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# Activity of Carbon in Liquid Iron-Carbon Solutions

## INTRODUCTION

The early physical chemistry of steelmaking was content with applying the law of mass action in its original form to solutes in liquid iron. Much was written then on how to express the concentration of carbon. Was carbon dissolved as atoms or as molecules such as  $\text{Fe}_3\text{C}$ ? Precarious phase-diagram and thermal data could not help to settle the issue.<sup>1</sup> As metallurgical chemistry was gradually approached from a more thermodynamical point of view, non-ideal solutions gained recognition, and the necessity to establish activity-concentration relationships was realized. The nature of the solution, now known to be interstitial in the case of carbon,<sup>2</sup> could be ignored for that purpose.

The attention given by metallurgists to the reaction of carbon and oxygen in the open-hearth bath greatly delayed the study of the simple binary iron-carbon system. The equilibrium of laboratory melts with  $\text{CO}-\text{CO}_2$  mixtures, defining fixed carbon and oxygen potentials, was used by a number of workers<sup>3, 4, 5, 6, 7</sup> to study the equilibrium value

of the product  $[\text{C}] \cdot [\text{O}]$ . Such experiments may give information on the activity of carbon if accurate gas analyses are obtained. In fact, Phragmén and Kalling<sup>6</sup> did compute an activity coefficient for Henry's law from their data which ranged below 0.1% carbon. They remarked that the value which they found had to increase very fast with concentration if the solubility limit was to be accounted for. Marshall and Chipman<sup>7</sup> reached carbon contents as high as 2.0% by operating under pressure. They found that the activity coefficient of carbon may be regarded as constant up to 1% and that it increases thereafter. Later work was not to confirm this view.

In 1953, Richardson and Dennis<sup>8</sup> contributed the first study devoted primarily to the determination of the carbon activity in liquid iron. Melts with carbon contents between 0.1 and 1.1% were equilibrated with controlled  $\text{CO}-\text{CO}_2$  mixtures at 1560, 1660, and 1760° C. The experiments were carried out with extreme care, and the data are very consistent. They point to an appreciable deviation from Henry's law down to the lowest carbon investigated.

The work of Richardson and Dennis is authoritative and covers most of the range of interest in steelmaking. Nevertheless, it seemed desirable, for the sake of completeness as well as to provide data for ironmaking, to explore the entire liquid field. The present work, although it met with limited success, was undertaken with this purpose.

Concentrated iron-carbon solutions have already been studied by Esin and Gavrilov<sup>9</sup> and by Sanbongi and Ohtani.<sup>10</sup> These authors built electrochemical cells of the type:

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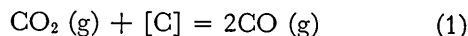
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Liquid iron-carbon alloy (sat.)	Carbide slag	Liquid iron-carbon alloy
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and measured their electromotive forces at various concentrations of the alloy on the right-hand side.

### STATEMENT OF THE PROBLEM AND METHOD

It was proposed to measure the activity of carbon dissolved in liquid iron as a function of concentration and temperature through the study of the equilibrium:



where  $[\text{C}]$  represents carbon dissolved in liquid iron. The equilibrium constant for the reaction at temperature  $T$  is

$$K_1 = \frac{(p_{\text{CO}})^2}{p_{\text{CO}_2} \cdot a_{\text{C}}}$$

where  $p$ 's represent partial pressures in the gas phase and  $a_{\text{C}}$  is the activity of carbon in solution.

Temperature and the "gas ratio"  $(p_{\text{CO}})^2/p_{\text{CO}_2}$  are taken as the two independent variables. The activity is proportional to the gas ratio, the proportionality factor  $1/K_1$  being determined at each temperature by the choice of a standard state for carbon. In the experiments, gas ratio and temperature are maintained constant, and the metal which is exposed to the flowing gas adjusts its composition to the carbon activity imposed by the gas phase. The study is thus designed to yield the activity-composition relationship.

The main experimental problems are: the con-

trol and measurement of the gas composition, the control and measurement of temperature, and the analysis of the metal.

In order to cover the range of high carbon concentration, high gas ratios must be attained with mixtures extremely dilute with respect to carbon dioxide. A situation thereby arises in which composition control in the gas is difficult (and, in fact, becomes impossible when carbon deposition steps in), the reaction is slow, and side reactions between melt and crucible are favored.

### APPARATUS AND EXPERIMENTAL PROCEDURE

#### Preparation of the Gas Mixtures

Ternary gas mixtures of  $\text{CO}_2$ ,  $\text{CO}$ , and argon were used, argon being added in order to benefit by the effects of an increased total flow rate. The sketch of Fig. 1 shows clearly the three gas lines.

Argon was purified from water vapor, carbon dioxide, and oxygen in columns containing anhydron, ascarite, and magnesium turnings at  $590^\circ\text{C}$ . Carbon dioxide was dried over anhydron and purified from oxygen over copper at  $450^\circ\text{C}$ . Carbon monoxide was manufactured by passing dry carbon dioxide over graphite at  $1100^\circ\text{C}$  and then purified from residual carbon dioxide over a concentrated potassium hydroxide solution and ascarite.

The flow rates of the component gases were controlled by adjusting the pressure drops across capillary flow meters. Through most of the experiments the flow rates of  $\text{CO}$  and argon were kept constant

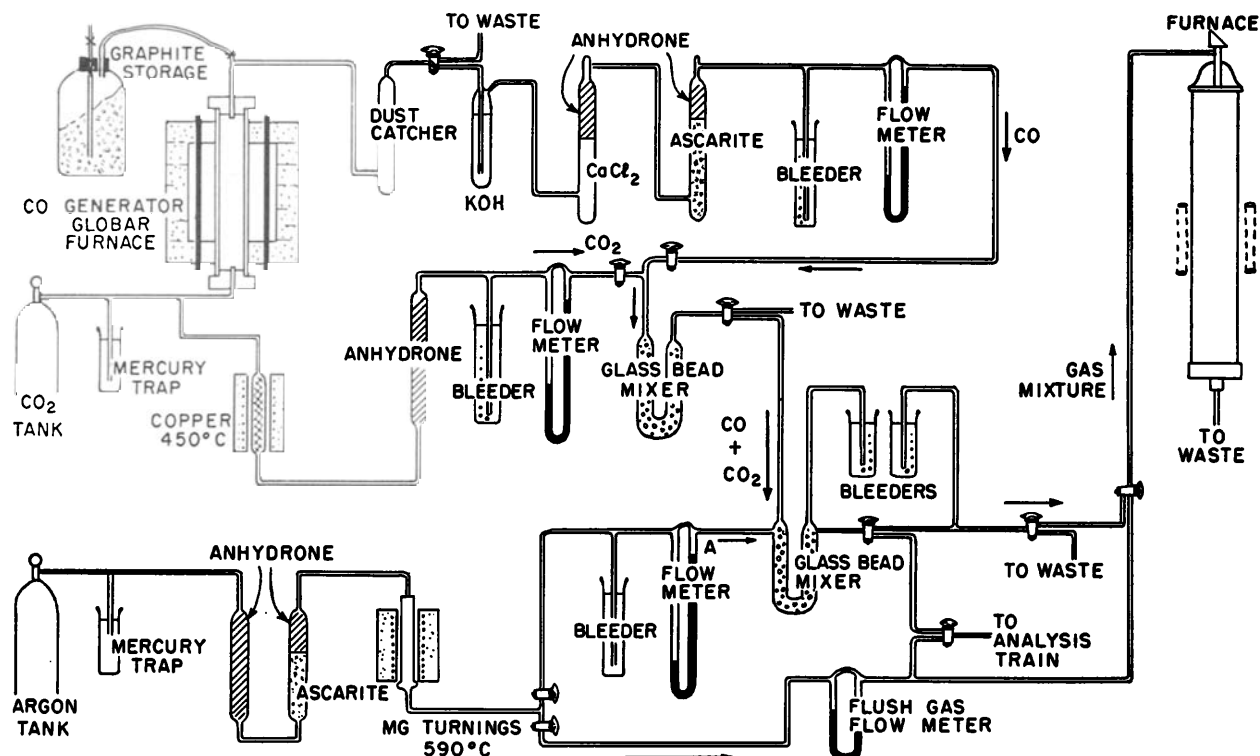


Fig. 1. Diagram of gas system.

and each equal to about 300 ml/min while the flow rate of CO<sub>2</sub> was varied to obtain the required gas ratios. The entire range of gas ratios (100 to 4300) was covered with CO<sub>2</sub> flow rates ranging roughly from 2 to 0.03 ml/min.

### Gas Analysis

The apparatus was equipped with facilities for the gravimetric analysis of CO<sub>2</sub> by absorption on ascarite and of CO by conversion to CO<sub>2</sub> in a cupric-oxide furnace followed by absorption on ascarite. Analysis was used to establish or check the calibration of the capillary flow meters. In the case of argon, a volumetric method was used.

The analysis of CO<sub>2</sub> required special care in view of the small quantities involved. Over 4 hr were necessary to collect about 15 mg at the lowest flow rate. Two ascarite bulbs were put in series, the first one being capable of absorbing over 99% of the incoming CO<sub>2</sub>. Argon had first been used as a flushing gas; later, hydrogen was substituted for it to minimize the weight fluctuations of the enclosed gas, and a dummy bulb was used to suppress buoyancy corrections.

### Furnace Design

The metal was contained in alumina crucibles and was heated and stirred by high-frequency in-

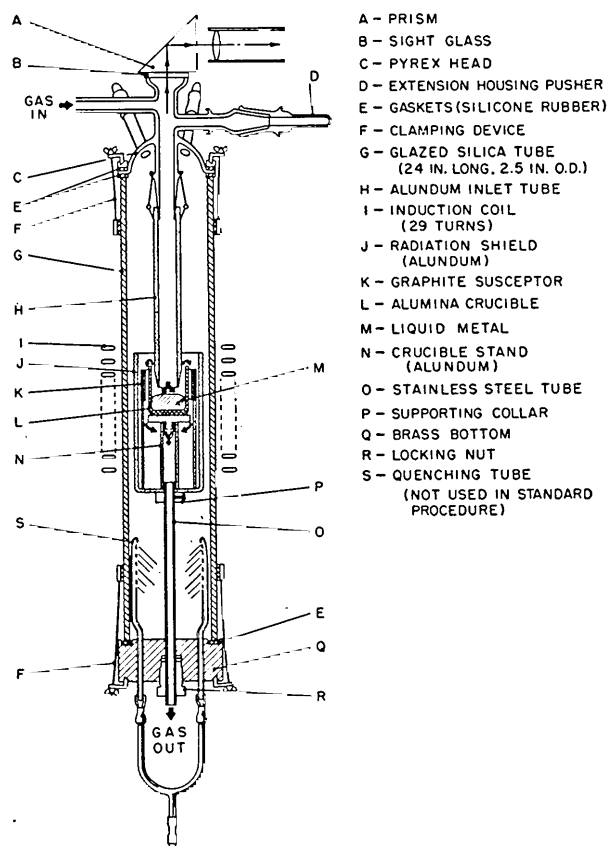


Fig. 2. Furnace arrangement.

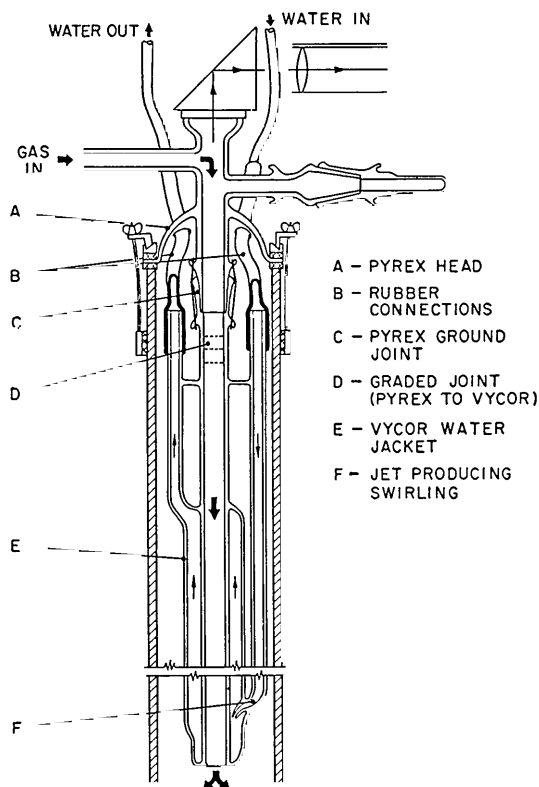


Fig. 3. Furnace head mounted with watercooled Vycor tube.

duction. The furnace, as first designed and mounted, is shown in Fig. 2. An Alundum tube, 13 mm i.d., led the gas flow downward to the melt surface. The crucible was surrounded by an annular graphite susceptor in order to delay cooling of the gases as they left and thereby to delay carbon deposition. The furnace enclosure was a glazed silica tube equipped with a sight glass and prism at the top to permit optical temperature readings.

The above version of the furnace failed at gas ratios higher than 1150 when carbon deposition began to appear in the Alundum inlet tube. A new inlet tube was installed, made of Vycor and water-cooled all the way down to its mouth above the melt (see Fig. 3). That second version, which was successful in preventing carbon deposition at the lower temperatures used (1360 and 1260°C) introduced other errors to be discussed later.

### Temperature Measurement

Temperature was measured with a disappearing-filament pyrometer. Previous work<sup>11</sup> gave information on the emissivity of pure iron and its variation with temperature, thus permitting calibration of the instrument at the melting point of iron and providing an optical temperature scale over a range of temperatures. The validity of the calibration has been extended to iron-carbon alloys at lower temperatures by using the eutectic point (1153°C) as a reference in conjunction with a

linear extrapolation of the emissivity curve for pure iron. Agreement was found within two degrees by observing the solidification of alloys of slightly hypoeutectic composition.

## Running Procedure

For each run a temperature and a gas ratio were selected. A 30-gram charge was prepared from electrolytic iron and a very pure grade of graphite. Air was flushed out of the furnace with argon, and the charge was heated under argon. Melting was completed under the ternary gas mixture to avoid excessive reaction between metal and crucible, and temperature was stabilized at the assigned value after 15 min of heating.

The heat was held at temperature for times which varied between a few minutes in recovery runs and a maximum of 31 hr (see Tables 1 and 2). Temperature was controlled manually through the power output of the high-frequency converter unit. Fluctuations in temperature were normally less than  $\pm 10$  degrees.

At the end of the run, argon was substituted for the gas mixture, the power turned off, and the melt cooled under argon. The heats containing less than 2.0% carbon were killed with aluminum. Quenching had been planned originally and was to be effected between two helium jets at the bottom of the furnace. It was abandoned, however, to suppress opportunities for scraping or shaking loose any carbon deposited on the exit path of the gas.

## Metal Analysis

The metal analysis was performed by the conventional combustion method. One-gram samples were taken from milling chips representing one-half of the solidified ingot and thoroughly mixed. The analysis was thus made insensitive to segregation if any was present. When solidification had produced grey or mottled iron, a certain amount of graphite powder was present with the chips. It was carefully screened out and weighed, and proportional amounts of powder and chips were taken for each analytical sample. The spread of duplicate carbon determination was constant at all carbon levels and equal to  $\pm 0.01\%$  carbon.

## EXPERIMENTAL RESULTS

The experiments reported are divided into series A and series B according to the furnace setup used. As a rule, only the heats corresponding to the closest approach to equilibrium are listed.

**Series A.** The heats were made with Alundum inlet tubes, and results were obtained free of any recognized systematic error at 1560 and 1460°C with gas ratios up to 1150. The data are recorded

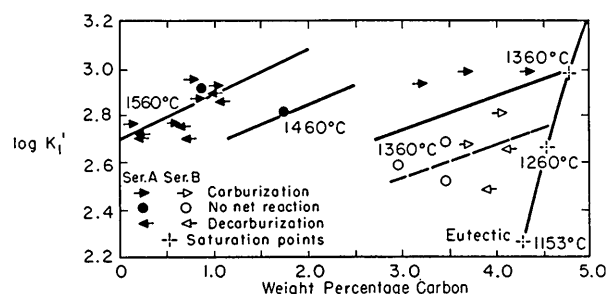


Fig. 4. Experimental data;  $K'_1 = p_{CO}^2 / (p_{CO_2} \cdot \% C)$ . The solid lines represent equilibrium; broken line at 1360° represents series B, known to be subject to errors of thermal diffusion and incomplete equilibrium.

in Table 1 and plotted in Fig. 4. In the fifth column of Table 1, the "initial % C" of a heat was

Table 1. Experimental Results, Series A

Heat No.	Temperature, °C	Gas Ratio	Time, hr	% C Initial	% C Final	$\Delta\% C$	$\log K'$
53	1560	104	4.0	0.16	0.19	+0.03	2.750
53	1560	103	6.8	0.31	0.20	-0.11	2.710
54	1560	102	3.0	0.20	0.19	-0.01	2.725
58	1560	336	4.0	0.55	0.57	+0.02	2.770
59	1560	325	6.0	0.64	0.62	-0.02	2.720
61	1560	325	6.0	0.59	0.56	-0.03	2.765
72	1560	1045	6.0	1.12	1.14	+0.02	2.965
68	1560	1030	5.0	1.17	1.17	0.00	2.945
63	1560	990	6.0	1.18	1.19	+0.01	2.920
66	1560	1030	5.25	1.29	1.27	-0.02	2.910
65	1560	1035	6.0	1.23	1.22	-0.01	2.930
75	1560	1150	6.0	1.28	1.29	+0.01	2.950
133	1460	1140	6.0	1.76	1.76	0.00	2.810
81	1360	2750	6.0	3.19	3.21	+0.02	2.930
82	1360	3705	6.0	3.78	3.81	+0.03	2.995
83	1360	4290	6.0	4.37	4.38	+0.01	2.990

$$* K' = \frac{(p_{CO})^2}{p_{CO_2} \cdot \% C}$$

calculated after recovery runs showing that over 99% of the carbon charged was recovered. In the seventh column,  $\Delta\% C$  is the difference between final and initial % C. The ranges of temperatures and gas ratios which could be investigated were limited by the occurrence of carbon deposition, which is discussed later. Justification for quoting heats 81, 82, and 83 is also given later.

**Series B.** The heats were made with the Vycor

Table 2. Experimental Results, Series B

Heat No.	Temperature, °C	Gas Ratio	Time, hr	% C Initial	% C Final	$\Delta\% C$	$\log K' \dagger$
195	1360	1160	9.0	2.98	2.98	0.00	2.590
194	1360	1165	10.0	3.48	3.48	0.00	2.525
196	1360	1160	10.3	3.88	3.86	-0.02	2.480
201*	1360	1700	30.25	3.48	3.48	0.00	2.690
188	1360	1820	10.5	3.73	3.75	+0.02	2.685
204	1360	1840	31	4.08	4.05	-0.03	2.660
187	1360	2720	10.5	4.17	4.18	+0.01	2.815
203	1260	1150	27.2	4.17	4.15	-0.02	2.450
186	1260	1475	10.5	4.07	4.08	+0.01	2.560
182	1260	1810	10.0	4.07	4.08	+0.01	2.645

\* In heat 201, helium was substituted for argon.

$$\dagger K' = \frac{(p_{CO})^2}{p_{CO_2} \cdot \% C}$$

water-cooled tube mostly at 1360° C. The results have been recognized to be affected by a large systematic error, other than carbon deposition, and are discussed later. They are reported, however, in Table 2 since they suggest some interesting comments. For the sake of clarity, only the 1360° C heats are shown in Fig. 4.

The co-ordinates selected to plot the data on Fig. 4 are % C as abscissa and  $\log K_1' = \log ((p_{\text{CO}})^2 / p_{\text{CO}_2} \cdot \% \text{ C})$  as ordinate. They are well suited to the case where the standard state for carbon is defined by the condition that its activity should become equal to its weight % at infinite dilution. The plot yields readily:

(a) The logarithm of the equilibrium constant,  $\log K_{1(T)}$ , by extrapolation to zero % carbon of the isotherm  $T$ .

(b) The logarithm of the activity coefficient,  $\log f_{\text{C}}$  (where  $f_{\text{C}} = a_{\text{C}} / \% \text{ C}$ ), at any concentration by reading off the plot  $\log f_{\text{C}} = \log K_{1(T)}' - \log K_{1(T)}$ .

Similar plots will be presented where the mole fraction  $N_{\text{C}}$  is used as a unit of concentration.

The full lines on Fig. 4 have been drawn according to the treatment given below. At 1360° C the broken line is drawn through the experimental points and parallel to the full line.

## DISCUSSION OF THE MAIN SOURCES OF ERROR

### Carbon Deposition

Carbon deposition is the reaction  $2\text{CO} \rightarrow \text{CO}_2 + \text{C}$  (amorphous). Its effect is to lower the carbon potential in the gas and correspondingly in the metal. Carbon deposition could affect the measurements only if it occurred:

(a) During preheating in the inlet tube so as to alter the composition of the fresh gas.

(b) During cooling on the exit path of the gas at such a short distance from the melt as to permit mixing of used and fresh gas (see Fig. 5). Con-

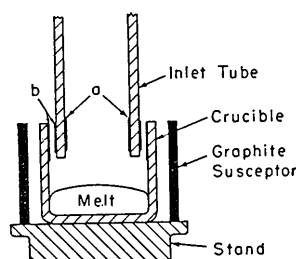


Fig. 5. Most harmful locations for carbon deposition.

densed iron was especially efficient in catalyzing the formation of such a deposit.

Heats retained in series A were free of both types. Type b could be suppressed by heating the crucible externally with the graphite susceptor. Type a ap-

peared only at temperatures above 1600° C or at gas ratios higher than 1150. All heats made under the latter conditions were discarded, except heats 81, 82, and 83, which were run at 1360° with gas ratio much above 1150. In spite of visible carbon deposition, they still showed carburization, and therefore, they set lower limits of the equilibrium concentrations.

In the heats of series B, carbon deposition of type a was suppressed since the gas was kept cold in the inlet tube. Type b deposits tended to be heavier because of increased iron condensation on cold surfaces. Heats were retained at 1360 and 1260° C when carbon deposition was not visible or when it was light, provided its level on the crucible wall did not reach below the tube mouth. More serious errors were to affect series B heats which will be discussed presently.

### Thermal Diffusion

Thermal diffusion in the gas phase, if it is appreciable, will result in an excessive carburization of the melt since CO, the lighter gas, tends to diffuse toward the hot surface. Other workers in gas-metal equilibrium studies<sup>12, 13</sup> have resorted to full preheating of the gas to suppress the temperature gradient in the vicinity of the melt. This could not be done here because of carbon deposition. Addition of a heavy inert gas, which was found beneficial by the same authors to preserve the ratio  $p_i/p_j$  of gases  $i$  and  $j$  in a mixture, is slightly detrimental when it comes to preserving the ratio  $(p_{\text{CO}})^2/p_{\text{CO}_2}$ . Comparison with the experiments of Dastur and Chipman<sup>12</sup> on thermal diffusion in  $\text{H}_2$ — $\text{H}_2\text{O}$  mixtures under very similar conditions bears out the fact that, in series A, the error on  $\log K_1'$  ( $\Delta \log K'$ ) is less than 0.03 at 1560° C. In fact, the agreement of the present data with those of Richardson and Dennis obtained at the same temperature in a resistance furnace confirms that no large error was introduced in series A heats by thermal diffusion.

In the heats of series B, there is no other basis for estimating the error than comparison with measurements of thermal diffusion at equilibrium in similar gas mixtures, although such an equilibrium is not likely to be reached in the fast-flowing system under consideration. Gillespie's equation,<sup>14</sup> when tested on the available data,<sup>15</sup> is found to exaggerate the thermal separation of CO and CO<sub>2</sub>. If applied to the maximum temperature gradient found here, it gives:

$$-\Delta \log K_1' \leq 0.13$$

Although every step of the calculation exaggerates the estimate of the error, an even larger error is found, approaching 0.2. This is evidenced by the discrepancy between the known saturation points (equilibrium of graphite with CO and CO<sub>2</sub>) and the extrapolation to saturation of series B data at 1360° C (see Fig. 4).

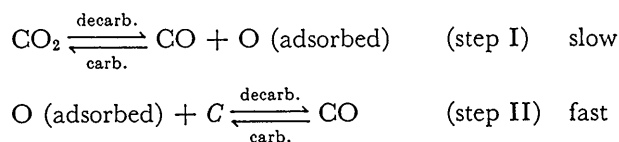
A few heats in which conditions were identical in series A and B show a displacement of the points of the same order. These facts suggest the existence of another large error affecting the measurements in the same direction as thermal diffusion, which, according to the authors, is lack of thermal equilibrium.

### Lack of Thermal Equilibrium

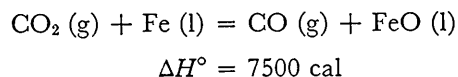
The heat transfer from the hot metal to the cold gas is not instantaneous and, for short retention times, the gas at the interface will contain "cold" molecules (i.e., the average stored energy is less than the average at thermal equilibrium). Fewer molecules will reach the activated state required for them to react, and reaction rates will be slower. Chemical equilibrium, which is a balance between the rates of two opposite reactions, may be displaced if one of them is slowed down more than the other. This may happen in two ways:

- (a) The reactants being equally "cold" in both, one reaction requires more activation energy than the other, or
- (b) Activation energies being equal, the reactants for one reaction are "colder" than for the other.

Short of any better working hypothesis, the mechanism proposed by Doehlemann<sup>16</sup> for carburization and decarburization of austenite is applied to liquid iron:



Step I is rate controlling. The difference between the heats of activation for the forward and the backward reactions is equal to  $\Delta H_{(I)}$ , the heat of reaction (I), a low estimate of which may be obtained by the standard heat of the reaction:



One may, therefore, write:

$$\Delta H_{I(\text{forward})}^* > \Delta H_{I(\text{backward})}^* + 7500 \text{ cal}$$

If it is assumed that the reactants be equally "cold," decarburization is, therefore, slowed down more than carburization.

Had the activation energies turned out to be equal, the same conclusion could be reached by arguing that the  $\text{CO}_2$  molecules (reactants in decarburization) which have more degrees of freedom may be expected to stay "colder" than CO molecules (reactants in carburization). In all cases, therefore, if the mechanism is correct, the total effect is a displacement of equilibrium towards higher carbon content, this is indeed found by experiment.

A quantitative evaluation of the error introduced by lack of thermal equilibrium is not possible. The large systematic error which steps in when going from series A to series B (i.e., when cooling of the gas is substituted for natural preheating) can be interpreted merely as the joint contribution of thermal diffusion and lack of thermal equilibrium, without it being possible to determine how much each contributes. One may only show that both are independent of gas composition so that, for a given temperature, all the equilibrium points are displaced the same distance parallel to the ordinate axis on Fig. 4, the slope of the line being preserved.

### Other Sources of Error

When no such large errors as have just been discussed are present, minor errors become of interest to assess the precision of the measurements.

In series A, errors on  $\log K_1'$  due to carbon analysis, inlet gas ratio (impurities, flow measurement), and temperature simultaneously were such that:

$$\Delta \log K_1' \leq 0.033$$

At high-carbon contents, the reaction was so slow that equilibrium, or "pseudo-equilibrium," could not be approached closely. Analytical errors could theoretically result in the wrong interpretation of the sign of the concentration changes when those were smaller than 0.03% carbon. Consistency was, however, obtained when they were trusted as low as 0.005%.

All the impurities in the metal which might affect the activity coefficient of carbon, except aluminum and oxygen, were controlled by selecting pure charge materials and properly purifying the gases. Oxygen was controlled through the equilibrium:



and its concentration, according to Marshall and Chipman,<sup>7</sup> was always lower than 0.01 weight percentage. Aluminum was controlled through the reaction of the melt with the crucible. Aluminum was analyzed and found to be always less than 0.01% in the range of the data presented here. It increased rapidly with temperature (0.11 at 1760°C in a 1.2% carbon melt), and the evidence that the reaction reached equilibrium was spectacular at 1760, 1660, or even 1560°C at high carbon. Alumina particles on the melt surface could be formed or suppressed at will with temperature fluctuations in a 20° interval. Independently of carbon deposition, the crucible reaction sets a limit to this study at high temperatures.

### INTERPRETATION OF THE DATA AND THERMODYNAMIC CALCULATIONS

At 1560°C, three equilibrium points have been established with good accuracy. They are also in good agreement with those of Richardson and Den-

nis at the same temperature. At 1460° C, a single heat, showing no net reaction under conditions where reaction rates were high, is taken as defining equilibrium within the accuracy of the method. This point fits the temperature dependence of the equilibrium found by Richardson and Dennis at higher temperatures.

At 1360 and 1260° C, the equilibrium lines could not be determined in the present work. Reliable data are limited at the present time to the solubility limit and the equilibrium of graphite with CO and CO<sub>2</sub>. Successful experimental work is still needed between 2% carbon and saturation.

In view of the modest contribution of this work, it seems desirable to propose a joint interpretation of all the data available. All of the experimental points of Richardson and Dennis and of the authors have been plotted in Fig. 6. The choice of  $(1 -$

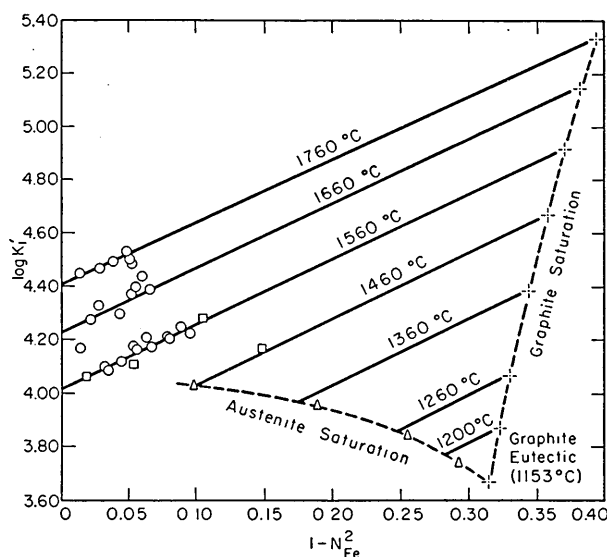


Fig. 6. Equilibrium of carbon with CO-CO<sub>2</sub> mixtures.  $K_1' = p_{CO}^2 / (p_{CO_2} \cdot N_C)$ .

$N_{Fe^2}$ ) as abscissa permits a linear extrapolation of the 1560° C data to a point determined by the known carbon content and gas ratio of the graphite-saturated melt. The relative position of the lines for other temperatures will be discussed presently.

The isotherms have equations of the type:

$$\log K_1' = \log K_1 + \log \gamma_C$$

$$K_1' = \frac{(p_{CO})^2}{p_{CO_2} \cdot N_C}$$

The 1560° C isotherm is the best defined experimentally and may be represented by the equation:

$$\log K_1' = 4.02 + 2.43(1 - N_{Fe^2})$$

where 4.02 is the value of  $\log K_1$  determined by the intercept and the last term represents  $\log \gamma_C$  at 1560° C over the entire range of liquid compositions.

To proceed further, two assumptions are made:

(a) The intercepts of the isotherms (i.e., values of  $\log K_1$ ) are a linear function of  $1/T$  which, in view of the relationship:

$$\frac{d \log K_1}{d(1/T)} = -\frac{\Delta H_1^\circ}{2.3R}$$

is equivalent to assuming that the standard heat of reaction 1 is independent of temperature.

(b) The slopes of the isotherms are proportional to  $1/T$ , following the treatment of the iron-carbon system by Darken and Gurry.<sup>17</sup> These authors assume the relationship:

$$\log \gamma_C = -\frac{A}{T}(1 - N_{Fe^2})$$

where  $A$  is a constant. Hence:

$$\frac{\partial \log K_1'}{\partial(1 - N_{Fe^2})} = \frac{\partial \log \gamma_C}{\partial(1 - N_{Fe^2})} = -\frac{A}{T}$$

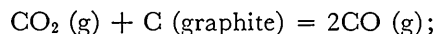
All slopes may, therefore, be calculated from the 1560° C isotherm, the value of  $A$  being  $A = -4450$ . A tentative general expression for the activity coefficient is therefore

$$\log \gamma_C = \frac{4450}{T}(1 - N_{Fe^2})$$

The data at 1760° C are used along with the previous equation for  $\log \gamma_C$  to establish the temperature dependence of  $K_1$  with the following result:

$$\log K_1 = \frac{-7280}{T} + 7.98$$

These equations reproduce the data of Richardson and Dennis and of the authors at carbon concentrations below 2%. The expression for the activity coefficient, however, is not valid at high carbon concentrations at temperatures other than 1560° C, and slight modification is required to conform with what is known about high-carbon solutions. The equilibrium constant of the producer-gas reaction is known from thermodynamic data<sup>18</sup> and may be represented by the equation:



$$\log K = \frac{-8460}{T} + 8.85$$

The solubility of graphite according to Chipman and co-workers<sup>19</sup> is:

$$\% C = 1.34 + 2.54 \times 10^{-3} t (^\circ C)$$

From these equations, values of  $\log K_1'$  were calculated and are shown along the line of saturation in Fig. 6. The lines are fitted to those points by a correction whereby  $A$  is made a function of temperature. The expression of  $\log K_1$  remaining unchanged, the best fit is obtained when  $\log \gamma_C$  is written:

$$\log \gamma_C = \frac{4350}{T} [1 + 4 \times 10^{-4} (T - 1770)] (1 - N_{Fe}^2)$$

The lines of Fig. 6 are drawn to conform to this equation, and values of  $\log \gamma_C$  are shown in Fig. 7.

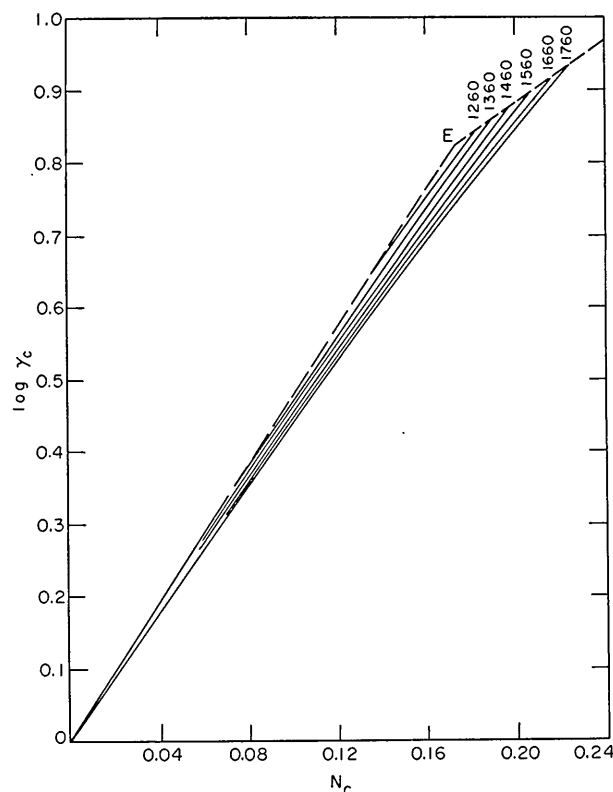


Fig. 7. Activity coefficient of carbon in liquid iron (mole fraction basis).

Figure 8 is a translation of Fig. 7 on the weight-percentage basis, and the line earlier proposed by Chipman<sup>20</sup> is shown on the same graph.

### Comparison with Data on Austenite

The data of Smith<sup>21</sup> on the equilibrium of carbon in austenite with CO—CO<sub>2</sub> mixtures may be extrapolated across the two-phase field where austenite is in equilibrium with liquid alloys. The points placed on the liquidus line on Fig. 6 have been calculated in a manner to be described here. First the liquidus and solidus lines of the iron-carbon diagram were redrawn on the following basis: the eutectic was taken at 1153° C<sup>17</sup> and 4.27% carbon<sup>19</sup> and the peritectic at 1499° C and 0.53% carbon.<sup>17</sup> The experimental points of several investigators,<sup>22, 23, 24, 25</sup> when corrected to fit the above end points, define the liquidus used here. The agreement with the line proposed by Darken and Gurry<sup>17</sup> is very close. The end points of the solidus are taken at 1499° C, 0.16% carbon, and at 1153° C, 2.01%. Short of any justified choice among the widely scattered experimental determinations of the solidus, a straight line was drawn between the two end points.

### 10—SOLUTES IN LIQUID IRON OR STEEL

Second, the data of Smith were extrapolated to the solidus concentrations at 1200° C (the highest experimental temperature), 1260, 1360, and 1460° C to yield the corresponding gas ratios. In doing so, the equilibrium isotherms were drawn as a set of parallel straight lines on a plot of

$$\log \left( \frac{p_{CO}^2}{p_{CO_2}} \cdot \frac{N_{Fe}}{N_C} \right) \text{ versus } \frac{N_C}{N_{Fe}}$$

and spaced on the assumption that the heat of transfer of carbon from gas to metal is independent of temperature.

Third, the gas ratios obtained were applied to the liquid alloys of the liquidus line at the same temperatures, and  $\log K_1'$  was calculated.

The agreement with the equilibrium lines of Fig. 6 is fair. It could be improved by selecting a solidus line slightly concave downward, since the location of the final points is rather sensitive to the choice of the solidus. In fact, the uncertainty regarding both solidus and liquidus is such that Darken and Gurry<sup>17</sup> preferred to calculate those lines from activity data.

### Thermodynamic Summary

The experimental data and the thermodynamic implications of the above treatment regarding the reactions of CO—CO<sub>2</sub> mixtures with carbon in solution or as graphite and the various solution and

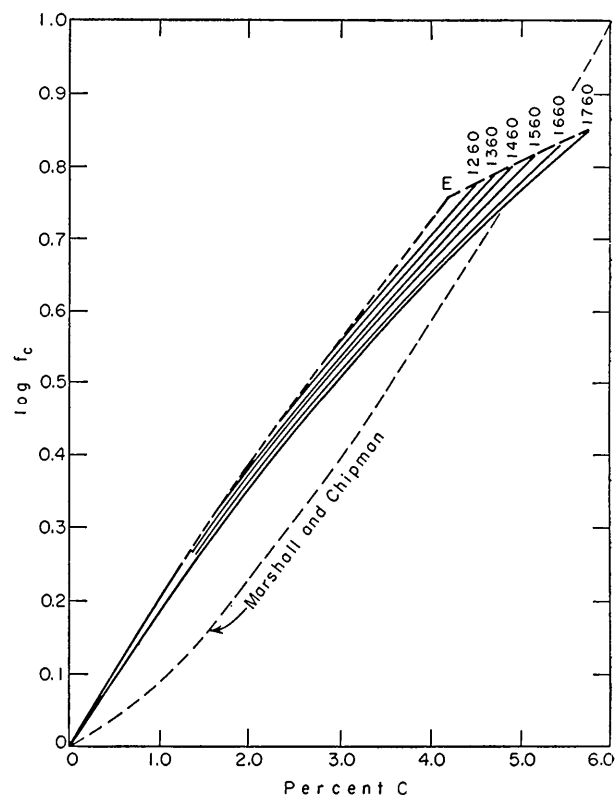
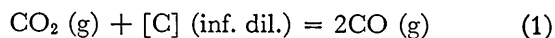


Fig. 8. Activity coefficient of carbon in liquid iron (weight-percentage basis). Broken line based on data of Marshall and Chipman.<sup>20</sup>



dilution processes for liquid iron-carbon alloys are summarized\* in the following statements and equations. In particular, expressions are given for the activity of carbon with respect to both graphite and the infinitely dilute solution as standard states. The free-energy equations are well established because they follow directly from the experimental data. The heat terms in equations 4 to 7 that follow should not be considered as accurate since they are very sensitive to small errors in the temperature coefficients of free-energy terms.



$$\Delta F_1^\circ = 33,300 - 36.5T$$

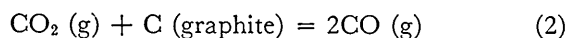
$$\log K_1 = \frac{-7280}{T} + 7.98$$

The standard state is defined by  $a_{\text{C}}/N_{\text{C}} = 1$  when  $N_{\text{C}} = 0$ . The enthalpy term,  $\Delta H_1^\circ = +33,300$  cal is an average for the experimental range and is assumed to be independent of  $T$ .

When it is desired to express carbon concentration in weight per cent, making  $a_{\text{C}}/[\% \text{C}] = 1$  when  $[\% \text{C}] = 0$ , the equation becomes

$$\Delta F_{1a}^\circ = 33,300 - 30.40T$$

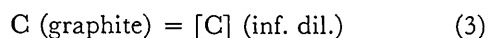
$$\log K_{1a} = \frac{-7280}{T} + 6.65$$



$$\Delta F_2^\circ = 38,700 - 40.5T$$

$$\log K_2 = \frac{-8460}{T} + 8.85$$

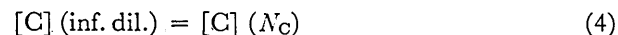
The enthalpy term is an average between 39,700 cal at 1150° C and 37,900 cal at 2030° C, based on National Bureau of Standards' data.



$$\Delta F_3^\circ = 5400 - 4.00T$$

$$\log K_3 = \frac{-1180}{T} + 0.87$$

The enthalpy term  $\Delta H_3^\circ = 5400$  cal is the heat of solution of graphite in the infinitely dilute solution.



$$\Delta F_4 = RT \ln N_{\text{C}} + \Delta F_4^\circ$$

$$\Delta F_4^\circ = +19,900[1 + 4 \times 10^{-4}(T - 1770)]$$

$$(1 - N_{\text{Fe}}^2)$$

$$\Delta H_4 = \bar{H}_{\text{C}} - \bar{H}_{\text{C}}^\circ (\text{inf. dil.}) = 5810(1 - N_{\text{Fe}}^2)$$

The excess partial molar free energy of carbon  $\Delta F_4^\circ$  and its relative partial molar enthalpy  $\Delta H_4$  are obtained directly from the equation for activity coefficient:

\* See Ref. 26.

$$\log \gamma_{\text{C}} = \frac{4350}{T} [1 + 4 \times 10^{-4}(T - 1770)](1 - N_{\text{Fe}}^2)$$



$$\Delta F_5 = \bar{F}_{\text{C}} - F_{\text{C}}^\circ (\text{graphite}) = \Delta F_4 + \Delta F_3^\circ$$

$$\Delta H_5 = \bar{H}_{\text{C}} - H_{\text{C}}^\circ (\text{graphite})$$

$$= 5400 + 5810(1 - N_{\text{Fe}}^2)$$

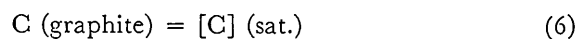
These equations give the free-energy and enthalpy change for dissolving graphite in a solution of mole fractions  $N_{\text{C}}$  and  $N_{\text{Fe}}$ . The activity of carbon in the graphite-saturated solution follows from 3:

$$\log a_{\text{C}} (\text{sat.}) = \frac{-1180}{T} + 0.87$$

If  $a_{\text{C}}'$  and  $\gamma_{\text{C}}'$  are the activity and activity coefficient referred to graphite as the standard state, then  $a_{\text{C}}' (\text{sat.}) = 1$  and

$$\log a_{\text{C}}' = \log N_{\text{C}} + \log \gamma_{\text{C}}'$$

$$\log \gamma_{\text{C}}' = \log \gamma_{\text{C}} + \frac{1180}{T} - 0.87$$



$$\Delta F_6 = 0$$

$$\Delta H_6 = \bar{H}_{\text{C}} (\text{sat.}) - H^\circ (\text{graphite})$$

$$= 5400 + 5810[1 - N_{\text{Fe}}^2 (\text{sat.})]$$

For a mean temperature of 1500° corresponding to  $N_{\text{C}} (\text{sat.}) = 0.2$ , the heat of solution of graphite is 7500 cal.



$$\Delta F_7 = RT \ln \frac{a_2}{a_1}$$

$$\Delta H_7 = 5810(N_{\text{Fe}1}^2 - N_{\text{Fe}2}^2)$$

The last is a general expression for the heat of dilution.

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## Discussion

DARKEN pointed out that in his laboratory they had made similar calculations several years ago. They concluded that the eutectic point provided the most reliable source of information. The activities at point E of Fig. 7 could be calculated from the thermodynamic properties of iron, the temperature and composition of the eutectic, and the assumption that the activity coefficients approach unity at high temperatures.

CHIPMAN said that their calculations did not include the thermodynamic functions of iron, but that  $\log K_1'$  at the eutectic was calculated from the graphite-gas equilibrium and the eutectic composition. The result was reasonably close to Darken's previous calculation. The discrepancy may be due in part to the values taken for

the eutectic composition. Darken used 4.24%, while Chipman and Rist used 4.27%.<sup>19</sup>

RICHARDSON discussed briefly some of the experimental difficulties inherent in a system where heating is by induction and a cold gas impinges on the surface of the melt. These conditions could be expected to have an influence on the constant  $K_1'$  and on the temperature measurement. CHIPMAN and RICHARDSON agreed that the general effect would tend to lead to too-low results, as shown in the experimental points on the right side of Fig. 4.

WAGNER brought out the fact that in a gas like  $\text{CO}_2$  there are several degrees of freedom. Equilibrium involving the vibrational energy is probably not readily attained. Therefore, it seems likely that  $\text{CO}_2$  is not in equilibrium with the melt, and on Richardson's question, he surmised that this effect would tend to shift  $K_1'$  as shown in Fig. 4.

PEARSON described a program of research being conducted in the Chemical Laboratories of B.I.S.R.A. in London. Initially the interest was in measuring the activity of carbon in iron-carbon alloys, but in reviewing the picture, it was decided that although the  $\text{CO}/\text{CO}_2$  ratio in equilibrium with liquid iron did not give trouble at low carbon levels, it would in the high carbon ranges. As a result, the  $\text{H}_2/\text{CH}_4$  reaction was tried. A mixture of hydrogen and methane was circulated over a liquid iron-carbon alloy contained in a lime crucible. The gas was recirculated continuously and was analyzed in an infrared gas analyzer. Equilibrium was established in approximately two hours. It was run for another two hours to be sure. Subsequently, the methane-hydrogen gas was replaced with argon, the sample was quenched, and analyzed for carbon. The general accuracy of the method was checked by using iron contained in graphite crucibles. Their results checked with the existing data on methane. A quick calculation from data sent recently from England showed that the results agreed reasonably well with Fig. 7. Up to 0.16 atom fraction of carbon, the agreement is good. At  $N_C = 0.18$ , they begin to drop a little bit below the line given.

MORRIS inquired whether the presence of the water-cooled Vycor tube influenced the temperature measurement by changing the emissivity of the iron surface. CHIPMAN said that it did not, as the emissivity values are for cold surroundings.