ries for his interest in this research and for suggestions in the preparation of this paper.

Summary

With the aid of a hollow, prismatic cell and the optical equipment of the Tiselius electrophoresis apparatus, the refractive index increments of solutions of some purified proteins have been measured as a function of the protein concentration, the temperature, and the wave length of the incident light. The changes in the specific refractive increment that occur on titration of the protein with alkali, in the presence of neutral salts and after equilibration with buffers have also been determined. Such data are necessary for a quantitative interpretation of the electrophoretic patterns of proteins.

NEW YORK, N. Y. RECEIVED APRIL 22, 1948

[CONTRIBUTION FROM THE RESEARCH LABORATORY, UNITED STATES STEEL CORPORATION]

Equilibrium of Iron–Carbon–Silicon and of Iron–Carbon–Manganese Alloys with Mixtures of Methane and Hydrogen at 1000°

BY RODNEY P. SMITH

Measurements of the equilibrium of iron–carbon alloys with mixtures of methane and hydrogen have been reported in an earlier paper.[1] Since most commercial steels contain various amounts of alloying elements, it is of considerable importance to know the effect of these additional elements on this equilibrium. Accordingly measurements were made of the carbon content of iron–silicon alloys containing up to 15% silicon and of iron–manganese alloys containing up to 15% manganese equilibrated at 1000°, with methane–hydrogen atmospheres of known composition. At this temperature the crystal structure of the silicon alloys may be either face-centered cubic (austenite or gamma iron) or body-centered cubic (ferrite or alpha iron) depending on the concentration of carbon and silicon. For these alloys measurements were made in the region in which austenite is stable and in the region in which ferrite is stable and an estimate is given of the phase boundaries in a portion of the isothermal section of the iron–silicon–carbon system. At 1000° the structure of the manganese alloys is austenitic at all compositions investigated. For the iron–manganese–carbon system an estimate is given of the position of the phase boundaries of the austenite–austenite+graphite and a portion of the austenite–austenite+carbide fields.

Experimental

The experimental procedure was similar to that previously described.[1] The dimensions of the samples used were about 1 × 1 × 0.4 cm. For each gas mixture a number of samples of either series of alloys and a sample of electrolytic iron were equilibrated simultaneously. The carbon content of samples containing more than 0.05% carbon were analyzed by the usual combustion method; those with less than 0.05% carbon by the low pressure combustion method described by Gurry and Trigg.[2] The silicon alloys were either milled or broken up in a steel mortar prior to combustion; the manganese alloys were burned without milling, 0.5 to 1.0 g. of Bureau of Standards sample 55b, 0.010% C, being added to start combustion.

The gas composition for each set of samples was derived from the carbon content of the electrolytic iron and the equilibrium data previously published[1] rather than from the analysis of the primary hydrogen–methane mixture and the flowmeter constants. This method has the following advantages: (1) an accurate knowledge of the composition of the primary hydrogen–methane mixture is not required; (2) it is not necessary to make corrections for the small deviations (less than ±1°) from 1000° of the furnace temperature. The minimum equilibration period was one week; that this time was sufficient was established by comparison of the analysis of the electrolytic iron, equilibrated together with a typical set of alloy samples using a primary mixture of known composition, with the results for pure iron–carbon alloys previously published.[1]

The silicon alloys of composition within the range 1.2 to 5.0% Si were commercial quality steels,[3] those between 7.0 and 15.0% Si were prepared from a high-grade ferrosilicon and electrolytic iron. Analysis of a sample of electrolytic iron and of the alloys containing 1.2 to 5.0% Si before and after equilibration with respect to carbon indicated a silicon pick up from the silica furnace tube of 0.02 to 0.06%. The results were not corrected for this small change in silicon content since its effect on the carbon concentration is nearly balanced by that of the manganese present in these alloys.

The manganese alloys were of commercial quality,[4] produced in a 250 lb. arc furnace. Since an alundum furnace tube was used in the equilibration of these alloys with respect to carbon, there was no change in their silicon content. There was, however, a small change in manganese content, that of the electrolytic iron increasing by 0.25%, that of the 14.67% Mn decreasing by 0.41%, the change in the other samples being nearly linear with the manganese content.

Results—Silicon Alloys

Equilibrium with Austenite.—The left portion of Table I gives the carbon content of the austenitic silicon alloys equilibrated with several CH_4–H_2 mixtures containing from 0.14 to 0.86% methane. The marked effect of silicon on this

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[1] R. P. Smith, THIS JOURNAL, 68, 1163 (1946).

[2] R. W. Gurry and H. Trigg, *Ind. Eng. Chem., Anal. Ed.*, 16, 248 (1944).

[3] Analysis. C, 0.05–0.07; Mn. 0.2–0.3; P. 0.005–0.01; S. 0.01–0.02.

[4] ANALYSES

Mn	C	P	S	Si
3.92	1.50	0.015	0.014	0.03
6.48	1.64	.023	.011	.01
9.10	0.30	.040	.008	.19
12.87	0.94	.043	.010	.11
14.67	1.33	.040	.007	.09

TABLE I

CARBON CONTENT OF IRON–SILICON ALLOYS EQUILIBRATED WITH CH_4–H_2 MIXTURES AT 1000°: $r_1 = p_{CH_4}/p_{H_2}{}^2$, WHERE p IS IN ATMOSPHERES

Initial Si content weight per cent.	0	1.23	2.10	3.41	4.39	5.00	7.8	10.3	15.6
	Final carbon content, weight per cet.								
$r_1 \times 10^3$		Austenite				Ferrite			
1.42	0.308	0.261	0.223	0.023		0.016			
1.40	.306			.021		.016	0.009	0.003	0.003
3.24	.666	.572	.485	.394		.039			
3.08	.638					.036	.017	.006	.003
5.31	.995						.028	.011	.006
5.56	1.032	.880	.764	.619		.383			
8.45	1.390						.048	.020	.004
8.65	1.412	1.218	1.080	.866	.729	.658			

equilibrium is shown better in Fig. 1, in which the weight per cent. carbon at equilibrium at 1000°, for various gas ratios, $r_1 = p_{CH_4}/p_{H_2}{}^2$ is plotted against the weight per cent. silicon. For a given gas ratio the decrease in carbon for each per cent. increase in silicon is roughly 10% of the carbon content of pure iron. The activity of dissolved carbon is proportional to r_1, thus each line for a given value of r_1 represents an iso-activity line, with respect to carbon.

Austenite, Austenite + Graphite Boundary.—At the gas ratio, $r_1 = 0.00950$, the gas phase is in equilibrium with graphite.[1] Therefore the iso-activity line for $r_1 = 0.00950$ gives the boundary of the single phase austenite field and the two phase austenite + graphite field. This boundary, line FB in Fig. 1, was determined by extrapolating curves of r_1, plotted against weight per cent carbon for each silicon alloy to $r_1 = 0.0095$. It may be noted that the decrease caused by silicon in the solubility of graphite in gamma iron is similar to that found by Herty and Royer,[5] in the case of liquid iron (see Fig. 2). The solubility of graphite in austenitic silicon alloys as given in Fig. 1 is somewhat higher than that given by Charpy and Cornu-Thenard,[6] and considerably higher than that given by Becker.[7] The solubility of graphite in pure iron given by Becker is lower than the value given by more recent determinations and it is probable that his values for the silicon steels are also low.

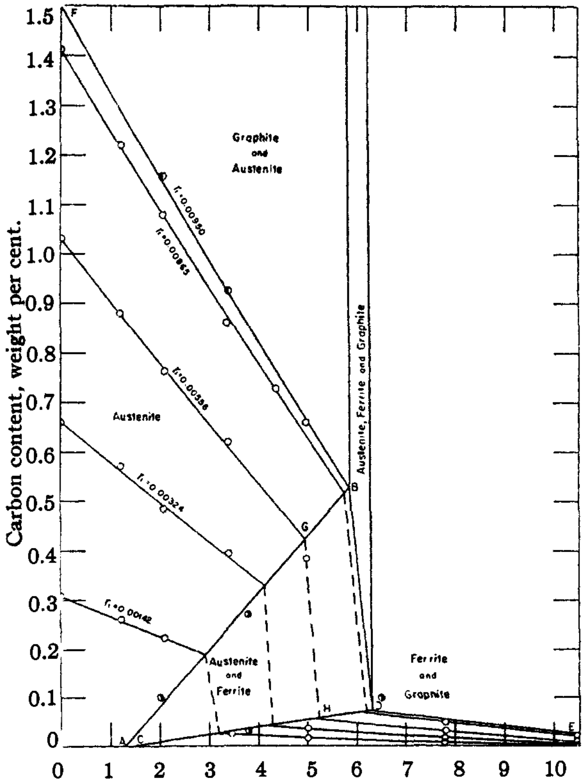

Fig. 1.—A portion of the iron–carbon–silicon equilibrium diagram at 1000°: O, experimental; ◐, extrapolated; ◑, "Alloys of Iron and Silicon"[12]; $r_1 = p_{CH_4}/p_{H_2}{}^2$.

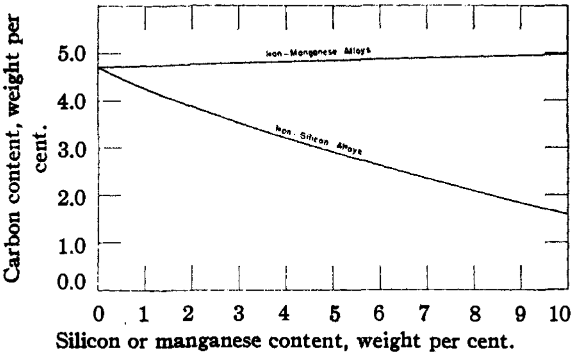

Fig. 2.—Effect of silicon and manganese on the solubility of graphite in iron at 1300° as given by Herty and Royer.[5]

Equilibrium with Ferrite.—The right portion of Table I gives the carbon content of the ferritic silicon alloys equilibrated with several CH_4–H_2 mixtures. These results are shown graphically in Figs. 1 and 5. The consistency of these results

(5) C. H. Herty and M. B. Royer, U. S. Bureau Mines, R. I. 3230 (1934).

(6) G. Charpy and A. Cornu-Thenard, *J. Iron Steel Inst.*, **91**, 276 (1915).

(7) M. L. Becker, *ibid.*, **112**, 239 (1925).

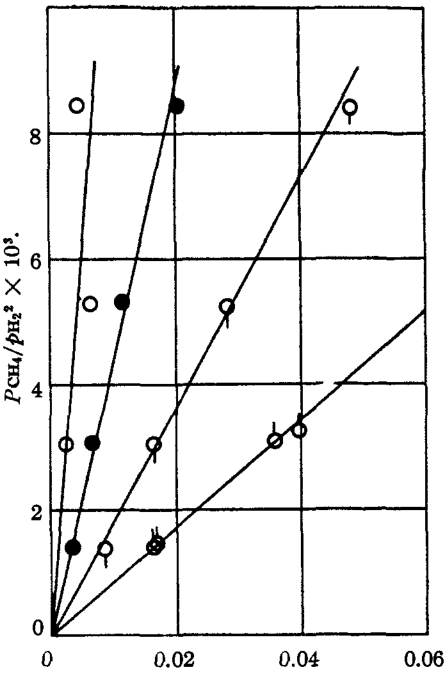

Fig. 3.—Carbon content of ferrite in relation to $p_{CH_4}/p_{H_2}^2$: ó, 5.0% Si; ♀, 7.8% Si; ●, 10.3% Si; O, 15.6% Si.

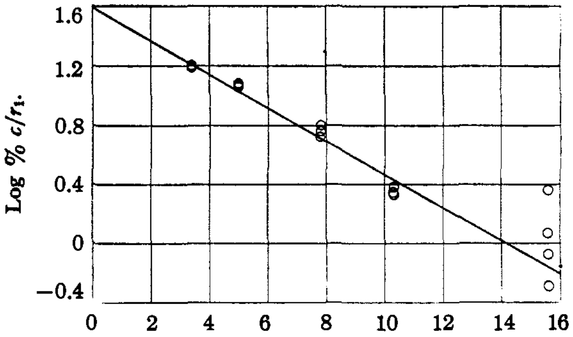

Fig. 4.—Plot of log $\%C/r_1$, against weight per cent. of silicon; $r_1 = p_{CH_4}/p_{H_2}^2$, % C = weight per cent. carbon.

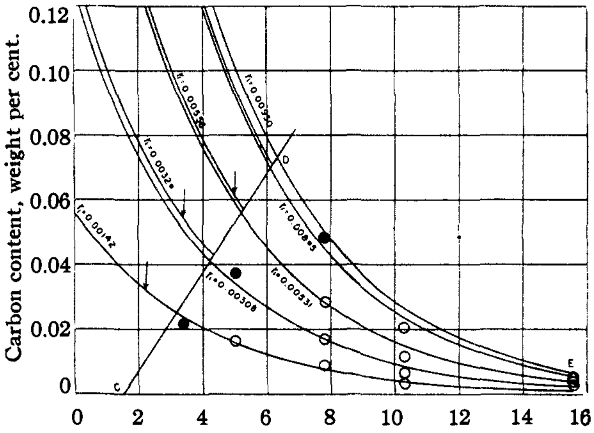

Fig. 5.—Carbon content of ferrite in relation to silicon content for various values of r_1 at 1000°: curves calculated from straight line of Fig. 4; O, ●, experimental points.

may be illustrated better in the following manner. The activity of carbon is proportional to r_1, and its activity coefficient is inversely proportional to $\%C/r_1$ where $\%C$ is the weight per cent. carbon of a sample equilibrated with a gas whose $p_{CH_4}/p_{H_2}^2$ ratio is r_1. Since the carbon content of ferrite is always less than 0.08 weight per cent. it is reasonable to assume that, for a given silicon alloy, the activity coefficient of carbon is independent of the carbon concentration. The validity of this assumption is illustrated in Fig. 3 in which r_1 is plotted against weight per cent. carbon for the alloys containing 5.0, 7.8, 10.3 or 15.6% Si; the points fall on straight lines, within the experimental error, demonstrating that the system conforms to Henry's law, or the activity coefficient of carbon in these alloys does not change with the carbon concentration. The activity coefficient of carbon does, however, change appreciably with the silicon content for the range of concentration of 0 to 15% Si. In general log $\%C/r_1$, rather than $\%C/r_1$, will be a nearly linear function of %Si; thus if log $\frac{\%C}{r_1}$ is plotted against weight per cent. silicon all points should fall on the same curve which will be either straight or nearly so. Fig. 4 shows such a plot; except for results for the alloy containing 15.6% silicon all the points fall on a straight line with ±10%. The curves of Fig. 5 represent smoothed results calculated from the straight line of Fig. 4 for the experimental values of r_1.

Extrapolation of the straight line, Fig. 4 to zero per cent. silicon allows the calculation of the hypothetical carbon content of alpha iron at 1000° for any given value of r_1; the corresponding carbon content of gamma iron is known,[1] thus a distribution coefficient for carbon between alpha iron and gamma iron may be calculated. The distribution coefficient, K, may be defined as

$$K = a_1/a_2 = \gamma_1 C_1/\gamma_2 C_2 \cong \gamma_1 C_1/C_2 \qquad (1)$$

where a_1 is the activity of carbon in gamma iron, when its concentration is C_1 weight per cent., a_2 is the activity of carbon in alpha iron, when its concentration is C_2 weight per cent., γ_1 and γ_2 are the activity coefficients of carbon in gamma iron and alpha iron, respectively. The standard state in each case is chosen so that the activity is equal to the weight per cent. when the latter approaches zero. The value of K at 1000° may then be compared with values calculated from the data of Smith[1] (at 800 and 1000°) and of Mehl and Wells[8] for the temperature range 723 to 849° and those of Adcock[9] at 1490° by the relation

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[8] Robert Mehl and Cyril Wells, *Trans. Am. Inst. Mining Met. Engrs.*, **125**, 429 (1937).

[9] Frank Adcock, *J. Iron Steel Inst.*, **135**, 281 (1937).

$$\Delta H = -4.575 \text{ d} \log K/(\text{d}1/T) \qquad (2)$$

where ΔH is the heat of transfer of carbon from alpha iron to gamma iron and T is the absolute temperature.

Since C_2 is always small, it is assumed that $\gamma_2 = 1$; γ_1 at 800 and 1000° may be determined from the deviation from Henry's law of the solid solution of carbon in gamma iron.[1] Within the experimental error γ_1 is the same at 800 and 1000° and in the calculation of K it is assumed to be independent of temperature. Fig. 6 shows a plot of log a_1/C_2 against $1/T$. The straight line through the points calculated from the data of Smith,[1] Mehl and Wells[8] and Adcock[9] gives 0.916 for log a_1/C_2 at 1000°. The value calculated from the equilibrium of CH_4–H_2 mixtures with austenite and the extrapolated value for ferrite, Fig. 4, is 0.826. Considering the uncertainties in each method of calculation, the agreement is satisfactory. The heat of transfer of carbon from alpha iron to gamma iron determined by equation (2) is −15,600 cal. per gram atom.[10] It may be noted that the quantity $RT \ln (3N_1/N_2)$ where N_1 and N_2 are the equilibrium atom fractions of carbon in gamma iron and alpha iron, respectively, which is considered constant with temperature by Zener,[11] varies from 9000 to 5400 cal. per mole for the temperature range 800 to 1490°.

Ferrite, Ferrite + Graphite Boundary.—The solubility of graphite in silicon ferrite, line DE, Figs. 1 and 5, was determined from the straight line of Fig. 4 and $r_1 = 0.0095$, the value for equilibrium of the gas phase with graphite.[1]

Ferrite, Ferrite + Austenite Boundary.—For the binary iron–silicon system the limit of the ferrite field at 1000° is 1.5% silicon.[12–14] This locates one terminus, C, in Fig. 1, of the boundary between the ferrite and the ferrite + austenite fields, line CD Fig. 1, for the three component system. Other points on this boundary, may be estimated in the following manner. In Fig. 5 the circles represent experimental data when the solid phase is ferrite, the vertical arrows indicate samples whose carbon content is too great for the solid phase to be ferrite for the particular value of r_1. The boundary between the ferrite and the ferrite + austenite fields lies at compositions to the right of those represented by the vertical arrows and to the left of the solid circles and is best represented by the straight line, CD Fig. 5, starting at 1.5%Si, 0%C, and which averages the difference in composition of points known to be in the ferrite field and those known to be in the austenite or austenite + ferrite fields. The other terminus of this boundary line is given by the intersection of line CD, Fig. 5, with the curve for $r_1 = 0.0095$. This intersection gives the composition for one corner of the three phase, austenite, ferrite, graphite, triangle. The position of the boundary is in fair accord with the best estimate from previous results.[12]

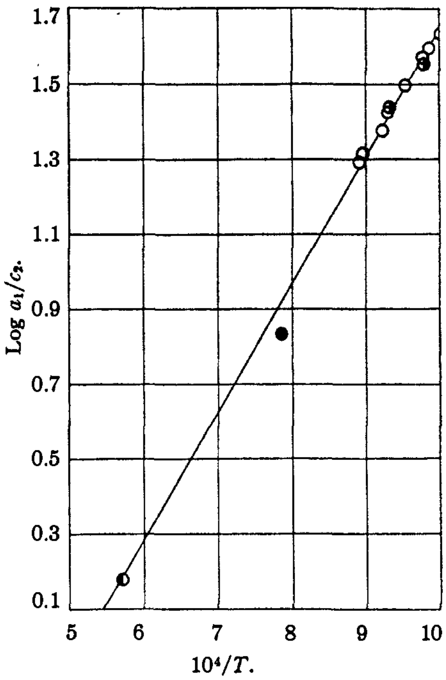

Fig. 6.—Plot of log a_1/C_2 against $10^4/T$: ◑, Smith[1]; ●, extrapolation of data for silicon alloys; ○, Smith,[1] Mehl and Wells[8]; ◐, Adcock.

Austenite, Austenite + Ferrite Boundary.—One terminus of this boundary, line AB, Fig. 1, is at 0%C, 1.3%Si.[12–14] A second point on this boundary may be estimated in the following manner. The carbon content, 0.383%C of the 5.0% silicon sample for $r_1 = 0.00556$ is below that of the smooth curve through the other points, Fig. 1, in the austenite field by an amount considerably greater than the probable experimental error. It is therefore reasonable to assume that this point lies in the austenite + ferrite field. The composition of ferrite at the ferrite, ferrite + austenite boundary in equilibrium with the gas mixture $r_1 = 0.00556$ is 0.057%C and 5.25%Si. The gross composition of all mixtures of ferrite and austenite in equilibrium with a gas of this composition will lie on a straight line, GH Fig. 1 (an isoactivity line with respect to carbon), through these two points. The intersection, G Fig. 1, of this straight line with the curve, $r_1 = 0.00556$, through the points in the austenite field gives a second point on the austenite, austenite + ferrite boundary. From these data the boundary may be represented by a straight line through points A and G, the other terminus will be at the intersection of this line with the austenite–graphite boundary. Although

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(10) This result is in good agreement with the value −15,900 cal. given by the difference in heat of solution of graphite in alpha iron and gamma iron.[1]

(11) C. Zener, *Trans. Am. Inst. Mining Metal Engrs.*, **167**, 513 (1946).

(12) Greiner, Marsh and Stoughton, "Alloys of Iron and Silicon," McGraw-Hill Book Co., Inc., New York, N. Y., 1933.

(13) R. L. Rickett and N. C. Fick, *Trans. Am. Inst. Mining Met. Engrs.*, **167**, 346 (1946).

(14) C. Zener, *ibid.*, **167**, 354 (1946).

the location of this boundary depends mainly on a single experimental point, it agrees well with previous estimates,[12] especially in the range 1.3 to 4% silicon.

The Activity of Carbon Relative to Graphite.—The activity, a_c, of carbon relative to graphite is given by the equation

$$a_c = p_{CH_4}/p_{H_2}^2K_3 = r_1/K_3 = r_1/0.0095 \qquad (3)$$

where K_3 is the equilibrium constant for the reaction $2H_2 + C$ (graphite) $= CH_4$.[1] Table II gives values of a_c at 1000° for austenitic silicon alloys interpolated to even values of the concentration of carbon and silicon.

TABLE II

THE ACTIVITY OF CARBON, RELATIVE TO GRAPHITE IN AUSTENITIC IRON SILICON ALLOYS AT 1000°

	%Si				
%C	0.2	0.4	0.6	0.8	1.0
0	0.097	0.195	0.301	0.424	0.563
1	.107	.226	.358	.507	.674
2	.127	.267	.427	.607	.810
3	.157	.334	.533	.762	
4	.197	.415	.662	.945	

Values of a_c for ferritic silicon alloys may be calculated from the equation of the straight line in Fig. 4 and the equilibrium constant K_3 by the equation

$$-\log a_c = 1.60 - 0.113\ (\%\mathrm{Si}) + \log K_3/\%\mathrm{C} \qquad (4)$$

where 1.60 is the intercept of the straight line at zero silicon and −0.113 is its slope.

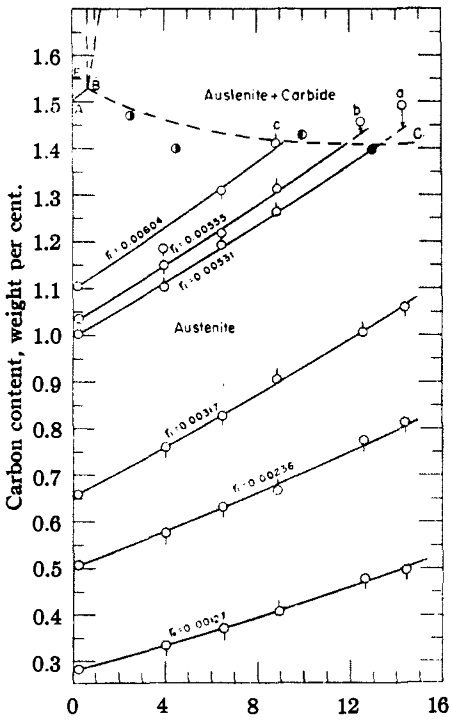

Fig. 7.—A portion of the iron-carbon-manganese equilibrium diagram at 1000°: δ, equilibrium by carburization; ♀, equilibrium by decarburization; ◑, Gensamer[15]; ◐, Eckel and Krivobok[16]; ●, Wells and Walters[17]; $r_1 = p_{CH_4}/p_{H_2}^2$.

Results—Manganese Alloys

Equilibrium with Austenite.—The experimental results for equilibrium of CH_4–H_2 mixtures with iron-manganese alloys containing from 0 to 15% Mn, are given in Table III and shown graphically in Fig. 7. For a given gas atmosphere the carbon content increases markedly with increase in manganese. A similar, but less pronounced, effect has been observed in the case of the solubility of carbon in liquid iron-manganese alloys[5] (see Fig. 2).

TABLE III

CARBON CONTENT OF IRON-MANGANESE ALLOYS EQUILIBRATED WITH CH_4–H_2 MIXTURES AT 1000°

$r_1 = p_{CH_4}/p_{H_2}^2$ where p is in Atmospheres

	Initial manganese, weight Mn per 100 g. of Fe + Mn					
	0	4.04	6.54	8.95	12.69	14.52
$r_1 \times 10^3$	Final carbon content, weight per cent.					
1.27	0.277	0.333	0.371	0.406	0.478	0.495
2.36	.501	.576	.632	.667	.775	.815
3.17	.653	.760	.827	.906	1.009	1.061
5.31	.996	1.102	1.193	1.264		1.493
5.55	1.029	1.148	1.219	1.313	1.458[a]	
6.04	1.096	1.184	1.312	1.413		
9.45	1.496	1.861				

[a] Microscopic examination of a polished sample indicated carbide at temperature.

The consistency of these results may be illustrated better by a plot suggested by the semi-empirical equation

$$\log r_1/N_2 + 1.86\ (1 - N_2)^2 = kN_3\ (1 - N_2) + I \qquad (5)$$

where N_2 and N_3 are the atom fractions of carbon and manganese respectively at equilibrium with a gas atmosphere whose $p_{CH_4}/p_{H_2}^2$ ratio is r_1; k and I are constants. If this relation is valid all the experimental points should fall on one straight line when the left side of equation (5) is plotted against $N_3\ (1 - N_2)$. Such a plot is shown in Fig. 8, and

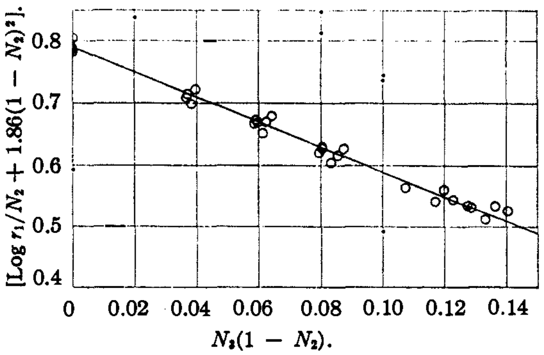

Fig. 8.—Plot of $\log r_1/N_2 + 1.86\ (1 - N_2)^2$ against $N_3\ (1 - N_2)$: $r_1 = p_{CH_4}/p_{H_2}^2$; N_2 = atom fraction of carbon; N_3 = atom fraction of manganese.

since there is no consistent deviation from a straight line it would appear that equation (5) is valid in this system within the experimental error. The greater number of the points fall on the straight line within ±5%. The slope of this line (k) is -2.05 and the intercept, I, at $N_3(1 - N_2) = 0$ is 0.792.

Austenite, Graphite + Austenite Boundary.—It has been shown that equation (5) is valid, within the experimental error, for $r_1 = 0.0013$ to 0.006 and it is not unreasonable to assume that it also holds for $r_1 = 0.0095$, the value for equilibrium with graphite.[1] The concentration of carbon at this boundary when $N_3 = 0$ given by equation (5) is 1.47 weight per cent. A better estimate of this value, determined from a consideration of several investigations, is 1.50 weight per cent. carbon.[1] The boundary, line AB, Fig. 7, is drawn parallel to the line given by equation (5) but higher in carbon by 0.03 weight per cent. The other terminus of this line will be its intersection with the line representing the austenite, austenite + carbide boundary.

Austenite, Austenite + Carbide Boundary.—The limiting solubility of carbide in pure iron–manganese alloys has been determined by microscopic examination of quenched samples for 2.5 and 4.5% Mn alloys by Gensamer,[15] for a 10% Mn alloy of Eckel and Krivobok,[16] and for a 13% Mn alloy by Wells and Waters[17]; also for commercial quality alloys of the same range of composition by Bain, Davenport and Waring.[18] These two sets of measurements do not agree too well as to the carbide solubility but do give the same general form for the solubility curve at a given temperature. Since manganese forms an orthorhombic carbide, Mn_3C, which is isomorphous with cementite, Fe_3C, and apparently forms a continuous series of solid solutions with it,[19] it is to be expected that the extension of the solubility curve to zero Mn will intersect the carbon axis at the composition of gamma iron in equilibrium with cementite, E, Fig. 7. The boundary, line BC Fig. 7, is estimated from these data. While our equilibrium data are not sufficiently extensive to establish this boundary it may be shown that they are consistent with it. Point a, Fig. 7, has a carbon content considerably higher than that indicated by the smooth curve through the points in the austenite field and may be assumed therefore to be in the austenite + carbide field, and the boundary at 14.3% Mn must lie below 1.44%C (extension of the austenite curve to 14.3% Mn, indicated by arrow). Likewise at 12.5% Mn, point b, the boundary lies at a carbon content below 1.43%C.[20] Within the experimental error, point c, 8.84% Mn, 1.413%C, is on the smooth curve through the points for $r_1 = 0.00604$ and is therefore considered to be in the austenite field. Thus the boundary for 9 to 15% Mn lies between 1.40 and 1.43% carbon, which is consistent with the boundary as determined from microscopic examination of quenched alloys.

Activity of Carbon Relative to Graphite.—The activity, a_c, of carbon relative to graphite in austenitic iron manganese alloys is given in Table IV. The method of calculation was identical with that described for austenitic silicon alloys.

TABLE IV

THE ACTIVITY OF CARBON, RELATIVE TO GRAPHITE, IN AUSTENITIC IRON–MANGANESE ALLOYS AT 1000°

	%Mn					
%C	0.2	0.4	0.6	0.8	1.0	1.2
0	0.097	0.195	0.301	0.424	0.563	0.720
2	.085	.175	.277	.391	.521	.665
4	.078	.161	.253	.358	.479	.616
6	.071	.148	.233	.328	.441	.569
8	.065	.137	.214	303	.405	.526
10	.060	.127	.198	.280	.373	.484
12	.055	.117	.183	.258	.347	.445
14	.050	.107	.167	.237	.318	.408

Summary

The carbon content of several iron–silicon alloys (1.2 to 15% Si) and of a number of iron–manganese alloys (4.0 to 14.5% Mn) in equilibrium with various mixtures of methane and hydrogen of known composition at 1000° has been determined. For the silicon alloys the measurements cover both the region in which the crystal structure is face-centered cubic (austenite) and body-centered cubic (ferrite).

The activity of carbon, relative to graphite, is given for each system.

An estimate is given of the phase boundaries in a portion of each of the two three component systems. The phase boundaries determined by equilibrium measurements are in good agreement with those determined by others by microscopic methods.

KEARNY, N. J. RECEIVED MARCH 30, 1948

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(15) M. Gensamer, *Trans. Am. Soc. for Steel Treating*, **21**, 1028 (1933).

(16) John Eckel and V. N. Krivobok, *ibid.*, **21**, 846 (1933).

(17) Cyril Wells and Francis Walters, Jr., *ibid.*, **21**, 830 (1933).

(18) E. C. Bain, E. S. Davenport and W. S. N. Waring, *Trans. Am. Inst. Mining Met. Engrs.*. **100**, 228 (1932).

(19) J. B. Austin, *Trans. Am. Soc. Metals*, **38**, 28 (1947).

(20) The presence of carbide in this sample was confirmed by microscopic examination.