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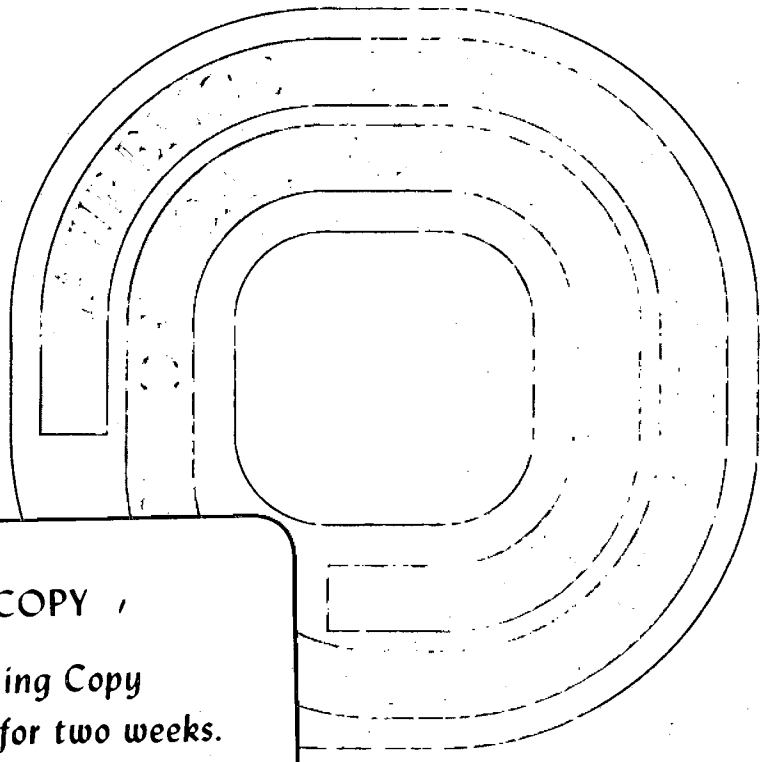

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ABSTRACT

A critical review of published data provides a fairly accurate knowledge of the thermodynamic properties of all of the phases of the system Fe-C that are stable or metastable at atmospheric pressure. Selected data are shown as tables and equations. A proposed phase diagram differs only slightly from others recently published but has the following features. Peritectic compositions and the α-γ equilibrium are shown to agree with measured values of the activity of Fe in the solid and liquid solutions and the thermodynamic properties of pure Fe. Of all the reported carbides of iron only two may be studied under equilibrium conditions. The solubilities of cementite and of χ-carbide in α-Fe are deduced from measured equilibria. Both are metastable at all temperatures with respect to graphite and its saturated solution in iron. The χ-carbide becomes more stable than cementite below about 230°C. Certain published data on ε-carbide permit an estimate of its free energy as a precipitate during the aging process.

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THERMODYNAMICS AND PHASE DIAGRAM OF THE IRON-CARBON SYSTEM

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I. INTRODUCTION

Probably everyone who attempts to do precise experimental measurements on binary alloys of iron and carbon feels tempted to try his hand at revising the iron-carbon diagram. Now that I have been asked to prepare a diagram for the Metals Handbook of the American Society for Metals. I am no longer able to resist this temptation. Actually the diagram of Hansen and Anderko[1] is very good and the amount of revision required is quite minimal. The same can be said of the more recent diagram of Elliott, Gleiser and Ramakrishna[2]. The latter had the advantage of the very accurate determination of the γ-solidus by Benz and Elliott[3] but omitted the nearly simultaneous publication of data on the liquidus by Buckley and Hume-Rothery[4]. In their somewhat older diagram Darken and Gurry[5] saw to it that the boundary lines were consistent with measured properties of the phases involved and with the laws of thermodynamics. This procedure can be recommended to anyone who sets out to construct a phase diagram. The thermodynamic properties of the individual components and in particular their partial molar properties within the homogeneous phases provide a more complete picture of the system than does the phase diagram alone. It is intended that this paper serve as a review and evaluation of this kind of data with a view to revision of the compilation of Hultgren, Orr, Anderson,

and Kelley[6].

The possibilities for meaningful revision rest on several more recent publications. Scheil, Schmidt and Wünning[7] determined the thermodynamic properties of Fe-C austenites and cementite using the $CO-CO_2$ equilibrium. A similar study of austenite by Ban-ya, Elliott and Chipman[8] extended the temperature range and derived simple mathematical statements for the thermodynamic properties of the components. Former discrepancies regarding solubilities of graphite and cementite in the α-phase have apparently been greatly reduced by the recent work of Swartz[9].

Of equal importance has been the recent marked improvement in the data on the properties of pure iron. The heat of fusion of iron has been lowered some 10 percent by recent studies of Ferrier and Olette[10] and of Morris, Foerster, Schultz and Zellars[11]. The heat capacity of the solid, particularly in the γ-range has been revised by the work of Olette and Ferrier[12], Anderson and Hultgren[13], Dench and Kubaschewski[14], Braun[15], and of Wallace, Sidles and Danielson[16]. All of these studies of the thermal properties of iron have been reviewed by Orr and Chipman[17] who derived precise values for the differences in Gibbs free energy between the several stable or metastable phases.

In addition it must be pointed out that revision is required by the adoption of the new International Practical Temperature Scale of 1968[18] according to which a secondary reference, the melting point of palladium has been raised from 1552° to 1554°C. On this scale the melting point of

iron becomes 1538°C while lower fixed points require smaller or negligible adjustment. Since practically all useful data are given on the 1948 scale, this scale will be used in some calculations and adjustments will then be applied to conform to the new scale. To avoid ambiguity, temperatures will be designated (48) or (68). For many purposes the difference is trivial.

II. THE AUSTENITE FIELD

The f.c.c. solid solution is the heart of the binary system and its properties and boundary lines are rather well known. The activity of carbon as a function of temperature and composition has been determined by many observers, chiefly through studies of the equilibria

$$\underline{C} + 2H_2 = CH_4 \qquad [1]$$

$$\underline{C} + CO_2 = 2CO \qquad [2].$$

Among the older investigations of reaction [2] those of Dünwald and Wagner[19] and of Smith[20] are in agreement with the more recent work of Scheil[7] et al. (except at the highest carbon concentrations) and of Ban-ya[8] et al. Studies of reaction [1] have been subject to errors especially at low carbon levels, due to reaction of methane with residual gas impurities. This is thought to have been responsible for the differences observed by Smith[20] between activity coefficients determined by the two equilibria. It may have accounted also for the disagreement between the values accepted here and those of Schenck and Kaiser[21] and of Schürmann, Schmidt, and Wegener[22]. Studies based on reaction [2] have not been immune to similar but generally smaller errors which tend to become greater with increasing temperature and carbon

content.

Ban-ya, Elliott and Chipman[8] covered a wide range of composition and temperature and in their analysis of the data included consideration of the earlier work. They expressed their results in terms of a very simple model in which the activity of an ideal interstitial solute is proportional to the ratio of filled to unfilled interstitial sites. Since there is one interstitial site per lattice atom, the ideal activity at great dilution is

$$a_C \sim n_C/(n_{Fe}-n_C) = y_C/(1-y_C) = z_C \qquad [3]$$

where y_C is the atom ratio n_C/n_{Fe} and the term $y_C/(1-y_C)$ may be abbreviated as z_C. Deviations from the ideal at finite concentrations were represented by an activity coefficient $\psi_C = a_C/z_C$ which was found to be related to the concentration, y_C by the simple equation

$$\ell n\psi_C = \ell n\psi_C^\circ + \theta_C y_C \qquad [4]$$

where ψ_C° is its value at infinite dilution and θ_C is an interaction coefficient, both being functions of temperature.

In their plot of log K versus 1/T they found that a straight line based on data at 900°- 1150°C fell outside the 2 σ limits at 1300°. A slightly curved line was therefore suggested and an equation was devised to fit it. It was known that some dissociation of CO had occurred at the higher temperature and it now appears that they may have been overoptimistic with regard to the accuracy of the 1300° data. For this reason a simpler equation closely approximating line A of reference 8 will be used here for all compositions and temperatures (1968 scale) within the austenite field:

$$\log a_C^{\gamma} = 2300/T - 0.920 + (3860/T)y_C + \log\left(y_C/(1-y_C)\right) \quad [5].$$

The activity of iron, by the Gibbs-Duhem equation is:

$$\log a_{Fe}^{\gamma} = -(1930/T)y^2_C + \log(1-y_C) \quad [6]$$

The solubility of graphite in austenite is readily calculated from equation [5] by setting a_C^{γ} equal to unity. Two other kinds of data are also available: the direct measurements of Wells[23] and of Gurry[24] and a downward extrapolation of the solidus line of Benz and Elliott[3] to the eutectic temperature. All of these data are in rather good agreement and average values are shown in Table I. For convenience the data on solubility of cementite are included but a discussion of these and of the α-γ boundary will be deferred to later sections. Both solubility lines are shown in figure 1.

III. THE GAMMA-LIQUID EQUILIBRIUM

The solidus line of Benz and Elliott[3] and a portion of the liquidus line of Buckley and Hume-Rothery[4] corrected to the 1968 scale are shown in figure 1. The solidus has been given a slight inflexion with downward curvature near its lower end to conform to the data of Ban-ya[8] et al. Both lines are superior in accuracy to those of earlier investigators but are strongly supported by the earlier work of Adcock[25]. The liquidus line includes a dotted extension to the calculated[17] melting point of γ-Fe. Interpolated values are listed in Table II and the entire liquidus line appears in figure 4. The activity of carbon at any temperature is the same at the liquidus and solidus compositions. Values calculated from equation [5] are included in the table.

IV. THE LIQUID PHASE

The activity of carbon in liquid Fe-C alloys has been determined by a number of investigators using several methods. The best accuracy has been achieved by Richardson and Dennis[26] using the equilibrium of Eq. [2]. It is known that serious errors occur at high carbon content and the precision of the data improves as the carbon content and the CO content of the gas decrease. Their experimental temperatures (48) were 1560°, 1660° and 1760°C. For lower temperatures I have used the activity in austenite at points along the solidus (Table II) to determine the activity coefficient in the liquid for compositions along the liquidus. For higher concentrations the solubility of graphite furnishes a secure base where $a_C = 1$. Using these data, and adopting the form of Eq. [4] I have obtained the equation[27]:

$$\log a_C^{\ell} = 1180/T - 0.870 + (0.72 + 3400/T)y_C + \log(y_C/(1-y_C)) \qquad [7].$$

It was shown that this equation agrees fairly well with that of Ban-ya et al.[8] where liquid and solid data could be compared. The agreement with Eq. [5] is distinctly better as shown in Fig. 2 where the points marking the liquidus have been calculated from the activity in the solid. At the peritectic the activity of carbon in the solid by Eq. [5] is 0.0199 while in the liquid by Eq. [7] it is 0.0185. The discrepancy is negligible since it is equivalent to an error of less than 0.01 pct C in the peritectic austenite. Accordingly the activity at the peritectic is taken as 0.019±0.001.

A summary of the activity of carbon in austenite and in liquid iron is given in Fig. 3. The chemical potential of carbon may be read as $\mu_C - \mu_C^o = 4.575T\log a_C$.

Tie lines in the 2-phase field are shown. A line for cementite would be almost indistinguishable on this scale from the graphite line at log $a_C = 0$. It would lie slightly above this line at all temperatures below the eutectic.

The activity of iron in the liquid as found by the Gibbs-Duhem equation is:

$$\log a^{\ell}_{Fe} = -(0.36+1700/T)y_C^2+\log(1-y_C) \qquad [8].$$

It has been shown[27] that this agrees with the data of Syu, Polyakov and Samarin[28] at 1560°.

The solubility of graphite in liquid iron has been measured by many investigators. Up to 1800°C excellent agreement is found among the data of Ruer and Biren[29], Chipman, Alfred, Gott et al.[30], and of Kitchener, Bockris, and Spratt[31]. Data up to 2500° were reported by Ruer and Biren, up to 2875° by Cahill, Kirshenbaum and Grosse[32] and at 2050-2375° by Vertman, Grigorovich, Nedumov and Samarin[33]. Averaged values are shown in Fig. 4; interpolated data together with estimates of probable accuracy are given in Table III. The selected eutectic at 1154°C and 4.26±0.02pct C. has been confirmed by Ruth and Turpin[34] who report 4.28±0.02 and 4.32±0.03 respectively for the Fe-C and Fe-Fe_3C eutectics.

The normal boiling point of iron (68) according to Hultgren, Orr, Anderson, and Kelley[35] is 2870°C. The effect of carbon on the vapor pressure may be calculated on the basis of Eq. [8] for temperatures up to 1800°C. At higher temperatures the solubility of graphite increases more rapidly, resulting in a somewhat lowered activity coefficient. Making allowance for this effect, the boiling points of alloys and temperatues at which the vapor pressure reaches 0.1 and 0.01 atm have been calculated and the results are

shown in Fig. 4.

V. THE δ-PHASE AND PERITECTIC

The melting point of δ-Fe according to Boulanger[35] adjusted to the 1968 scale is 1538°C. The metastable melting point of γ-Fe is found from thermal data[17] to be 1527°. The γ-δ inversion for pure Fe[35] is 1394°. Fig. 1 shows the δ-Fe region with the peritectic at 1495° (68) as recommended by Buckley and Hume-Rothery[4b]. The δ liquidus also depends on these authors. It is shown as a straight line from the melting point to 0.53 pct C at the peritectic. The δ-solidus also is based on results of the above investigators. The compositions of the peritectic are δ, 0.09 pct C; γ, 0.17 pct C; liquid, 0.53 pct C.

That the above peritectic compositions selected from published phase diagrams are in fact in accord with the laws of thermodynamics is shown in the following calculations. It has already been shown that the activity of carbon calculated from data on the liquid agrees well with that calculated from the solid $a_C = 0.019 \pm 0.001$. A more precise check can be obtained by consideration of the activity of iron in the several phases. In the liquid phase this is found from Eq.[8] which gives $\log a^{\ell}_{Fe} = -0.0117$. The activity in the γ-Fe phase must be the same at equilibrium. From Eq.[6] it is found that at 0.17 pct C $\log a^{\gamma}_{Fe} = -0.0035$ where pure γ-Fe is the standard state. To compare these two values of $\log a_{Fe}$ both must be referred to the same standard state. The difference in standard free energy between liquid and γ-Fe from the tables of Orr and Chipman[17] is $\Delta G^{\circ}_{1766} = 67$ cal which corresponds to a difference $\Delta \log a^{\gamma-\ell}_{Fe}$ of 0.0083. This, added to the value of

log a^{γ}_{Fe} gives -0.0118 in agreement with the value found for log a^{ℓ}_{Fe}.

A similar calculation may be made for δ-Fe which differs from γ-Fe in standard free energy by only 13 or 14 cal. This corresponds to $\Delta \log a^{\gamma-\delta}_{Fe} = 0.0016$ or 0.0017. Adding this to the value $\log a^{\gamma}_{Fe} = -0.0035$ we find $\log a^{\delta}_{Fe} = -0.0019$ to -0.0018. The activity coefficients in δ-Fe are unknown and theoretically the activity of carbon is proportional to $n_C/(n_{Fe}-n_C/3)$. For the small carbon concentrations considered this is equivalent to y_C, the activity coefficient of iron is unity and $a_{Fe} = (1-y_C)$. It follows that log $(1-y_C)$ is -0.0019 to -0.0018; $y_C = 0.0044$ to 0.0041 which is equivalent to a rounded value 0.090 pct C. The method of calculation is more accurate than the usual "freezing point lowering" and emphasizes the precision required in free energy data to make a significant calculation of a phase boundary. The results substantiate the published thermal data on δ, γ, and liquid iron and indicate their concordance with the data on the peritectic.

VI. THE ALPHA-GAMMA EQUILIBRIUM

The A3 line, the composition of γ-Fe in equilibrium with α-Fe, is based almost entirely on the work of Mehl and Wells[36], corrected by 1° at the pure iron end with negligible correction at the eutectoid. The intersections of our solubility lines place the graphite and cementite eutectoids respectively at 738° and 0.68 pct C and at 727° and 0.77 pct C. The latter temperature agrees with an observation of Smith and Darken[37] and is 4° higher than that of Mehl and Wells. The selected line and the observed points of Mehl and Wells are shown in Fig. 5.

The α-phase boundary was determined by Smith[20] at 800° and 750°C. These data form the basis for the line shown in Fig. 5 which is extrapolated to 0.0206 and 0.0218 pct C at the graphite and cementite eutectoids. The data of Schürman, Schmidt and Tillmann[38] indicate a graphite eutectoid of 0.029 pct C. The weight of evidence however favors Smith's value.

It is readily shown that this portion of the diagram is in fairly good agreement with the thermodynamic data on α- and γ-Fe. The value of $\log a_{Fe}^{\gamma}$ is simply $\log (1-y_C^{\alpha})$. To refer this to a standard state of Fe^{γ} we add $\Delta G^{\circ}{}_{\alpha\rightarrow\gamma}/4.575T$ obtained from the tables of Orr and Chipman. The corresponding carbon concentration is then obtained from Eq. [5]. Points thus calculated are shown by dots in Fig. 5. The agreement merely indicates a fairly high degree of internal consistency among the various data, perhaps as good as can be expected in the absence of information on the partial molar heat capacity of carbon.

The solubility lines for graphite and cementite will be discussed in a later section.

VII. ACTIVITY AND SOLUBILITY OF GRAPHITE IN FERRITE

The activity of carbon in bcc iron has been determined in the range 590°-1495°C with a wide void in the fcc region. Since the highest concentration is 0.09 pct C, Henry's law may be assumed and a_C may be taken as proportional to either x_C or y_C or z_C within the precision of the data. For the activity coefficient I shall use $\psi_C = a_C/y_C$, the value of a_C for graphite being taken as unity. A plot of $\log \psi_C^{\alpha}$ vs. $10^4/T$, shown in Fig. 6 permits a

comparison throughout the entire range. For the two points of Smith on the α boundary the activity of carbon is calculated from the γ boundary at the same temperature, using Eq. [5]. The value credited to Schürmann et al.[38] is their graphite solubility at the eutectoid. At the peritectic temperature, a_C is taken from an earlier section of this paper. Other points, including one by Smith[39] at 619°C are based on gas equilibria and the corresponding equilibrium with graphite. In the one point of Dünwald and Wagner[19], a modern value of p^2_{CO}/p_{CO_2} for graphite has been substituted for the erroneous value accepted in 1931. Other data are as reported by their authors. The plotted data of Swartz[9] include only those based on combustion analysis of carbon. The straight line based on the assumption that $\Delta C_p = 0$ has the equation:

$$\log \psi_C^{\alpha} = 5550/T - 2.49 \qquad [9]$$

which corresponds to a heat of solution of graphite, $\Delta H = 25.40$ kcal., a value larger than was previously accepted. Below the graphite eutectoid, Eq. [9] may be solved for the solubility of graphite ($a_C = 1$). Expressed in parts per million, with a slight adjustment to agree with Fig. 5, this gives for the solubility of graphite:

$$\log [C]^{\alpha}_{ppm} = 7.81 - 5550/T \qquad [10].$$

The indicated graphite solubilities are shown in Table IV. It should be mentioned that while the data seem fairly concordant some uncertainty remains concerning Smith's residual inactive carbon and Swartz's mysterious "traps" for carbon in δ-Fe.

VIII. THE IRON CARBIDES

Numerous carbides of iron are reported in the chemical and metallurgical literature ranging in composition from FeC to Fe_4C. Only two of these have been studied under metastable equilibrium conditions and it is only for these two that thermodynamic data are available.

Cementite is usually assigned the formula Fe_3C but its exact conformance to the stoichiometric composition has not been proved and variations in composition have been suggested[8]. Petch[40] quenched carbide-saturated alloys from various temperatures and found that the lattice parameter of the cementite varied with quenching temperature. Other observers have reported similar differences[41,42]. The structure is orthohombic and the Curie temperature is approximately 210°C with variations dependent upon the previous history. It is sometimes called θ (theta) carbide.

The possible existence of Fe_2C was suggested by Glud, Otto and Ritter[41]. An X-ray diffraction pattern of Hofmann and Groll[42] for iron carburized at temperatures below 400°C showed lines of an unknown carbide along with those of Fe_3C. When carburization was done above 400°C only the latter was found. Bahr and Jessen[43] developed a hydrogen-reduction method for independent determination of carbidic and free carbon. With its aid they were able to show that when iron, reduced from oxide by hydrogen at about 260°C, was carburized with CO at 225° the product contained 9.7 percent C corresponding to Fe_2C. At higher carburizing temperatures a mixture of Fe_2C and Fe_3C was formed and at 400° or above the carbidic carbon corresponded to the formula Fe_3C. The X-ray diffraction pattern of

this new carbide was determined a year later by Hägg[44] and it is generally called the Hägg carbide or χ (chi). Jack[45] obtained the same carbide by carburization of the nitride. Its analysis showed a slightly variable composition approximating $Fe_{2.2}C$.

Cementite, θ.

Twenty years ago Darken and Gurry[46] reviewed the properties of cementite and developed tables of its thermodynamic properties. They were able to show that Fe_3C is metastable at all temperatures with respect to graphite and its saturated solution in iron. Thus they produced the first modern phase diagram of the system; all subsequent diagrams, including the present, have added only refinement in detail.

The line in Fig. 1 representing the solubility of cementite in austenite is taken from the paper by Ban-ya, et al.[8] and is based on the direct measurements of solubility by Smith[47] and the CO-CO_2 equilibrium measurements of Scheil et al.[7] With the aid of Eqs. [5] and [6] interpolated points from these data and a point calculated from the eutectic composition have been used to establish the standard free energy change in the reaction:

$$3Fe(\gamma) + C(\text{graphite}) = Fe_3C(\text{equilib.}) \qquad [11].$$

The result is shown in Fig. 7. The curvature is somewhat greater than is ordinarily expected in a plot of this kind. Uncertainty remains as to whether this is to be ascribed to a change in heat capacity in the reaction or to variations in composition of the cementite phase, or to experimental error. Assuming the first, a value of $\Delta Cp = -3.4$ cal. $deg^{-1}mol^{-1}$ could be used to reproduce the observed curvature in the range 1000-1421K. However it will be preferable to return to this question after consideration of the solubility of Fe_3C in α-Fe.

The observed free energy and heat of formation at the eutectic provide a basis for calculation of the solubility of cementite in liquid iron. The other

data required are the activities of Fe and C in the liquid by Eqs.[7] and [8] and the free energy difference[17] between γ and liquid Fe. There are no experimental data on this problem and no measurements of the melting point. Various estimates have been made including a recent one by Hillert[48]. The result of the calculation is a very flat maximum shown by a dotted line in Fig. 4, and a calculated melting point of 1227°C.

At lower temperatures there are two distinct and conflicting lines of evidence on the free energy of formation of Fe_3C from α-Fe and graphite. The activity of carbon as shown by Fig. 6 or Eq.[9] can be used to calculate the free energy from the observed solubility. It happens that the solubility is quite small and the data conflicting. Moreover the solubility may be affected by precipitation stresses as shown by Swartz[9]. His more recent observation on self-stressed and stress-free cementite must be regarded as superceding the earlier work by the same technic, determination of the Snoek peak in the internal friction spectrum. It appears[9b] that with longer aging the precipitated cementite has about the same solubility as the stress-free. The free energy calculated from the solubility data is shown, along with other determinations in Fig. 8.

More direct information on cementite comes from studies of the equilibrium,

$$Fe_3C + 2H_2 = 3Fe(\alpha) + CH_4 \qquad [12]$$

and the known free energy of methane. The equilibrium was studied in the range 725°-875°K by Watase[49] and at lower temperatures by Browning, DeWitt, and Emmett[50]. The latter investigators drew separate lines through the two sets of results and computed the free energy and heat of formation. The latter, though poorly determined by the data, has been widely quoted. It is now

possible to improve on this treatment by consideration of the data at higher temperatures (Fig. 7) and the thermal properties of the reacting species. This was done by Darken and Gurry[46] with whose results the following calculations are in good agreement. The data points corresponding to the observed methane equilibrium are shown in Fig. 8.

The high-temperature data of Fig. 7 are easily recalculated using the free energy differences tabulated by Orr and Chipman[17] to show the feee energy of formation from metastable α-Fe. The results are shown in Fig. 8. In order to establish the thermodynamic properties from these data it is first necessary to examine the data on the enthalpy and entropy of Fe_3C.

At low temperatures (68°-298°K) the heat capacity was determined by Seltz, McDonald, and Wells[51] whose value for S°_{298} was 25.7±1.0. From this and data of Schwarz and Ulich[52] and Naeser[53], Kelley and King[54] proposed an average value S°_{298} = 24.2±1.0. More recent measurements by Mazur and Zacharko[55] have covered the range 2°-20°K thus filling part of the uncertainty in Seltz's estimate of the entropy. A recalculation of Seltz's data made very little change in his original figure but probably improved its overall reliability. The high-temperature data on free energy shown in Figs. 7 and 8 are better fitted by the value S°_{298} = 25.00. This value, which lies well within the range of uncertainty, is adopted for the calculations and tables.

Estimates of the thermodynamic properties of Fe_3C at high temperatures are based principally on the measurements of Naeser[53] and Umino[56]. The latter were recalculated by Darken and Gurry[46] and included in their tabulated enthalpy data. Corresponding values of the free energy function came from the entropy and equilibrium data mentioned above. Kelley[57] used the same data

plus Schwarz and Ulich[52] to arrive at a similar tabulation.

It is now possible to make some numerical adjustment in the data to conform more closely with the directly determined data on the free energy of formation. The selected values shown in Table V are based primarily on the equilibrium data at 500°-700°C and the solubility in α-Fe at 1000°K. The line in Fig. 8 representing the free energy of formation of Fe_3C from α-Fe follows the tabulated values up to 1000°K. Corresponding values for its solubility in α-Fe are shown in Fig. 9. These lie slightly below the line obtained by Swartz from internal friction measurements and decidedly below earlier values by that method. The line may be represented by the equation for the solubility of Fe_3C

$$\log[C]^{\alpha}_{ppm} = 6.38 - 4040/T \qquad [13]$$

which corresponds to a heat of solution of cementite, $\Delta H = 18.47$ kcal. This is to be compared with 24.0 kcal from Swartz's data.

Borelius and Berglund[58] measured the heat evolved on precipitation of cementite from α-Fe which had been equilibrated at temperatures of 350-700°C and from the results calculated the solubility. Their results at 700° are lower than those of Swartz or of Smith or of Eq. [13] and their heat of solution was only 12.5 kcal per gram atom of C. At 500-600° their values agree with the calculated curve of Fig. 9 while at lower temperatures they are more nearly in line with the data of Swartz.

The curvature in the line for the free energy of Fe_3C shown in Fig. 7 may now be reconsidered. This is not to be brushed aside as experimental error since it is based on closely agreeing investigations which in all other respects have been well substantiated. It was shown that the curvature could be accounted for by a heat capacity change in the reaction of $\Delta C_p = -3.4$ cal/deg mole. This would make

its molar heat capacity at 1200K about 26.4 cal. per degree. In view of Table V only an abrupt change at 1000°K could lead to such a low value. It is to be remembered that the standard free energy of formation shown in Fig. 7 is based on the assumption that the composition is Fe_3C. Variations from this composition could be expected to affect the thermodynamic properties. At the present time, however, no quantitative explanation of the curvature can be offered. Further research on this question is clearly needed.

In Fig. 7 a point is shown at 1000°K which is calculated from the solubility of cementite in α-Fe and the known free energy difference between α and γ-Fe. A straight line from this point to that calculated from the eutectic at 1421° is represented by the equation

$$3Fe(\gamma) + C(gr.) = Fe_3C$$

$$\Delta G^\circ_f = 2685 - 2.625T \qquad [14].$$

This approximate equation reproduces the data within ±60 cal and should serve well enough for practical purposes until a better knowledge of the composition of cementite is available.

The Hägg Carbide, χ.

Browning, DeWitt and Emmett[50] also measured the equilibrium

$$Fe_2C + 2H_2 = 2FE(\alpha) + CH_4 \qquad [15]$$

in the temperature range 296-359°C. Their carbide was prepared by treatment of hydrogen-reduced iron with butane at 275° and was identified by its diffraction pattern as the same as that prepared by Hägg at 225°. Both observers found that this carbide was converted to Fe_3C by heating to 500°.

Jack[45] obtained the same carbide which he called $Fe_{20}C_9$. The X-ray pattern was indexed as orthorhombic with the added notation that a monoclinic or triclinic structure was not excluded. More recently it was shown by Sénateur, Fruchart and Michel[59] that the structure is monoclinic and isotypic with Mn_5C_2. For purposes of the present discussion it is represented as $Fe_{2.2}C$. Its Curie temperature is given by Hofer[60] as 247°C.

Average equilibrium values of Browning et. al. for Eq. [15] are shown in Fig. 8. The slope of the line is not well defined but the data are represented approximately in the equation:

$$2.2Fe(\alpha) + C(gr.) = Fe_{2.2}C(\chi);\ \Delta G^\circ = 4850-2.5T \qquad [16]$$

Extrapolation to lower temperatures indicates that χ becomes a more stable phase than Fe_3C at temperatures below about 500°K. The triple point χ-θ-α is not accurately determined by the data. Krisement[61], using the method of Borelius and Berglund[58], found that the precipitate formed at 230°C was cementite whereas at 188° to 218°C a different carbide which he called Fe_2C appeared. The cause of the break in his curve remains obscure. Jack found that χ persisted for 50 hours at 350°, but was converted to cementite at 450°. Lesage[62] reported the formation of χ only at 230-450°. It is difficult to distinguish thermodynamic from kinetic effects but there would seem to be the possibility that the cross-over point is somewhat higher than the 500°K indicated.

The ε Carbide

Another well-defined carbide, ε (epsilon) occurs as a transition phase in the tempering and ageing of steel. It has not been isolated and its thermodynamic properties are unknown. It is described[60]

as close-packed hexagonal with a Curie temperature of 370°C and a variable composition, commonly about $Fe_{2.4}C$. It was recognized by Jack[63] as a result of the tempering of martensite and by Tsou, Nutting and Menter[64] in the quench-aging of iron. The voluminous and confusing literature on these phenomena contains little on which an estimate of its free energy can be based. Butler, Chollet and Crussard[65] estimated its apparent solubility in αFe from the shape of the aging curve and proposed the formula

$$\%C^{\alpha} = 1.15e^{-6100/RT} \qquad [17]$$

This would make its solubility a thousand fold greater than that of either of the other carbides. Arndt and Damask[66] measured the energy released in the formation of the metastable carbide precipitate and reported this as 0.27 e.v. per C-atom. This is equivalent to 6200 cal in remarkable agreement with the value estimated from the solubility. This agreement suggests an equation for the free energy of formation of the precipitate. This is not a "standard" free energy since it ignores the effects of particle size and precipitation strain.

$$2.4Fe(\alpha) + \underline{C}(\alpha) = Fe_{2.4}C \text{ (}\varepsilon\text{ precipitate)} \qquad [18]$$

$$\log[C]^{\alpha} \text{ (ppm)} = 4.06 - 1335/T$$

$$\Delta G \text{ (ppm)} = -6100 + 4.27T$$

SUMMARY

A critical review of published data has resulted in a phase diagram for the Fe-C system which differs only slightly from others recently published. It brings into agreement the measured thermodynamic properties of iron and the observed activities of the components in α-, γ- and liquid solutions, and the free energies of the carbide phases. Properties of the α, γ, δ and liquid solutions are given in equations, graphs and tables from which the following free energy, enthalpy and entropy data are derived. In the equations y_C is the atom ratio n_C/n_{Fe}; $z_C = y_C/(1-y_C)$; and ψ_C is the activity coefficient a_C/z_C, the activity of graphite being taken as unity.

The change in free energy accompanying the solution of graphite in γ-Fe at infinite dilution is obtained from Eq.[5] which is now used in preference to the analogous Eq. [9] of reference 8:

$$C(gr) = \underline{C}(\text{in } \gamma\text{-Fe})$$

$$\Delta G^\circ(\text{cal.}) = 10520 - 4.21\,T \qquad [19].$$

This is the difference between the two standard states, graphite and the hypothetical state with $z_C = 1$ and all other properties those of the infinitely dilution solution. The effect of concentration on the partial molar free energy is

$$\bar{G}^{\gamma}_C = \bar{G}^{\circ}_C(\gamma, \text{inf. dil.}) + RT\,\ell n\, z_C + 17660\, y_C \qquad [20].$$

From these equations it is evident that when graphite dissolves in austenite the increase in entropy is $4.21 - R\ell nz_C$ cal/°Kg.atom, and its heat of solution in calories $10520 + 17660y_C$.

For iron the partial molar free energy by Eq.[6] is:

$$\overline{G}_{Fe}(\text{austenite}) = G^{\circ}_{Fe}(\gamma) - 8830y_C^2 + RT\ell n(1-y_C) \qquad [21]$$

For the solution of graphite in liquid iron Eq. [7] gives

$$C(gr) = \underline{C}(\text{in } \ell\text{-Fe})$$

$$\Delta G^{\circ}(\text{cal}) = 5400 - 3.98T \qquad [22]$$

and $$\overline{G}_C(\ell) = \overline{G}^{\circ}_C(\ell, \text{ inf.dil.}) + RT\ell nz_C + (3.29T + 15550)y_C \qquad [23]$$

From these it is evident that the heat of solution in calories is $5400 + 15550\ y_C$ while the increase in entropy is $3.98 - 3.29y_C - R\ell nz_C$.

For the liquid solution the partial molar free energy of iron is

$$\overline{G}_{Fe}(\ell) = G^{\circ}_{Fe}(\ell) - (1.65T + 7770)y_C^2 + RT\ell n(1-y_C) \qquad [24]$$

In α-δ-Fe the free energy of solution of C by Eq.[9] in the range 500-1768°K is:

$$C(gr) = \underline{C}(\text{in } \alpha\text{-Fe})$$

$$\Delta G^{\circ}(\text{cal}) = 25400 - 11.40T \qquad [25]$$

The heat of solution is 25400 cal and the entropy increase is $11.40 - R\ell nz_C$. In δ-Fe the activity of Fe is appreciably different from unity and here the partial free energy is

$$\overline{G}_{Fe}(\delta) = G^{\circ}_{Fe}(\delta) - RT\ell n(1-y_C) \qquad [26]$$

The free energy of formation and other properties of cementite (assumed to be Fe_3C) in the α-Fe range up to 1000°K are given in Table V. In the γ-Fe range, 1000-1421°K, the free energy is approximately

$$3Fe^{\gamma} + C(gr) = Fe\ C(\Theta);\ \Delta G^{\circ} = 2685 - 2.625T \qquad [27]$$

The free energy of formation of the χ-carbide shown in Fig. 8 is, in the range 450°-650°K,

$$2.2Fe(\alpha) + C(gr) = Fe_{2.2}C(\chi)$$

$$\Delta G^\circ = 4850 - 2.50T. \qquad [28]$$

Both carbides are metastable at all temperatures with respect to grphite and its saturated solution in iron. Below a temperature estimated as 230 to 350°C the χ-carbide is more stable than cementite.

An estimate of the free energy of formation of ε carbide precipitate is made from reported observations during aging. From its apparent solubility and that of graphite in α-Fe we derive the equation

$$2.4Fe^{\alpha} + C(gr) = Fe_{2.4}C \text{ (ε precipitate)} \qquad [29]$$

$$\Delta G = 19300 - 6.13T$$

Other available data on the system including solubilities are shown in tables.

ACKNOWLEDGEMENTS

The author is indebted to Stuart Nelson and Donald T. Hawkins for assistance in computation and to Ralph Hultgren and to an anonymous reviewer for helpful comments on the manuscript. This study was supported at Massachusetts Institute of Technology by the Army Research Office, Durham and the American Iron and Steel Institute and at Berkeley by the Inorganic Materials Research Division of the Lawrence Radiation Laboratory and the U. S. Atomic Energy Commission.

Table I. Solubility of Graphite and Cementite in Austenite

Temperature °C	Graphite		Cementite	
	y_C	%C	y_C	%C
727[a]	-	-	0.0356	0.77
738[b]	0.0320	0.68	-	-
800	0.0408	0.87	0.0442	0.94
900	0.0561	1.19	0.0580	1.22
1000	0.0725	1.53	0.0730	1.55
1100	0.0896	1.89	0.0910	1.92
1148[c]	-	-	0.1000	2.11
1154[d]	0.0990	2.08	-	-

[a]Cementite eutectoid

[b]Graphite eutectoid

[c]Cementite eutectic

[d]Graphite eutectic

Table II. Solid-Liquid Equilibria

Temperature °C	γ-Solidus %C	y_C	a_C	Liquidus %C	y_C
1148[a]	2.11	0.1000		4.30	0.2092
1154[b]	2.08	0.0990	1.000	4.26	0.2072
1200	1.85	0.0877	0.720	3.93	0.1906
1250	1.59	0.0718	0.457	3.50	0.1689
1300	1.30	0.0613	0.323	3.02	0.1450
1350	1.01	0.0475	0.203	2.47	0.1179
1400	0.71	0.0333	0.117	1.88	0.0891
1450	0.42	0.0196	0.057	1.21	0.0570
1495[c]	0.17	0.0079	0.019	0.53	0.0248
1527[d]	0.00	0.0000	0.000	0.00	0.0000
1538[e]	-	-	-	-	-

[a] Cementite eutectic.

[b] Graphite eutectic.

[c] Peritectic. The value of a_C is an average from Eqs. [5] and [7].

[d] Metastable melting point of γ-Fe.

[e] Melting point of δ-Fe

Table III. Solubility of Graphite in Liquid Iron

Temperature °C	Carbon wt. pct.
1154	4.26 ± 0.02
1200	4.37
1300	4.63
1400	4.88
1500	5.14
1600	5.40 ± 0.03
1700	5.66
1800	5.94 ± 0.05
1900	6.26 ± 0.10
2000	6.63 ± 0.10
2100	7.05 ± 0.2
2200	7.56 ± 0.3
2300	8.1
2400	8.68
2500	9.28 ± 0.4
2600	9.87
2700	10.50
2800	11.12
2900	11.75 ± 0.5

Table IV. Solubility of Graphite and Carbides in α-Fe

Temperature °C	Parts per million Graphite[a]	Fe_3C[b]	$Fe_{2.2}C$[c]
738	206		
727		218	
700	127	160	
650	63	102	
600	28	57	
550	11.7	28	
500	4.3	13	
450	1.35	5.7	
400	0.37	2.3	
350	0.81	.75	1.3
300	0.013	.21	.30
250		.045	.050
200		.007	.0055

[a] Derived from Fig. 6.

[b] Calculated from observed value at 727°C and free energy of formation.

[c] From free energy of formation.

Table V. Thermodynamic Properties of Cementite, Fe_3C

T, °K	Cp	H_T-H_{st}	S_T-S_{st}	S°	$3Fe(\alpha) + C(gr) = Fe_3C$ ΔG°_T	ΔH°_T	ΔS°_T
298.15	25.40	0	0.00	25.00	4772	5985	4.07
400	27.93	2710	7.80	32.80	4274	6534	5.65
450	29.98	4140	11.21	36.21	3949	6802	6.34
480[a]	30.71	5052	13.17	38.17			
500	26.50	5624	14.34	39.34	3618	7083	6.93
600	27.20	8309	19.23	44.23	2916	7176	7.10
700	27.90	11064	23.48	48.48	2214	7121	7.01
800	28.60	13889	27.25	52.25	1524	6892	6.71
850	28.95	15328	28.99	53.99	1192	6692	6.47
900	29.30	16784	30.65	55.65	885	6411	6.14
950	29.65	18258	32.34	57.24	585	6019	5.72
1000	30.00	19749	33.78	58.78	300	5450	5.15

[a] Curie temperature.

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FIGURE TITLES

Fig. 1. Portion of the phase diagram Fe-C. Metastable γ-range and system Fe-Fe_3C shown by dashed lines. Curie temperature dotted.

Fig. 2. Activity coefficient of carbon in liquid iron. Lines Eq.[7] Δ graphite solubility; + gas equilibrium; □ points on liquidus.

Fig. 3. Activity of carbon in γ and liquid iron. Standard state is graphite.

Fig. 4. The iron-carbon phase diagram.

Fig. 5. Equilibria involving α-ferrite. Metastable system Fe-Fe_3C shown by dashed lines.

Fig. 6. Activity coefficient of carbon in α-δ-iron. The standard state is graphite; $\psi_C = a_C/y_C$.

Fig. 7. Standard free energy of the reaction $3Fe(\gamma) + C(graph) = Fe_3C$. Assumed formula: Fe_3C.

Fig. 8. Standard free energy of formation of $Fe_3C(\theta)$ and $Fe_{2.2}C(\chi)$ from α-Fe and graphite.

Fig. 9. Solubilities in α-Fe; line for $\chi(Fe_{2.2}C)$ and solid line for Fe_3C from free energy data.

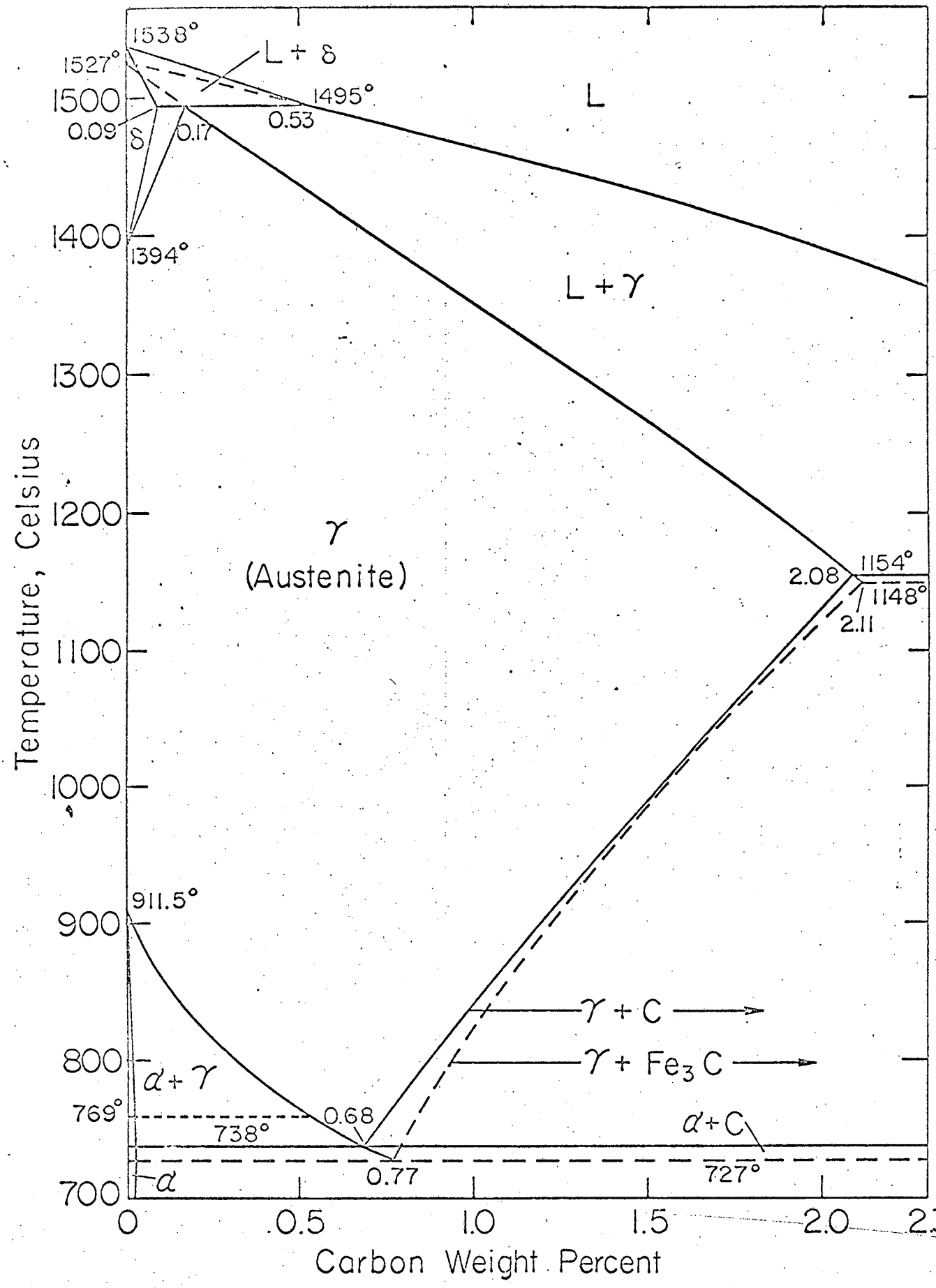

Fig. 1 Portion of the phase diagram

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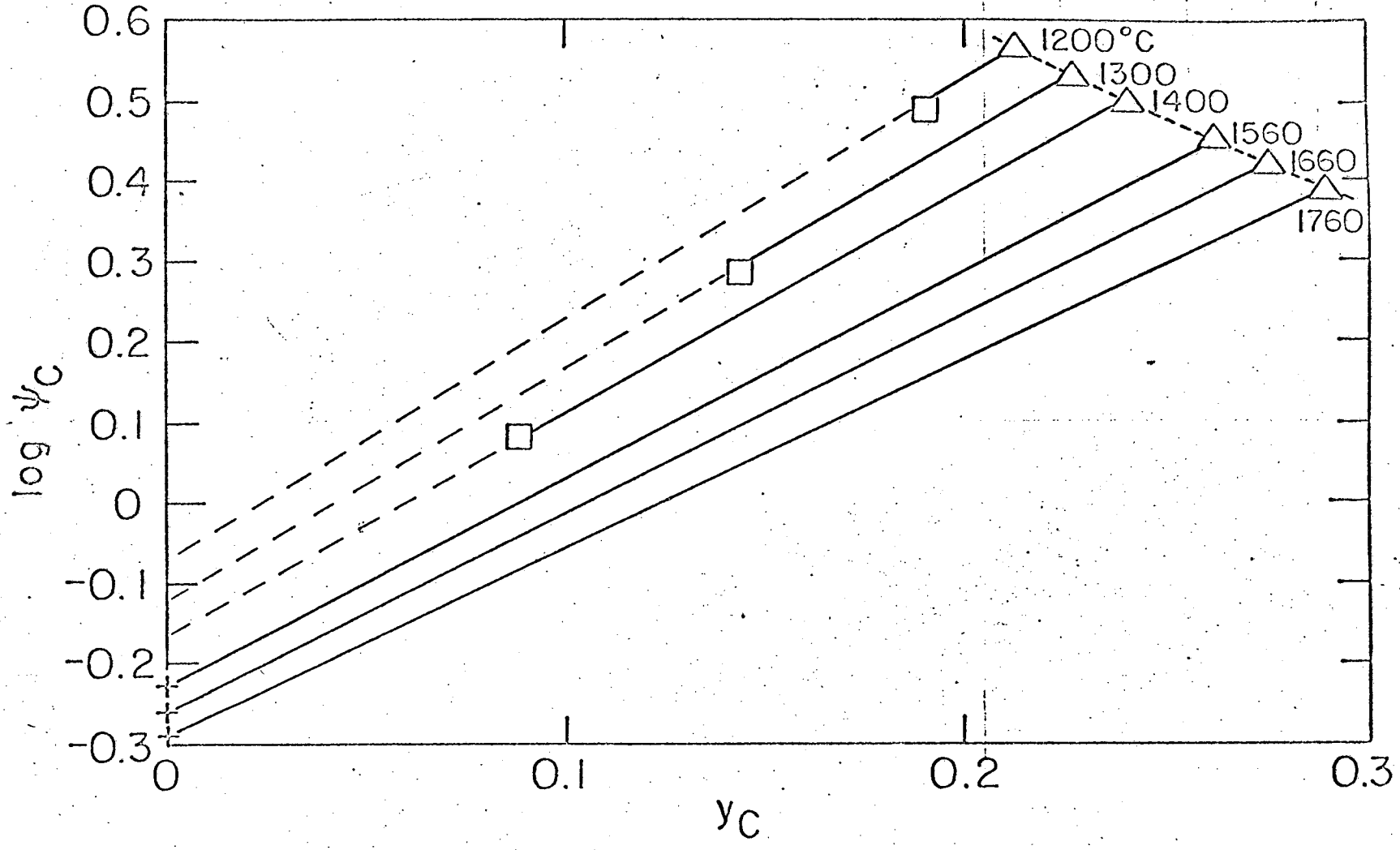

Fig. 2 Activity coefficient of Carbon in Liquid Iron.

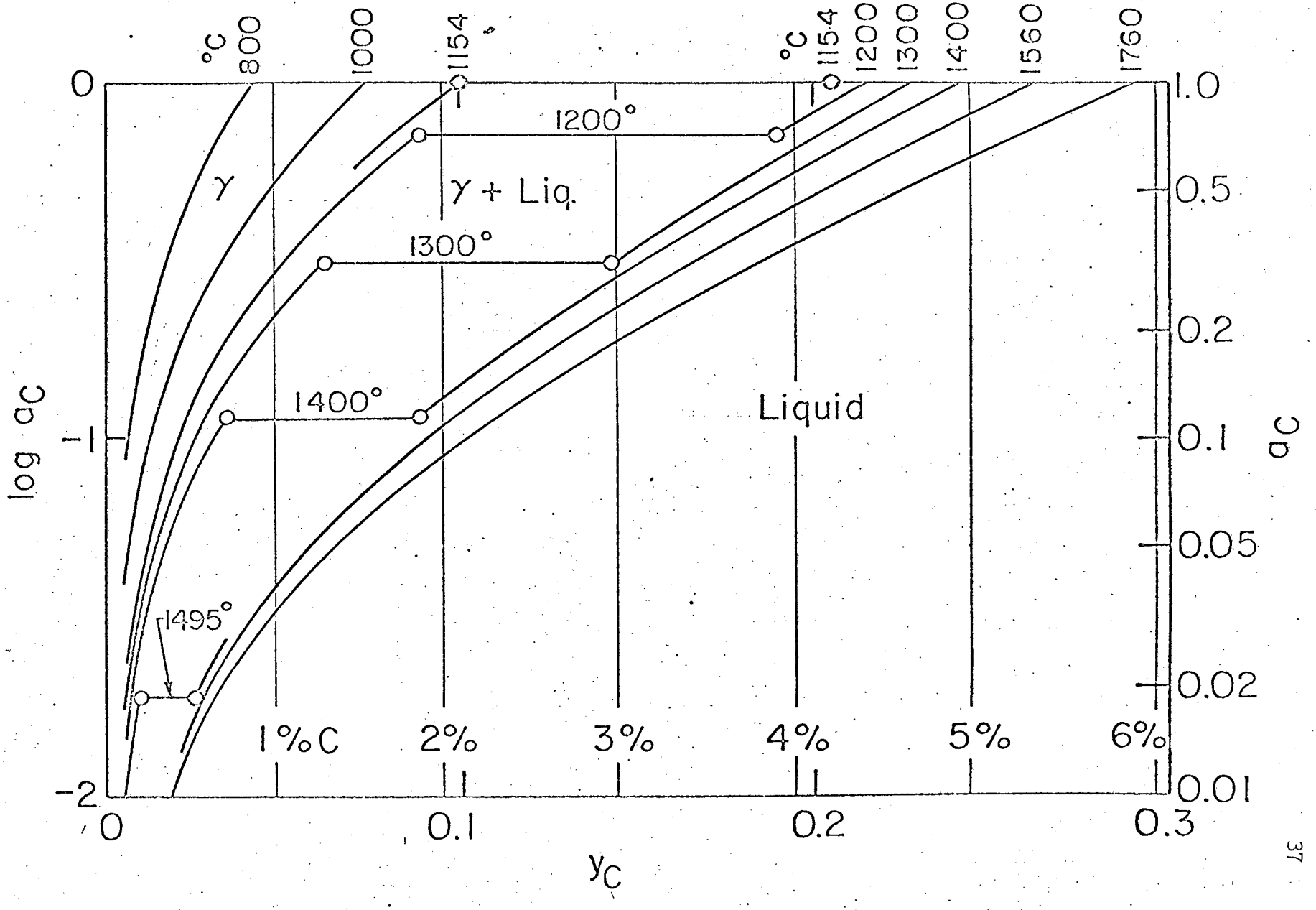

Fig.3 Activity of Carbon in γ and Liquid Iron.

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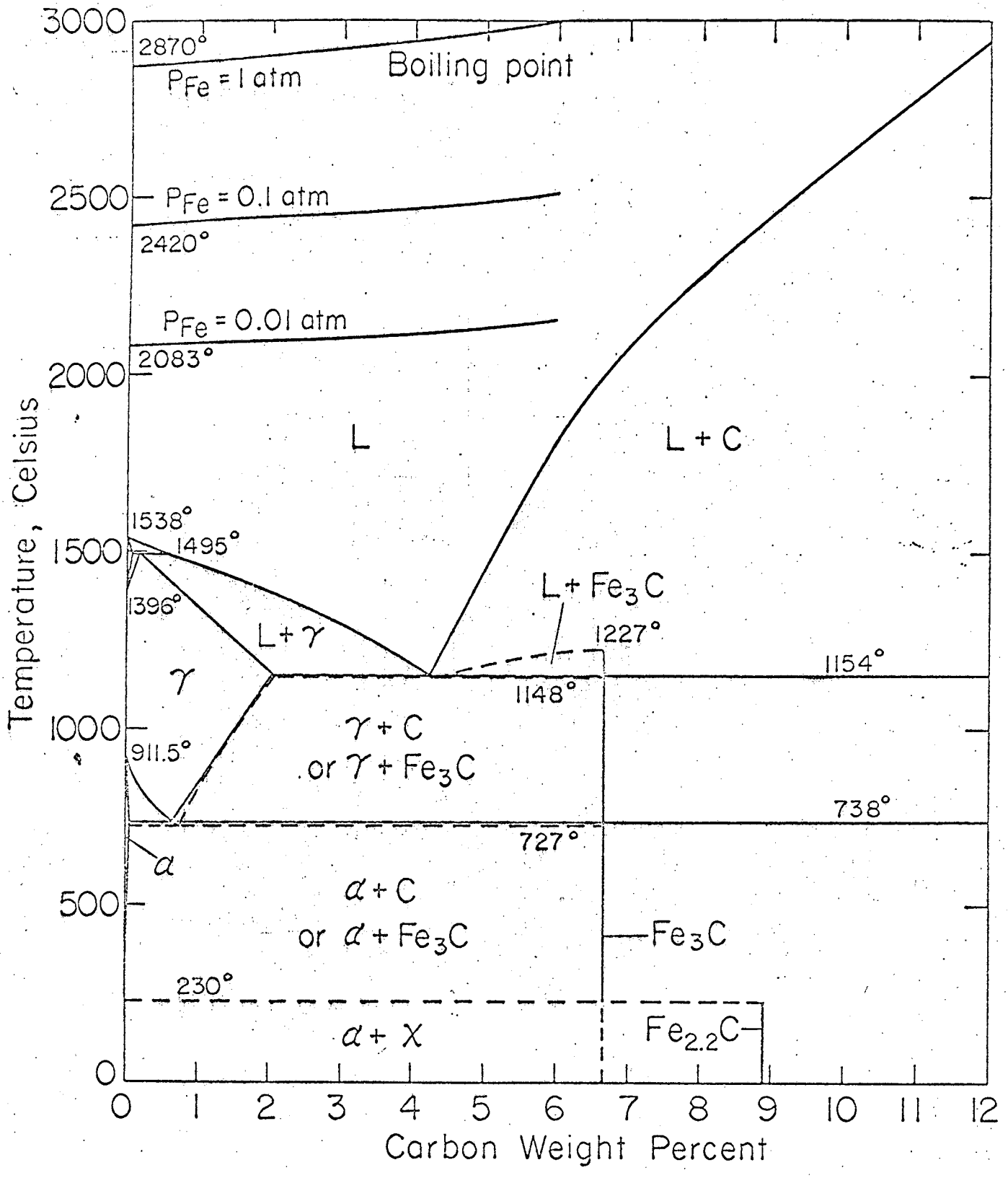

Fig. 4 The iron-carbon phase diagram.

XBL713-6591

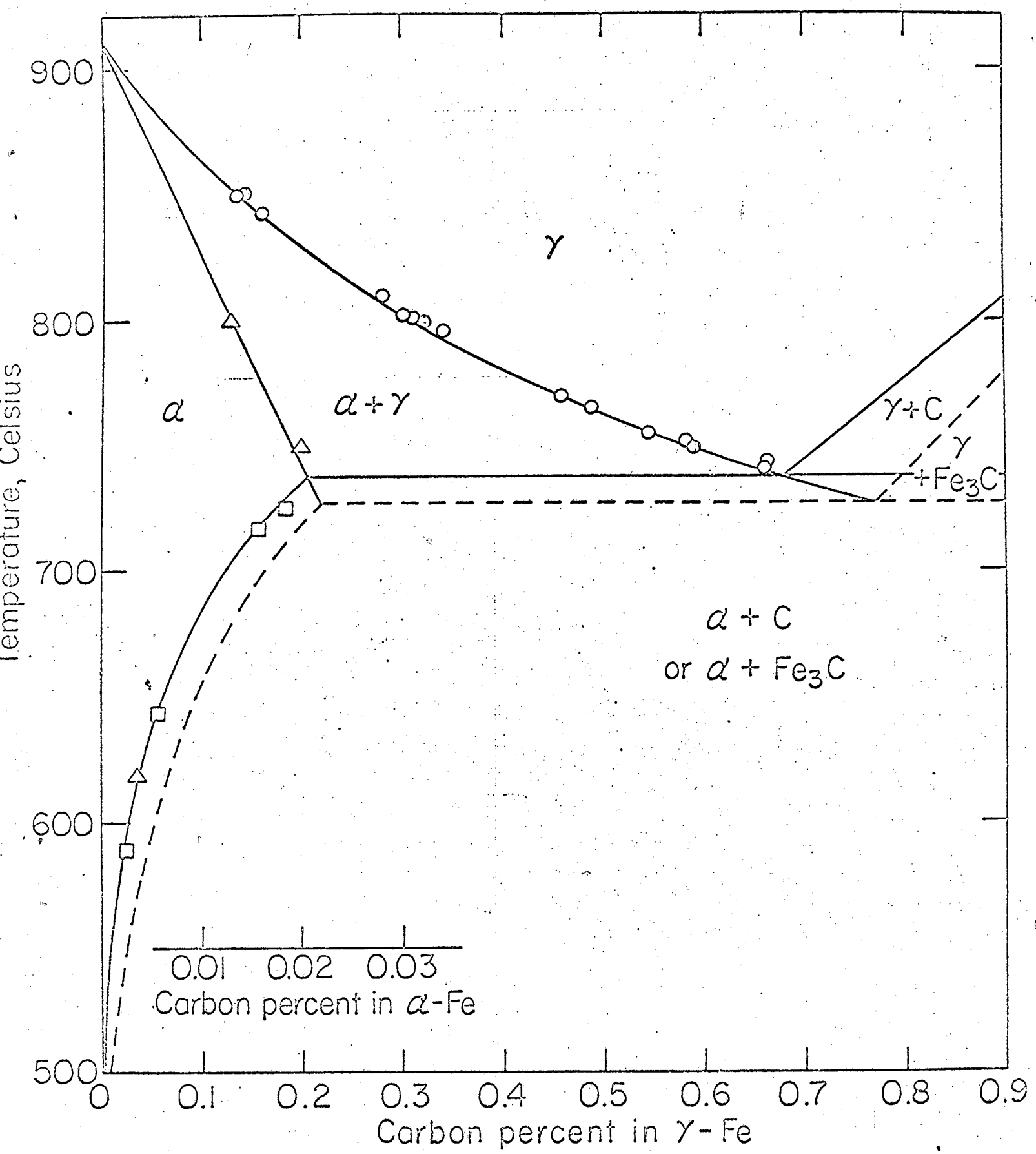

Fig. 5 Equilibria involving α-Ferrite.

XBL 713-6592

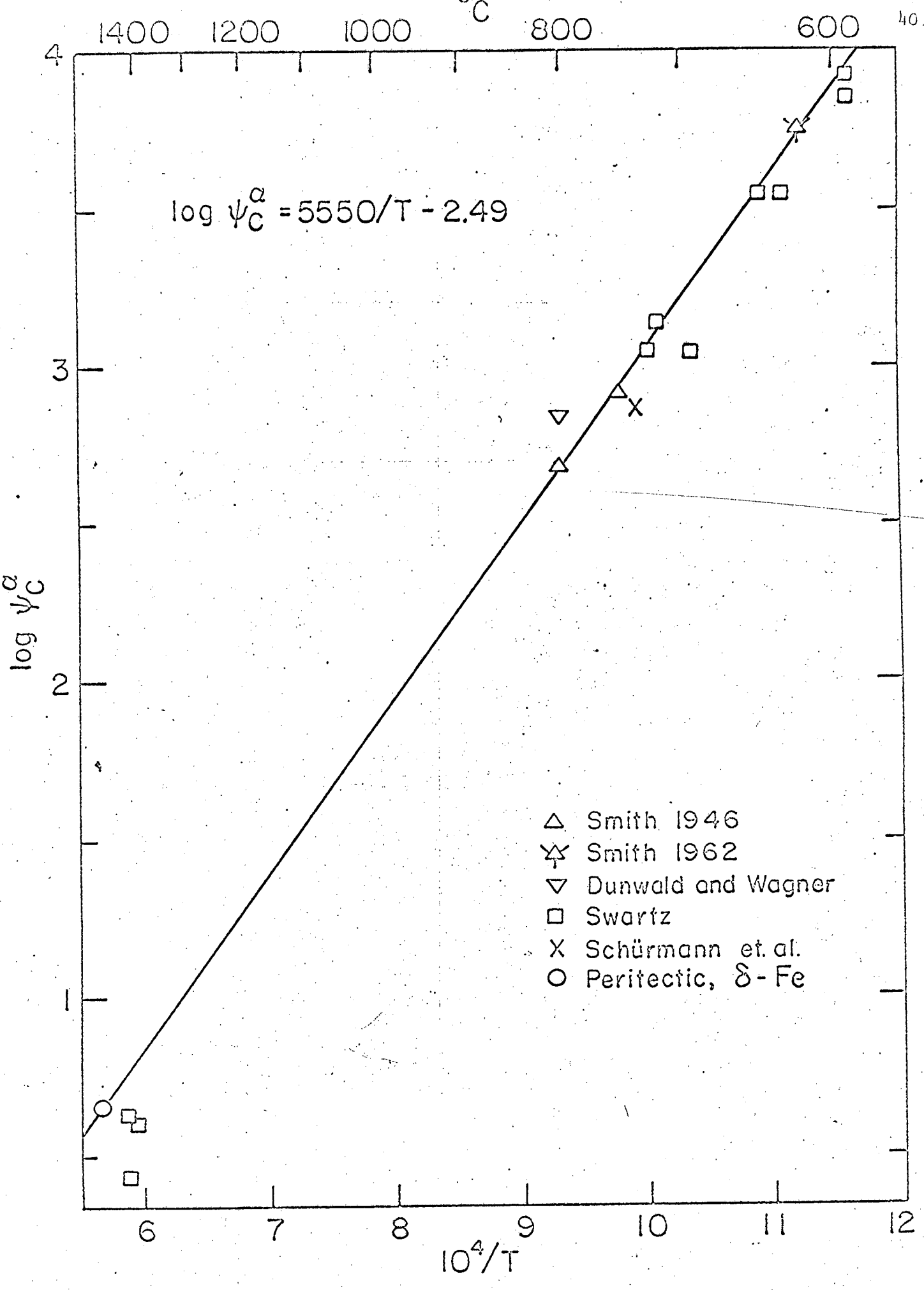

Fig. 6 Activity coefficient of Carbon in α - δ Iron.

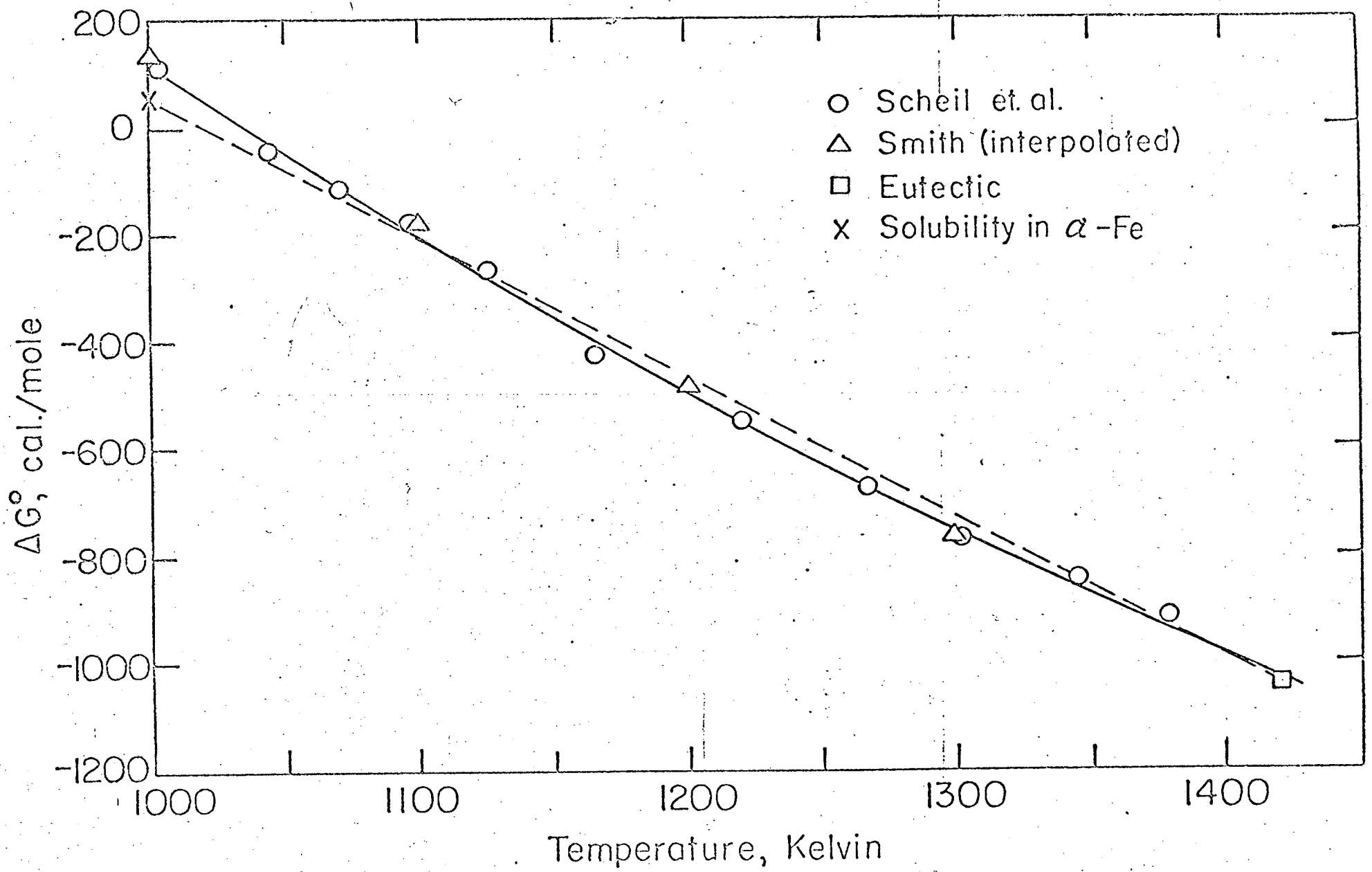

Fig. 7 Free energy of the reaction $3Fe(\gamma) + C(graph) = Fe_3C$.

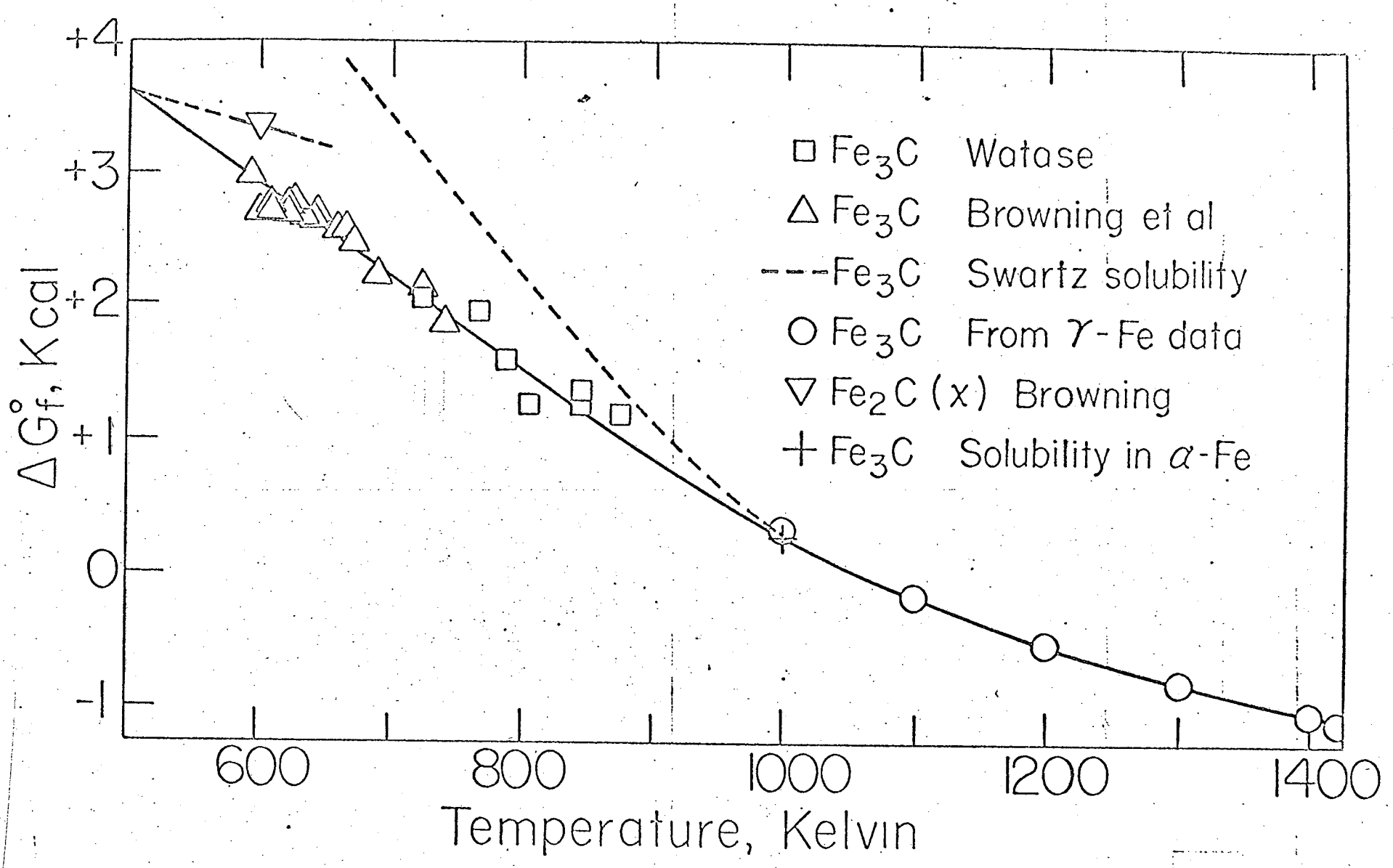

Fig. 8 Free energy of the reaction $3Fe(\alpha) + C(gr) = Fe_3C$

XBL713-6595

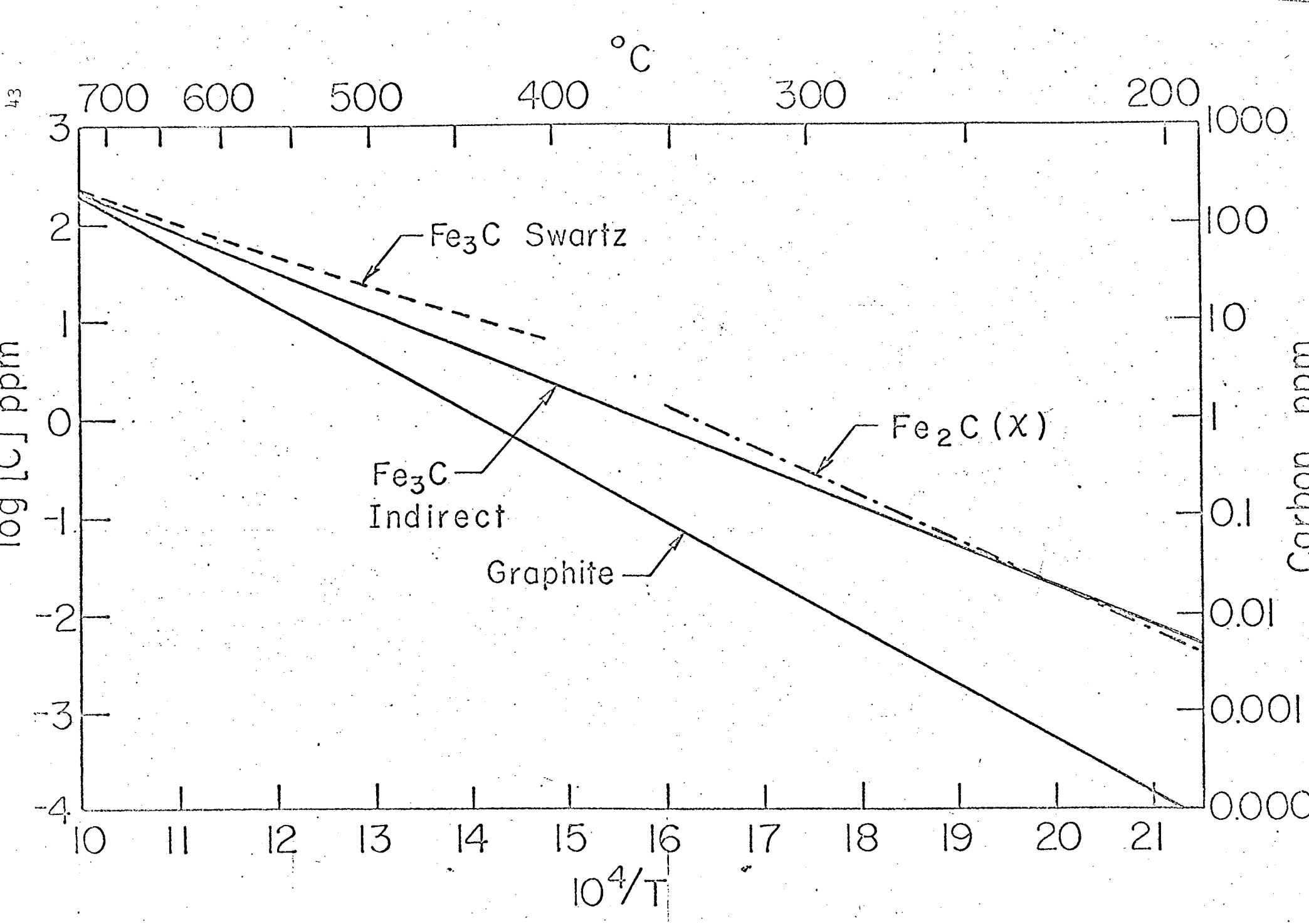

Fig. 9 Solubilities in α-Fe.

XBL 713-6596

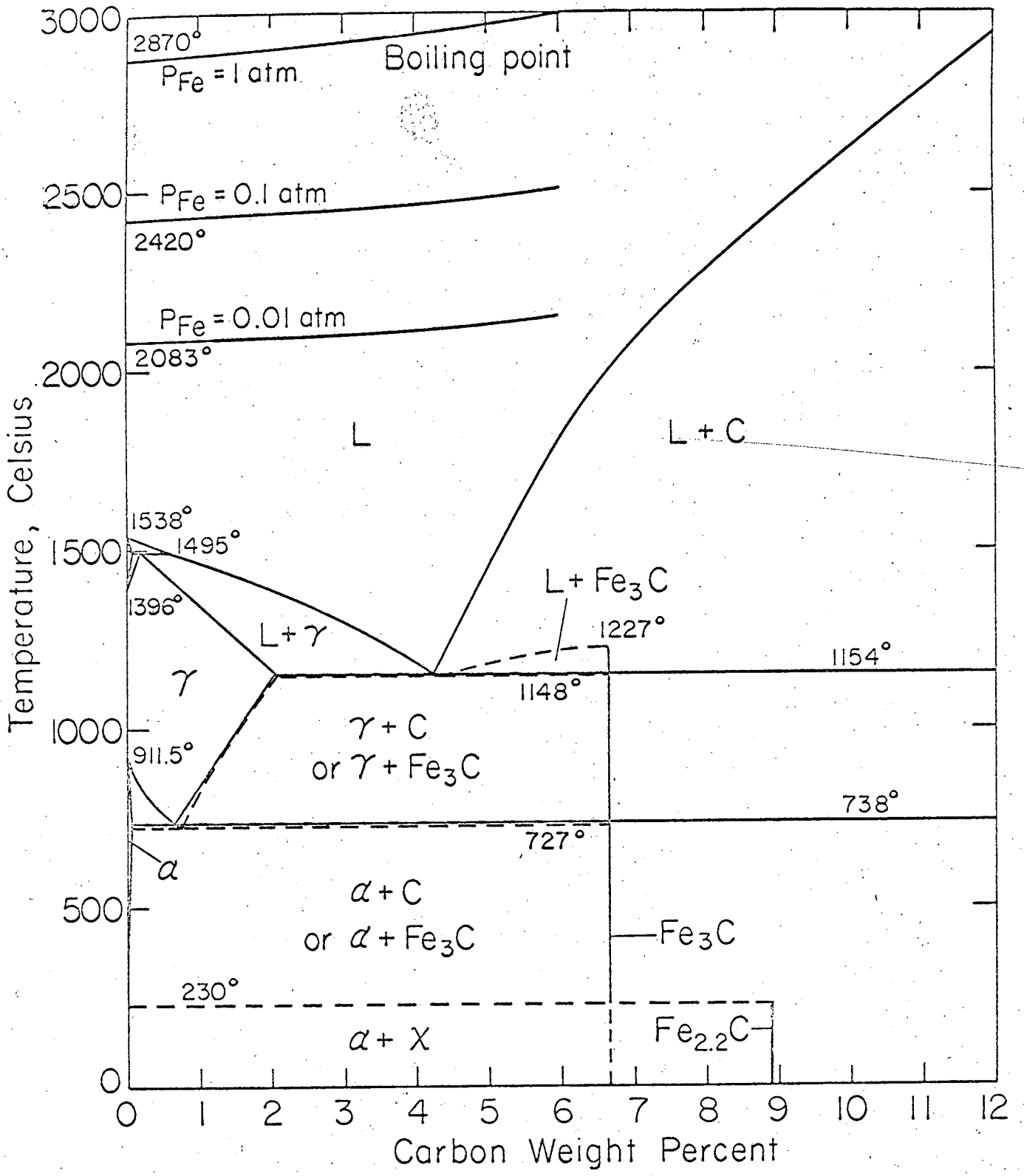

Fig. 4 The iron-carbon phase diagram.

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