon atoms are in a form that has not donated electrons. This reasoning is readily extended to postulate that the carbides of the composition Fe_2C also have two forms of carbon, and for this case $^1/_3$ of the carbon atoms donate no electrons.

Paramagnetism of Carbides.—The intercepts with the ordinate in Fig. 2 are the products of paramagnetic susceptibility and f (equation 1). Paramagnetic susceptibilities for χ-iron carbide and cementite are indicated in Table VIII. Their reciprocals, plotted as a function of temperature in Fig. 4, give paramagnetic Curie points for χ-iron carbide and cementite of 246 and 233°, respectively. The slopes of the functions as approximated by the indicated straight lines substituted into the equation

$$\chi M = N(n\beta)^2/3k(T - \theta) \qquad (11)$$

were used to evaluate "n" for these carbides, resulting in values of 5.55 Bohr magnetons per iron atom for χ-iron carbide and 3.89 for cementite. These values are larger than the corresponding ferromagnetic ones by factors of 3.2 and 2.2, respectively. This situation is usual for ferromagnetics; in the case of nickel, the ratio is 3.14. The lower points in Fig. 4 do not fall on the straight line because there is still some ferromagnetic effect just above the Curie point.

TABLE VIII

PARAMAGNETIC SUSCEPTIBILITIES OF IRON CARBIDES, 10^{-6} CC. GRAM^{-1}

Temp., °C.	χ-Iron carbide	Cementite
217.5	..	2640
232	..	2170
246	..	1480
260	2766	1065
274	2156	835
287.5	1604	647
302	1180	500
316	999	..
329.5	814	..
343	714	..
356.5	630	..

Acknowledgments.—We are indebted to P. L. Golden and A. M. Whitehouse for developing the magnetic balance; to M. Mentser for his able assistance in the experimental work; to E. H. Bean for preparation of the ϵ-iron carbide; to Dr. Elizabeth W. Toor for some of the calculations; to Mrs. W. C. Peebles for X-ray analysis and W.E. Dieter for chemical analyses. Our special thanks go to Dr. R. B. Anderson, without whose encouragement this study would not have been completed.

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[CONTRIBUTION FROM THE MINERALS THERMODYNAMICS EXPERIMENT STATION, REGION II, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

The Heats of Formation of Tungsten Trioxide and Tungsten Dioxide

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RECEIVED OCTOBER 29, 1958

Combustion calorimetry was used to find the standard heats of formation of tungsten trioxide, −201.46 ± 0.20 kcal./mole, and tungsten dioxide, −140.94 ± 0.21 kcal./mole.

The only previous direct measurement of the heat of combustion of tungsten dioxide is that of Delépine and Hallopeau,[2] who obtained −135 kcal./mole. Calculations from equilibrium data[3] give −137 ± 2 kcal./mole, which has a large uncertainty and is in poor agreement with the direct result. Although the work of Huff, Squitieri and Snyder[4] furnishes an accurate value for the heat of formation of tungsten trioxide (−200.84 ± 0.10 kcal./mole), it was decided to redetermine this value so that the heat of formation of the dioxide would be based entirely upon results from our calorimeter.

Materials

Two samples of metallic tungsten, both finely divided powders, were used. Sample A was made by reducing tungstic acid (C.A.F. Kahlbaum) with purified and dried hydrogen at 900°. Spectrographic analysis, together with the weight increase upon complete oxidation, indicated the following composition: 99.86% tungsten, 0.014% iron, 0.012% silicon, 0.06% molybdenum, 0.011% magnesium, 0.005% calcium and 0.04% oxygen. Sample B was obtained from Professor A. W. Searcy of the Division of Mineral Technology, University of California, Berkeley, California. This sample was treated with dried, purified hydrogen at 900° before use. Analysis as above showed 99.95% tungsten, 0.004% iron, 0.012% silicon, 0.02% molybdenum, 0.004% magnesium, 0.003% calcium and 0.01% oxygen.

Tungsten dioxide was prepared by oxidizing a portion of tungsten sample B to the trioxide and then reducing batches of it with purified hydrogen at 600° to near the dioxide composition. After analysis, batches with slight oxygen excess were mixed with batches slightly deficient in oxygen to ascertain the correct oxygen-to-tungsten ratio, and the mixture was homogenized by prolonged heating at 1000° in

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