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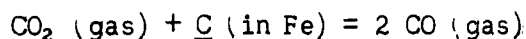
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ACTIVITY OF CARBON IN LIQUID IRON-CARBON SOLUTIONS

by André Rist and John Chipman

ABSTRACT

Experimental data are presented for the equilibrium



at 1360°, 1460°, and 1560°. Deposition of carbon on furnace parts limits accurate measurement to low carbon concentration. A water-cooled gas inlet led to errors of thermal diffusion and incomplete equilibrium but placed a lower limit on the equilibrium constant at 1360° up to four percent carbon. The data are in agreement with those of Richardson and Dennis, and these, together with other relevant data, are used to obtain the thermodynamic properties of the liquid solution at all compositions and at temperatures up to 1760° C.

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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 molecules such as Fe_3C ? Precarious phase diagram and thermal data could not help to settle the issue¹. 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 carbon², 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 CO-CO_2 mixtures, defining fixed carbon and oxygen potentials, was used by a number of workers^{3,4,5,5,6} 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 Kalling⁶ did compute an activity coefficient for Henry's law from their data which ranged below 0.1 percent 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 Chipman⁷ reached carbon contents as high as

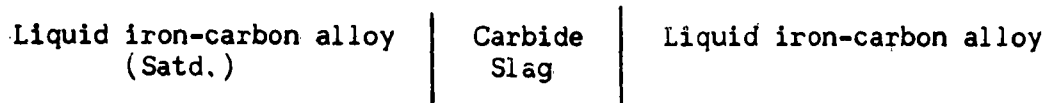
* Based on a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Science at MIT. Dr. Rist is now with the Institut de Recherches de la Sidérurgie, St. Germain-en-Laye, France.

2.0 percent by operating under pressure. They found that the activity coefficient of carbon may be regarded as constant up to one percent and increases thereafter. Later work was not to confirm this view.

In 1953, Richardson and Dennis⁸ 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 percent were equilibrated with controlled CO-CO₂ 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 Gavrilov⁹ and Sanbongi and Ohtani¹⁰. These authors built electrochemical cells of the type:



and measured their electromotive forces at various concentrations of the alloy on the right hand side. However, lack of knowledge of the ionic processes involved forced the authors to calibrate the electromotive force-activity relationship on previous gas-metal equilibrium studies. Their work cannot, therefore, be considered as independent.

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 $\underline{\text{C}}$ 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_{C} is the activity of carbon in solution.

Temperature and the "gas-ratio" $\frac{(p_{\text{CO}})^2}{p_{\text{CO}_2}}$ 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 control 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 CO_2 , CO , and argon were used, argon being added in order to benefit by the effects of an increased total flowrate. The sketch of Figure 1 shows clearly the three gas lines.

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

The flowrates of the component gases were controlled by adjusting the pressure drops across capillary flowmeters. Through most of the experiments the flowrates of CO and argon were kept constant and each equal to about 300 ml/min. while the flowrate of CO_2 was varied to obtain the required gas ratios. The entire range of gas ratios (100 to 4300) was covered with CO_2 flowrates ranging roughly from 2 to 0.03 ml/min.

Gas Analysis

The apparatus was equipped with facilities for the gravimetric analysis of CO_2 by absorption on ascarite and of CO by conversion to CO_2 in a cupric oxide furnace followed by absorption on ascarite. Analysis was used to establish or check the calibration of the capillary flowmeters. In the case of argon, a volumetric method was used.

The analysis of CO_2 required special care in view of the small quantities involved. Over four hours were necessary to collect about 15 mg. at the lowest flowrate. Two ascarite bulbs were put in series, the first

one being capable of absorbing over 99 percent of the incoming CO_2 . 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 induction. The furnace, as first designed and mounted, is shown in Figure 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 leave and thereby 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 watercooled all the way down to its mouth above the melt (see Figure 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 work¹¹ 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.

Burning Procedure

For each run a temperature and a gas ratio were selected. A 30 g. 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 minutes of heating.

The heat was held at temperature for times which varied between a few minutes in recovery runs and a maximum of 31 hours (see Tables I and II). Temperature was controlled manually through the power output of the high frequency converter unit. Fluctuations in temperature were normally less than ± 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 percent 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 ± 0.01 percent 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° C and 1460° C with gas ratios up to 1150. The data are recorded in Table I and plotted in Figure 4. In the fifth column of Table I, the "initial % C" of a heat was calculated after recovery runs showing that over 99 percent of the carbon charged was recovered. In the seventh column, Δ % C is the difference between final and initial percent C. The ranges of temperatures and gas ratios which could be investigated were limited by the occurrence of carbon deposition which is discussed below. Justification for quoting heats 81, 82, and 83 is also given below.

Series B. The heats were made with the Vycor watercooled 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 below. They are reported, however, in Table II since they suggest some interesting comments. For the sake of clarity, only the 1360° C heats are shown in Figure 4.

TABLE I. Experimental Results, Series A

<u>Heat No.</u>	<u>Temperature ° C</u>	<u>Gas Ratio</u>	<u>Time Hrs.</u>	<u>% C Initial</u>	<u>% C Final</u>	<u>Δ % C</u>	<u>log K'</u>
53	1560	104	4.0	0.16	0.19	+ 0.03	2.750
53	"	103	6.8	0.31	0.20	- 0.11	2.710
54	"	102	3.0	0.20	0.19	- 0.01	2.725
58	"	336	4.0	0.55	0.57	+ 0.02	2.770
59	"	325	6.0	0.64	0.62	- 0.02	2.720
61	"	325	6.0	0.59	0.56	- 0.03	2.765
72	"	1045	6.0	1.12	1.14	+ 0.02	2.965
68	"	1030	5.0	1.17	1.17	0.00	2.945
63	"	990	6.0	1.18	1.19	+ 0.01	2.920
66	"	1030	5.25	1.29	1.27	- 0.02	2.910
65	"	1035	6.0	1.23	1.22	- 0.01	2.930
75	"	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	"	3705	6.0	3.78	3.81	+ 0.03	2.995
83	"	4290	6.0	4.37	4.38	+ 0.01	2.990

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

TABLE II. Experimental Results, Series B

<u>Heat No.</u>	<u>Temperature ° C</u>	<u>Gas Ratio</u>	<u>Time Hrs.</u>	<u>% C Initial</u>	<u>% C Final</u>	<u>Δ % C</u>	<u>log K'</u>
195	1360	1160	9.0	2.98	2.98	0.00	2.590
194	"	1165	10.0	3.48	3.48	0.00	2.525
196	"	1160	10.3	3.88	3.86	- 0.02	2.480
201*	"	1700	30.25	3.48	3.48	0.00	2.690
188	"	1820	10.5	3.73	3.75	+ 0.02	2.685
204	"	1840	31	4.08	4.05	- 0.03	2.660
187	"	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	"	1475	10.5	4.07	4.08	+ 0.01	2.560
182	"	1810	10.0	4.07	4.08	+ 0.01	2.645

* In heat 201 helium was substituted for argon

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

The coordinates selected to plot the data on Figure 4 are percent C as abscissa and $\log K_1' = \frac{(p_{CO})^2}{p_{CO_2} \cdot \% C}$ 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 percent at infinite dilution. The plot yields readily:

the logarithm of the equilibrium constant, $\log K_1(T)$, by extrapolation to zero percent carbon of the isotherm T;

the logarithm of the activity coefficient, $\log f_C$ (where $f_C = a_C / \% C$), at any concentration by reading off the plot $\log f_C = \log K_1'(T) - \log K_1(T)$.

Similar plots will be presented where the mole fraction N_C is used as a unit of concentration.

The full lines on Figure 4 have been drawn according to the treatment given below. At 1360 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 $2 CO \rightarrow CO_2 + C$ (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, or

(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 Figure 5).

Condensed 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) only appeared 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 due to 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 towards the hot surface. Other workers in gas-metal equilibrium studies^{12,13} 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 $\frac{(p_{CO})^2}{p_{CO_2}}$. Comparison with the experiments of Dastur and

Chipman¹² on thermal diffusion in $H_2 - H_2O$ mixtures under very similar conditions bears out the fact that, in series A, the error on $\log K'$ ($\Delta \log K'$) 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 equation¹⁴, when tested on the available data¹⁵, is found to exaggerate the thermal separation of CO and CO_2 . If applied to the maximum temperature gradient found here, it gives:

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

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_2) and the extrapolation to saturation of series B data at 1360° C (see Figure 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 point to 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.

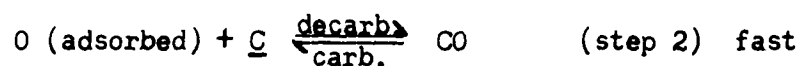
Lack of Thermal Equilibrium

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

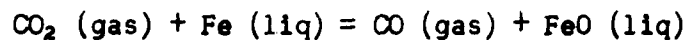
contain "cold" molecules (i.e., the average stored energy is less than the average at thermal equilibrium). Fewer molecules will reach the activated state required for them to react, and reaction rates will be slower. Chemical equilibrium, which is a balance between the rates of two opposite reactions, 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 Doehlemann¹⁶ for carburization and decarburization of austenite is applied to liquid iron:



Step 1 is rate controlling. The difference between the heats of activation for the forward and the backward reactions is equal to $\Delta H_{(1)}$, the heat of reaction (1), a low estimate of which may be obtained by the standard heat of the reaction:



$$\Delta H_3^\circ = 7500 \text{ cal.}$$

One may, therefore, write:

$$\Delta H_1^* \text{ forward} > \Delta H_1^* \text{ backward} + 7500 \text{ cal.}$$

Assuming the reactants to 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 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 which 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 merely be interpreted 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 Figure 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.

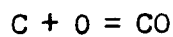
In series A, errors on $\log K'$ due to carbon analysis, inlet gas ratio (impurities, flow measurement), and temperature simultaneously were such that:

$$\Delta \log K' \leq 0.033$$

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 percent carbon. Consistency was, however, obtained when they were trusted as low as 0.005 percent.

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 Chipman⁷, was always lower than 0.01 weight percent. Aluminum was controlled through the reaction of the melt with the crucible. Aluminum was analyzed and found to be always less than 0.01 percent in the range of the data presented here. It increased fast with temperature (0.11 at 1760° C in a 1.2 percent carbon melt), and the evidence that the reaction reached equilibrium was spectacular at 1760, 1660, or even 1560 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 in good agreement with those of Richardson and Dennis 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 CO₂. Successful experimental work is still needed between two percent 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 the experimental points of Richardson and Dennis and of the authors have been plotted in Figure 6. The choice of $(1 - N_{Fe}^2)$ as abscissa permits a linear extrapolation of the 1560° 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 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:

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

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 Gurry¹⁷. These authors assume the relationship:

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

where A is a constant. Hence:

$$\frac{\partial \log K_1}{\partial (1 - N_{Fe}^2)} = \frac{\partial \log \gamma}{\partial (1 - N_{Fe}^2)} = - \frac{A}{T}$$

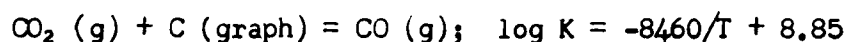
All slopes may, therefore, be calculated from the 1560° C isotherm, the value of A being $A = -4450$. A tentative general expression for the activity coefficient is therefore:

$$\log \gamma = \frac{4450}{T} (1 - N_{Fe}^2) \quad (\text{tentative})$$

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

$$\log K_1 = -7280/T + 7.98$$

These equations reproduce the data of Richardson and Dennis and of the authors at carbon concentrations below two percent. The expression for the activity coefficient, however, is not valid at high carbon concentrations at temperatures other than 1560, 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 data¹⁸ and may be represented by the equation:



The solubility of graphite according to Chipman and coworkers¹⁹ is:

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

From these equations, values of K_1 were calculated and are shown along the line of saturation in Figure 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 $\log \mathcal{J}$ is written:

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

The lines of Figure 6 are drawn to conform to this equation, and values of $\log \mathcal{J}_C$ are shown in Figure 7. Figure 8 is a translation of Figure 7 on the weight percent basis, and the line earlier proposed by Chipman²⁰ is shown on the same graph.

Comparison with Data on Austenite.

The data of R. P. Smith²¹ on the equilibrium of carbon in austenite with CO-CO₂ 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 Figure 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° C¹⁷ and 4.27 percent carbon¹⁹ and the peritectic at 1499° C and 0.53 percent carbon¹⁷. The experimental points of several investigators^{22,23,24,25} when corrected to fit the above end points define the liquidus used here. The agreement with the line proposed by Darken and Gurry¹⁷ is very close. The end points of the solidus are taken at 1499° C, 0.16 percent carbon, and at 1153° C, 2.01 percent. Short of any justified choice among the widely scattered experimental determinations of the solidus, a straight line was drawn between the two end points.

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

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

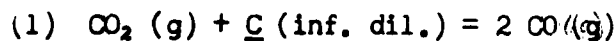
and spaced on the assumption that the heat of transfer of carbon from gas to metal is independent of temperature.

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 Figure 6 is fair. It could be improved by selecting a solidus line slightly concave downwards 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 Gurry¹⁷ 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 - CO₂ mixtures with carbon in solution or as graphite and the various solution and 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) should not be considered as accurate since they are very sensitive to small errors in the temperature coefficients of free energy terms.



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

$$\log K_1 = -7280/T + 7.98$$

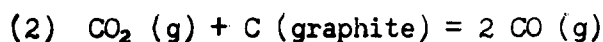
The standard state is defined by $a_C/N_C = 1$ when $N_C = 0$. The enthalpy term, $\Delta H_1 = +33,300$ cal. is an average for the experimental range and is assumed

independent of T.

(1a) When it is desired to express carbon concentration in weight percent, making $a_C / [\% C] = 1$ when $[\% C] = 0$, the equation becomes

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

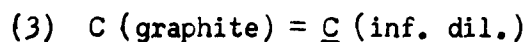
$$\log K_{1a} = -7280/T + 6.65$$



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

$$\log K_2 = -8460/T + 8.85$$

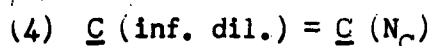
The enthalpy term is an average between 39,700 cal. at 1150° C and 37,900 cal. at 2030°, based on N. B. S. data.



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

$$\log K_3 = -1180/T + 0.87$$

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



$$\Delta F_4 = RT \ln N_C + \Delta F_4^x$$

$$\Delta F_4^x = +19,900 [1 + 4 \times 10^{-4} (T - 1770)] (1 - N_{\text{Fe}}^2)$$

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

The excess partial molar free energy of carbon ΔF_4^x and its relative partial molar enthalpy ΔH_4 are obtained directly from the equation for activity coefficient:

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



$$\Delta F_5 = \bar{F}_C - F_C^{\circ} (\text{graph}) = \Delta F_4 - \Delta F_3$$

$$\Delta H_5 = \bar{H}_C - H_C^{\circ} (\text{graph})$$

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

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

$$\log a_C (\text{sat.}) = -1180/T + 0.87$$

If a_C^* and γ_C^* are the activity and activity coefficient referred to graphite as the standard state, then $a_C^* (\text{sat.}) = 1$ and

$$\log a_C^* = \log N_C + \log \gamma_C^*$$

$$\log \gamma_C^* = \log \gamma_C - 1180/T + 0.87$$

$$(6) \quad C (\text{graph}) = \underline{C} (\text{sat.})$$

$$\Delta F_6 = 0$$

$$\Delta H_6 = \bar{H}_C (\text{sat.}) - H^\circ (\text{graph})$$

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

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

$$(7) \quad C (N_{C_1}) = C (N_{C_2})$$

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

$$\Delta H = 5810 (N_{Fe_1}^2 - N_{Fe_2}^2)$$

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

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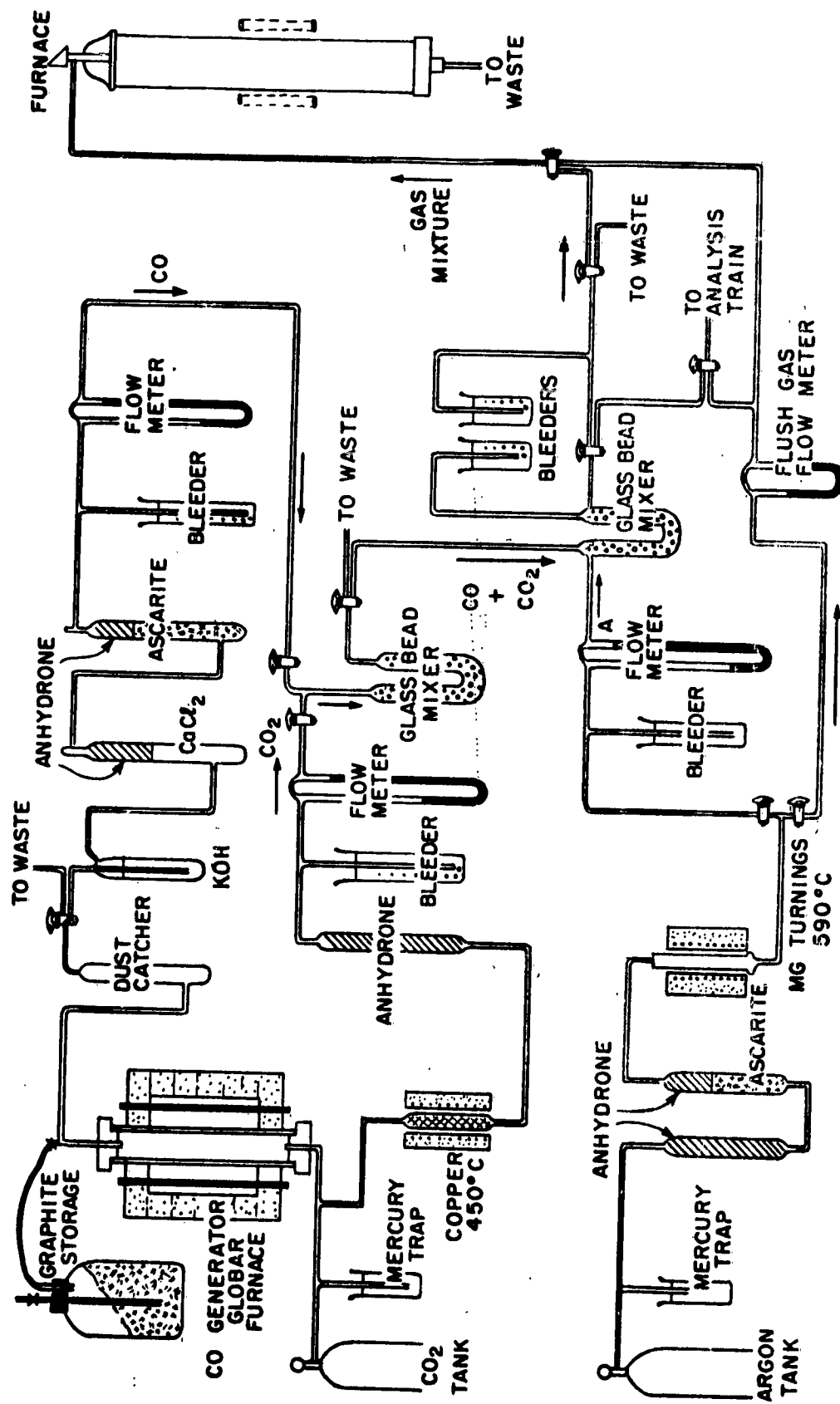
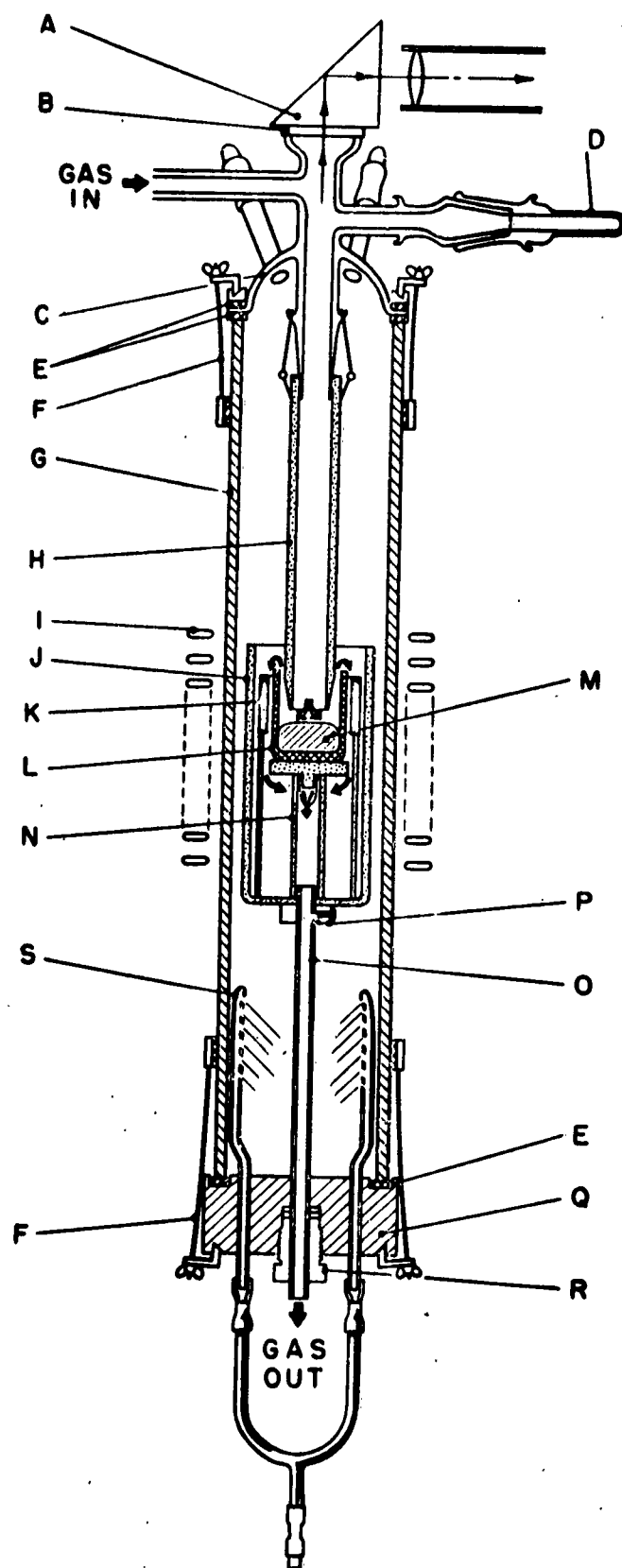


FIG. 1 - DIAGRAM OF GAS SYSTEM



- A - PRISM
- B - SIGHT GLASS
- C - PYREX HEAD
- D - EXTENSION HOUSING PUSHER
- E - GASKETS (SILICONE RUBBER)
- F - CLAMPING DEVICE
- G - GLAZED SILICA TUBE
(24 IN. LONG, 2.5 IN. O.D.)
- H - ALUNDUM INLET TUBE
- I - INDUCTION COIL
(29 TURNS)
- J - RADIATION SHIELD
(ALUNDUM)
- K - GRAPHITE SUSCEPTOR
- L - ALUMINA CRUCIBLE
- M - LIQUID METAL
- N - CRUCIBLE STAND
(ALUNDUM)
- O - STAINLESS STEEL TUBE
- P - SUPPORTING COLLAR
- Q - BRASS BOTTOM
- R - LOCKING NUT
- S - QUENCHING TUBE
(NOT USED IN STANDARD
PROCEDURE)

FIGURE 2 - FURNACE ARRANGEMENT

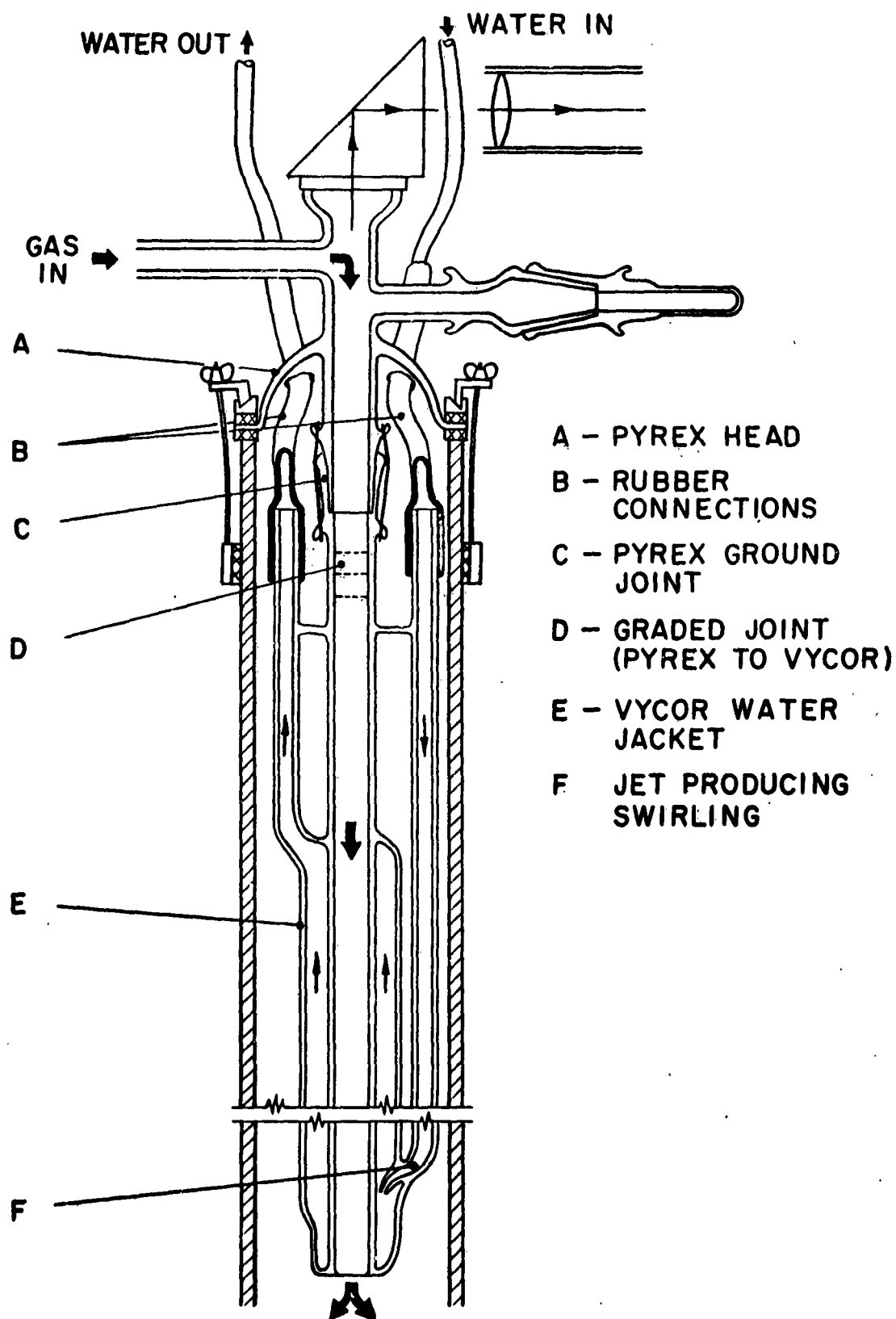


FIG. 3 — FURNACE HEAD MOUNTED WITH WATERCOOLED VYCOR TUBE.

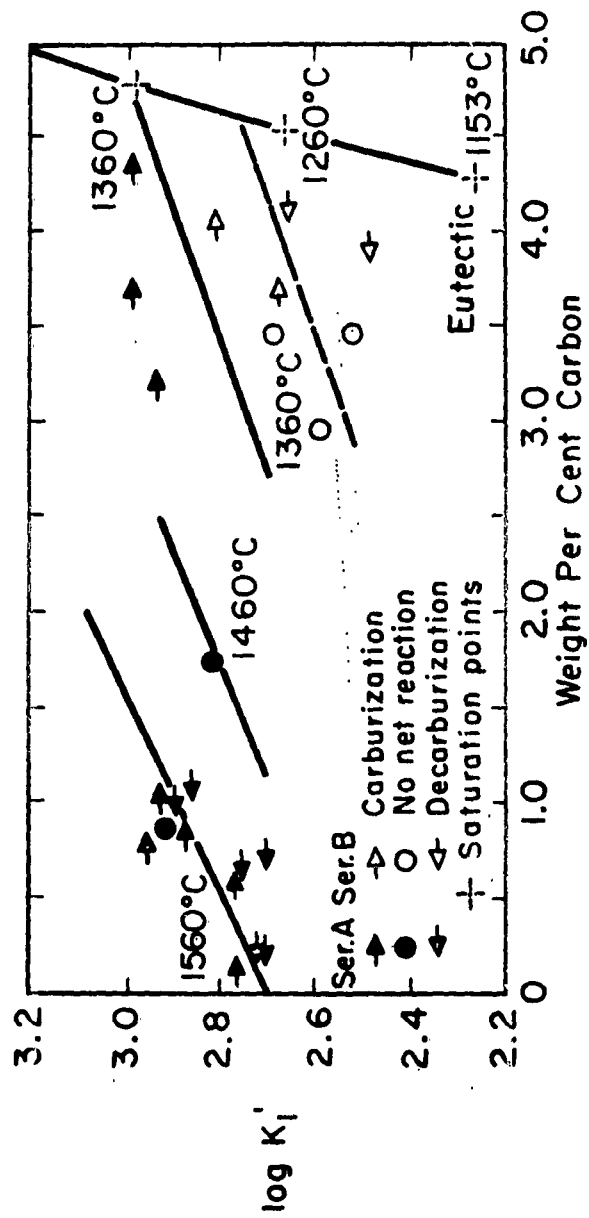


FIG. 4. Experimental data; $K' = p_{CO}^2 / (p_{CO_2} \cdot \% C)$. The solid lines represent equilibrium; broken line at 1360° represents Series B, known to be subject to errors of thermal diffusion and incomplete equilibrium.

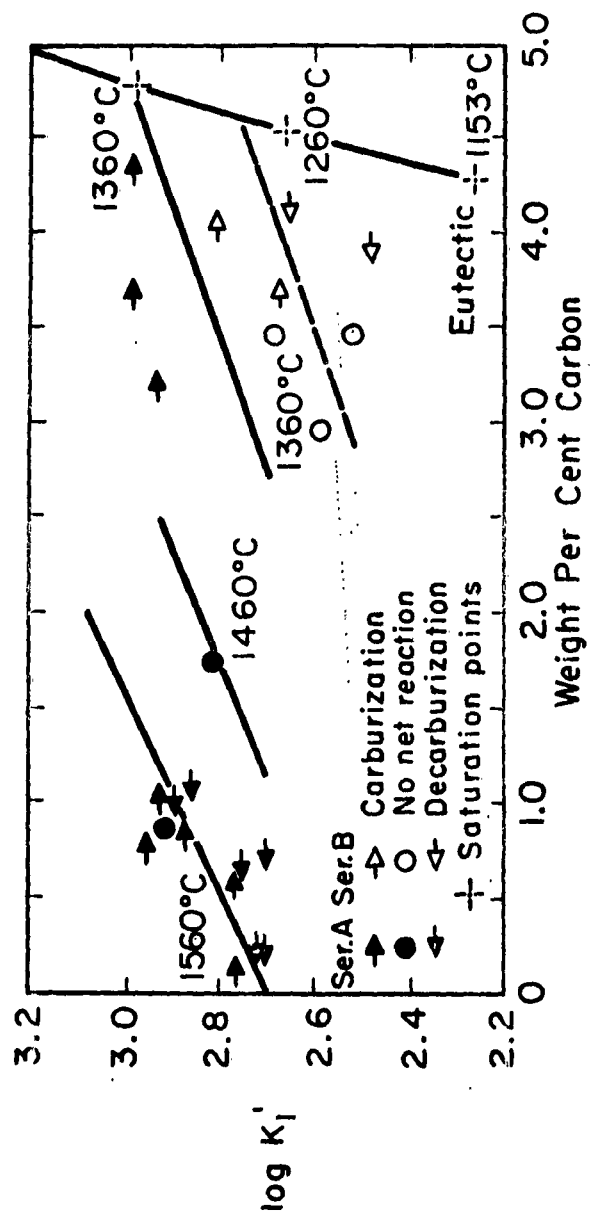


FIG. 4. Experimental data; $K' = p_{CO}^2 / (p_{CO_2} \cdot \% C)$. The solid lines represent equilibrium; broken line at 1360° represents Series B, known to be subject to errors of thermal diffusion and incomplete equilibrium.

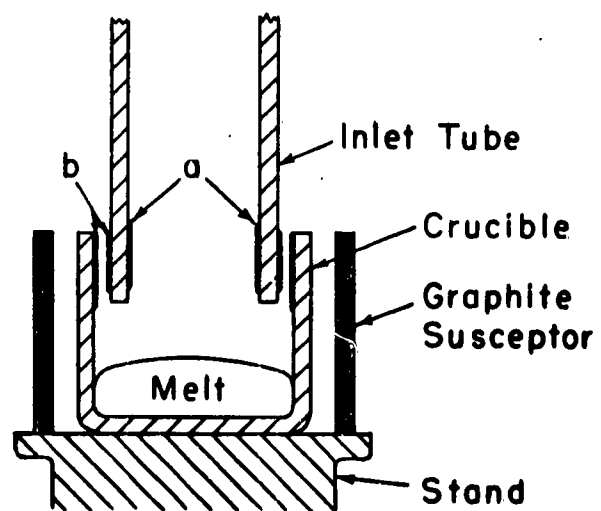


FIG. 5. Most harmful locations for carbon deposition.

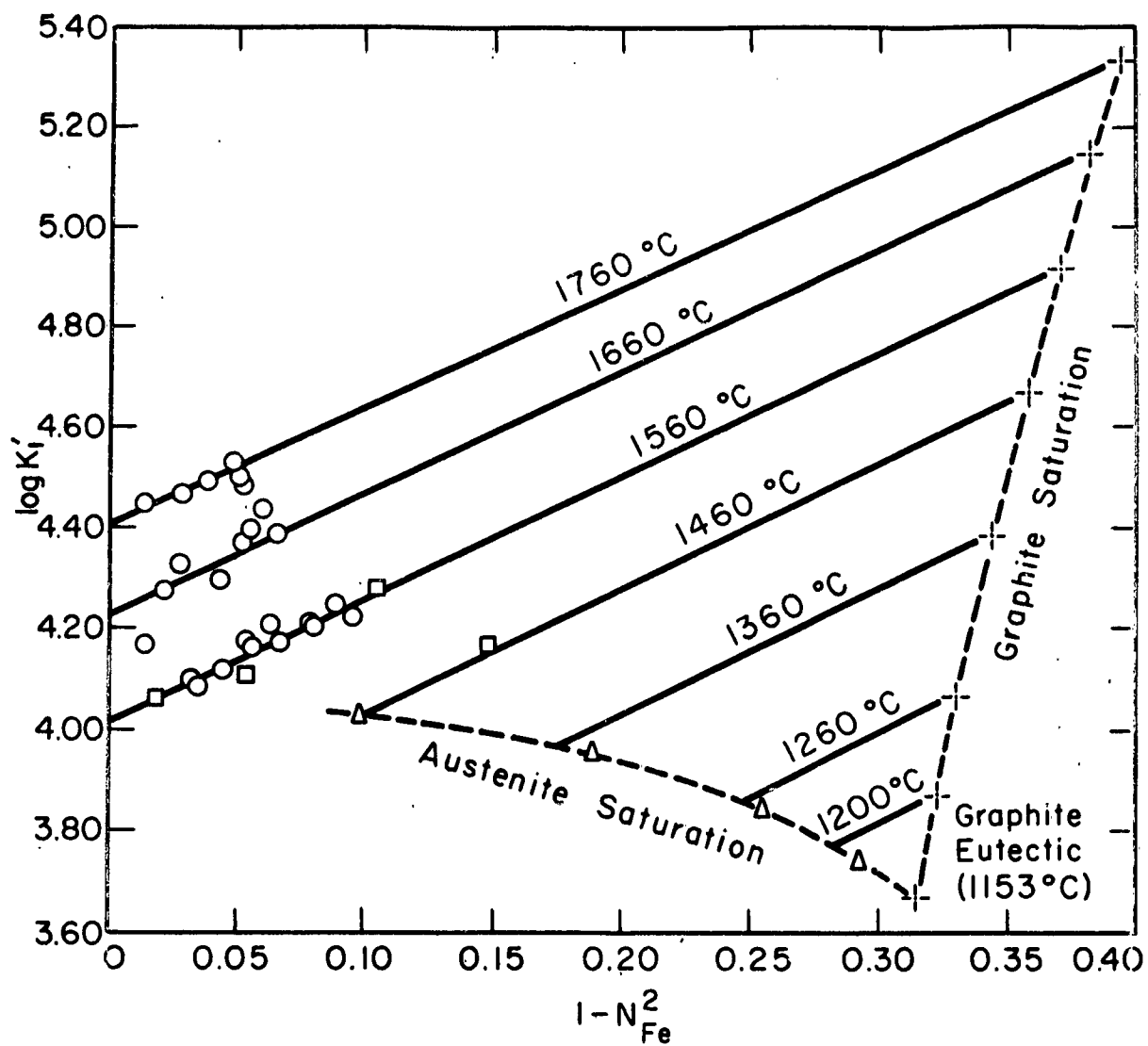


FIG. 6. Equilibrium of carbon with CO-CO₂ mixtures. $K' = p_{CO}^2 / (p_{CO_2} \cdot H_C)$

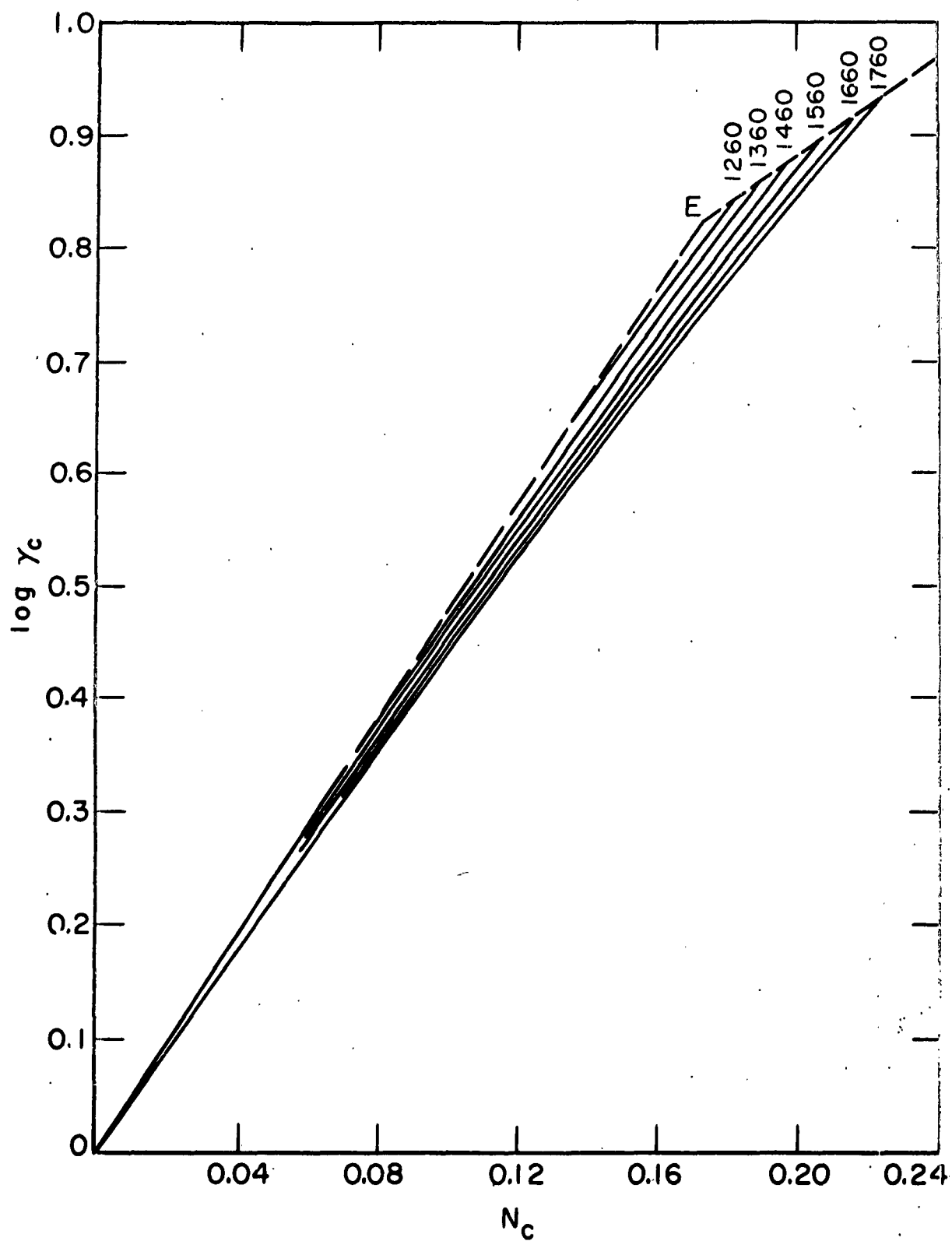


FIG. 7. Activity coefficient of carbon in liquid iron (mole fraction basis).

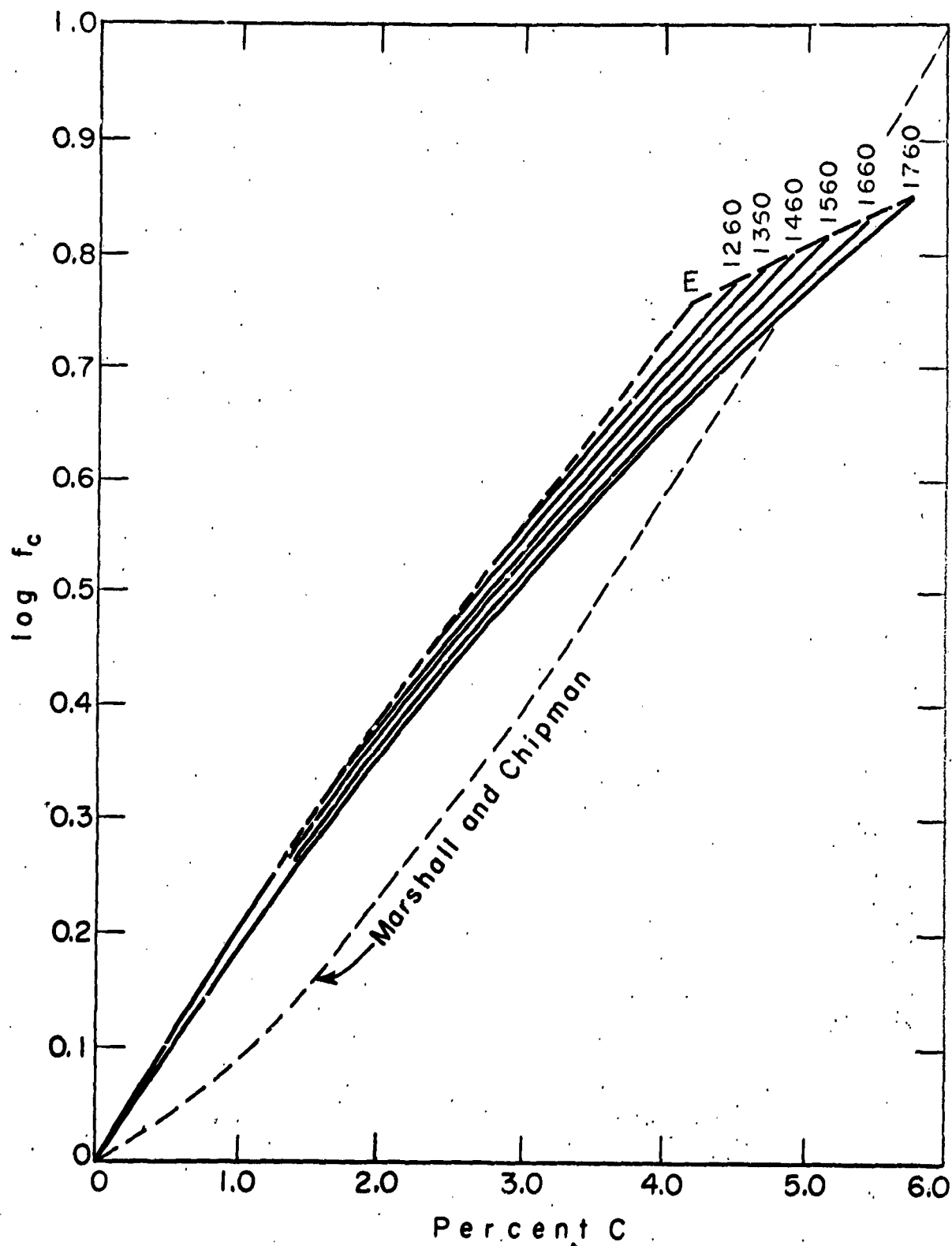


FIG. 8. Activity coefficient of carbon in liquid iron (weight percent basis). Broken line based on data of Marshall and Chipman²⁰.

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May 17, 1956

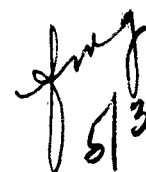
Gentlemen:

Attached is a copy of a paper on "Activity of Carbon in Liquid Iron-Carbon Solutions" by André Rist and John Chipman. This research was supported in part by ONR Contract No. N5ori-07816 (XVI).

Very truly yours


John Chipman

Enclosure

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