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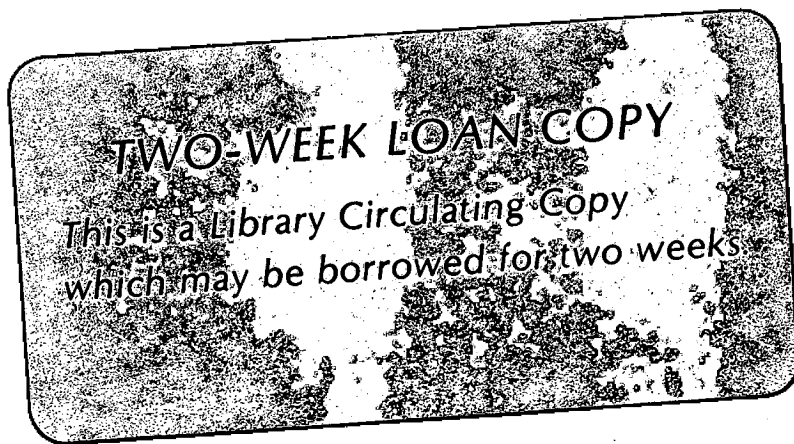
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THERMODYNAMICS AND PHASE DIAGRAM
OF THE IRON-CARBON SYSTEM

by

John Chipman

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 ϵ-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 ϵ-carbide becomes more stable than cementite below about 230°C. The data on cementite support the suggestion that it has a defect structure deviating from the stoichiometric composition Fe_3C.

THERMODYNAMICS AND PHASE DIAGRAM
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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

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

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

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

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

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:

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

The solubility of graphite in austenite is readily calculated from equation [5] by setting a_C 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 $\mu_C = 4.575 T \log a_C$.

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:

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

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-Fe₃C 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 $a_C = 0.019\pm0.001$. 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 $\log a_{Fe}^{\ell} = -0.0117$. 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 $\log a_{Fe}^{\gamma} = -0.0035$ 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 $\Delta G_{1766}^{\circ} = 67$ cal which corresponds to a difference $\Delta \log a_{Fe}^{\gamma-\ell}$ of 0.0083. This, added to the value of

$\log a_{Fe}^{\gamma}$ gives -0.0118 in agreement with the value found for $\log a_{Fe}^{l}$.

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 $\Delta\log$ $\Delta\log a_{Fe}^{\gamma-\delta}$ = 0.0016 or 0.0017. Subtracting from the value $\log a_{Fe}^{\delta}$ = -0.0035 we find $\log a_{Fe}^{\delta}$ = -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 Tellmann[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. ACITIVITY 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 since these are indistinguishable. 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 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 this gives

$$\log [C]^\alpha ppm = 7.82 - 5550/T \qquad [10].$$

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 appear to be capable of existing in metastable equilibrium 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 parameters of the cementite varied with quenching temperature. Other observers have reported similar differences[41,42]. The structure is orthorhombic and the Curie temperature is approximately 210°C with variations dependent upon the previous history.

The ϵ-carbide[41,42] is hexagonal (hcp) with a Curie temperature approximately 380°C. It has been called Fe_2C by some writers[43,44] but its composition appears to be more nearly $Fe_{2.4}C$. It appears to be the "Fe_2C" whose free energy was measured by Browning, DeWitt, and Emmett[45]. Because of its very small solubility, its heat and free energy of formation are independent of the assigned formula and pertain to an amount of the carbide containing 1 gram atom of carbon.

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 free energy change in the reaction:

$$3Fe(\gamma) + C(graphite) = Fe_3C(equilib.) \qquad [11].$$
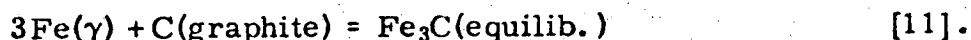
The result is shown in Fig. 7. The curvature is somewhat greater than is ordinarily expected in a plot of this kind. Uncertainty remains as to whether this is to be ascribed to a change in heat capacity in the reaction or to variations in composition of the cementite phase, or to experimental error. 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 its solubility 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 quenching stresses as shown by Swartz[9]. His more recent observations 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[45]. 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.

The thermal properties of Fe_3C are not known with accuracy and its heat

of formation is determined better by equilibrium than by calorimetric

measurements. Typical of the latter is Roth's 50 value 57±7 K cal.

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 $S°_{298} = 24.2 \pm 1.0$. 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°K and the solubility in α-Fe at 1000°K. The line in Fig. 8 representing the free enrgy of formation of Fe_3C from α-Fe follows the tabulated values up to 1000°K.

Browning et al.[45] also measured the equilibrium of Fe and "Fe_2C" with methane and hydrogen. It now appears that this was the ϵ-carbide, approximately $Fe_{2.4}C$. Since the activity of Fe is essentially unity the free energy data refer to 1 gram-atom of carbon regardless of the formula for the carbide. Their results appear in Fig. 8 and may be represented by the equation

$$2.4Fe(\alpha) + C(gr.) = Fe_{2.4}C$$

$$\Delta G° = 4850 - 2.5T \qquad [13].$$
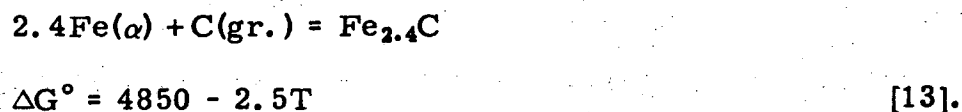
It is noted that below about 500°K the ϵ-carbide becomes metastable with respect to cementite. This is corroborated by a number of recorded observations. Krisement[58] found by calorimetric observations of precipitation in low-carbon alloys that below 230°C the precipitate was ϵ-carbide rather than cementite. Observations of tempering or quench aging at temperatures below 250° by studies of internal friction,[59] electrical resistivity,[60] and transmission electron microscopy[61] confirm the observation that below a certain temperature another carbide is more stable than Fe_3C. Tsou, Nutting, and Menter[62] had already identified this carbide by electron

diffraction as the ϵ-carbide.

Solubilities of graphite and of the two carbides are shown in Fig. 9.

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 $\Delta Cp = -3.4$ cal/deg mole. This would make its molar heat capacity at $1200°K$ about 26.4 cal. In view of Table V only an abrupt change at $1000°K$ could lead to such a low value. I think we must conclude that the composition of cementite is not the stoichiometric Fe_3C.

The activity data on which Fig. 7 was based are shown in Fig. 10. If $\Delta Cp = 0$ and the composition is constant at Fe_nC, the sum of $\log a_C + n \log a_{Fe}$ should give a striaght line when plotted against reciprocal temperature. This condition could be fulfilled by the formula Fe_4C, but such a wide difference could never have escaped detection. A variable composition is much more probable. A dashed straight line shows the calculated values if $n = 3$ at $1000°K$ and increases to about 3.6 at $1400°K$. Such a large increase however is not necessary. It is known[63] that in a defect structure small variations from the stoichiometric composition cause relatively large changes in the activities of the components. The activities represented in Fig. 10 are only those of the Fe-saturated phase and the free energy shown in Fig. 7 is not that of the stoichiometric Fe_3C. It seems possible that the structure is deficient in carbon, the deficit in the equilibrium composition being a function of temperature. Let no one underestimate the difficulties of obtaining

the thermodynamic properties of a phase of unknown and variable composition.

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

$$3Fe(\gamma) + C(gr.) = Fe_3C$$
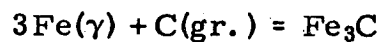
$$\Delta G_f^° = 2685 - 2.625\,T \qquad\qquad [14].$$

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.

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 observed activities of the components in α-, γ- and liquid solutions. The free energy of cementite and of ϵ-carbide and their solubilities in α-Fe are calculated from equilibrium data. Both are metastable at all temperatures with respect to graphite and its saturated solution in iron. Below 230°C the ϵ-carbide is more stable than cementite. The data indicate that cementite has a defect structure deviating from the stoichiometric formula Fe_3C.

The thermodynamic properties of cementite (assumed Fe_3C) up to 1000°K are summarized in Table V. Properties of the other phases 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 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.

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

$$\Delta G°(cal.) = 10520 - 4.21\,T \qquad [15].$$

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

$$\bar{G}_C^\gamma = \bar{G}_C°(\gamma, \text{inf. dil.}) + RT \ln z_C + 17660\,y \qquad [16].$$

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

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

$$\bar{G}_{Fe}(\text{austenite}) = G^\circ_{Fe}(\gamma) - 8830 y^2_C + RT \ln (1 - y_C) \qquad [17].$$

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

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

$$\Delta G^\circ(\text{cal}) = 5400 - 3.98 T \qquad [18]$$

and

$$\bar{G}_C(l) = \bar{G}^\circ_C(l, \text{inf. dil.}) + RT \ln z_C + (3.29 T + 15550) y_C \qquad [19].$$

From these it is evident that the heat of solution in calories is $5400 + 15550 y_C$ while the increase in entropy is $3.98 - 3.29 y_C - R \ln z_C$. For the liquid solution the partial molar free energy of iron is

$$\bar{G}_{Fe}(l) = G^\circ_{Fe}(l) - (1.65 T + 7770) y^2_C + RT \ln (1 - y_C) \qquad [20].$$

In α-δ-Fe the free energy of solution of C by Eq. [9] is

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

$$\Delta G^\circ(\text{cal}) = 25400 - 11.40 T \qquad [21].$$

The heat of solution is 25400 cal and the entropy increase is $11.40 - R \ln z_C$.

It is only in δ-Fe that the activity of Fe is appreciably different from unity and here the partial free energy is

$$\bar{G}_{Fe}(\delta) = G^\circ_{Fe}(\delta) - RT \ln (1 - y_C) \qquad [22].$$

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

$$2.4 Fe \, \alpha + C(gr) = Fe_{2.4}C(\epsilon) \qquad [13]$$

$$\Delta G^\circ = 4850 - 2.50 T.$$

The free energy of cementite in the α-range varies rapidly with temperature as shown in Table V and a linear equation is not recommended. It is also variable in the γ-range as shown in Fig. 7. In view of our ignorance of its composition an approximate linear equation is justified, assuming the formula Fe_3C in the range $1000°-1421°K$:

$$3Fe(\gamma) + C(gr) = Fe_3C$$
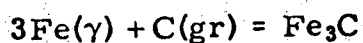
$$\Delta G° = 2685 - 2.625\,T \qquad\qquad [14]$$

Its average heat of formation from γ-Fe is therefore 2685 cal and its entropy is 2.625 units less than that of its elements.

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FIGURE TITLES

Fig. 1. Portion of the phase diagram Fe-C. Metastable γ-range and system

Fe-Fe$_3$C shown by dashed lines. Curie temperature dotted.

Fig. 2. Activity coefficient of carbon in liquid iron. Lines Eq.[7] Δ graphite

solubility; + gas equilibrium; $\square$ 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$_3$C 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. Free energy of the reaction $3Fe(\gamma) + C(graph) = Fe_3C$.

Assumed formula: Fe$_3$C.

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

Assumed formula: Fe$_3$C.

Fig. 9. Solubilities in α-Fe; line for ϵ and solid line for Fe$_3$C from free energy

data.

Fig. 10. Activities in cementite-saturated austenite. For a compound Fe$_n$C

a straight line is found if n = 4 or if n increases from 3 to about 3.6.

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	γ-Solidus			Liquidus	
°C	%C	y_C	a_C	%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]	-	-	-	-	-

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[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]	$Fe_{2.4}C$[c] ϵ
738	214		
727		218	
700	130	160	
650	64	102	
600	29	57	
550	11.9	28	
500	4.4	13	
450	1.4	5.7	
400	0.38	2.3	
350	0.08	.75	1.3
300	0.014	.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° | $3Fe(\alpha) + C(gr) = Fe_3C$ | | |
					$\Delta G_T^°$	$\Delta H_T^°$	$\Delta S_T^°$
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.
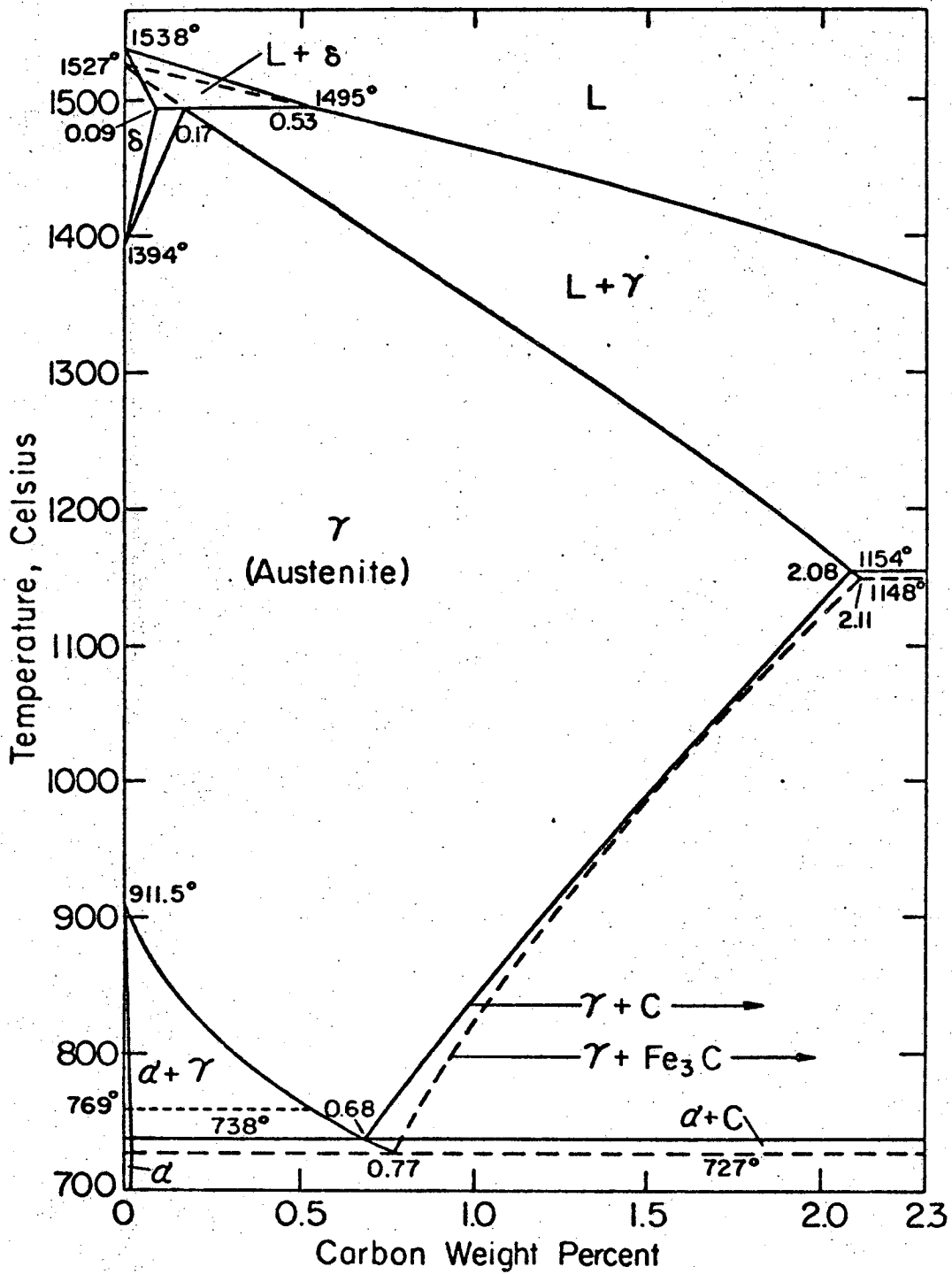
Fig. 1 Portion of the phase diagram.

XBL713-6588
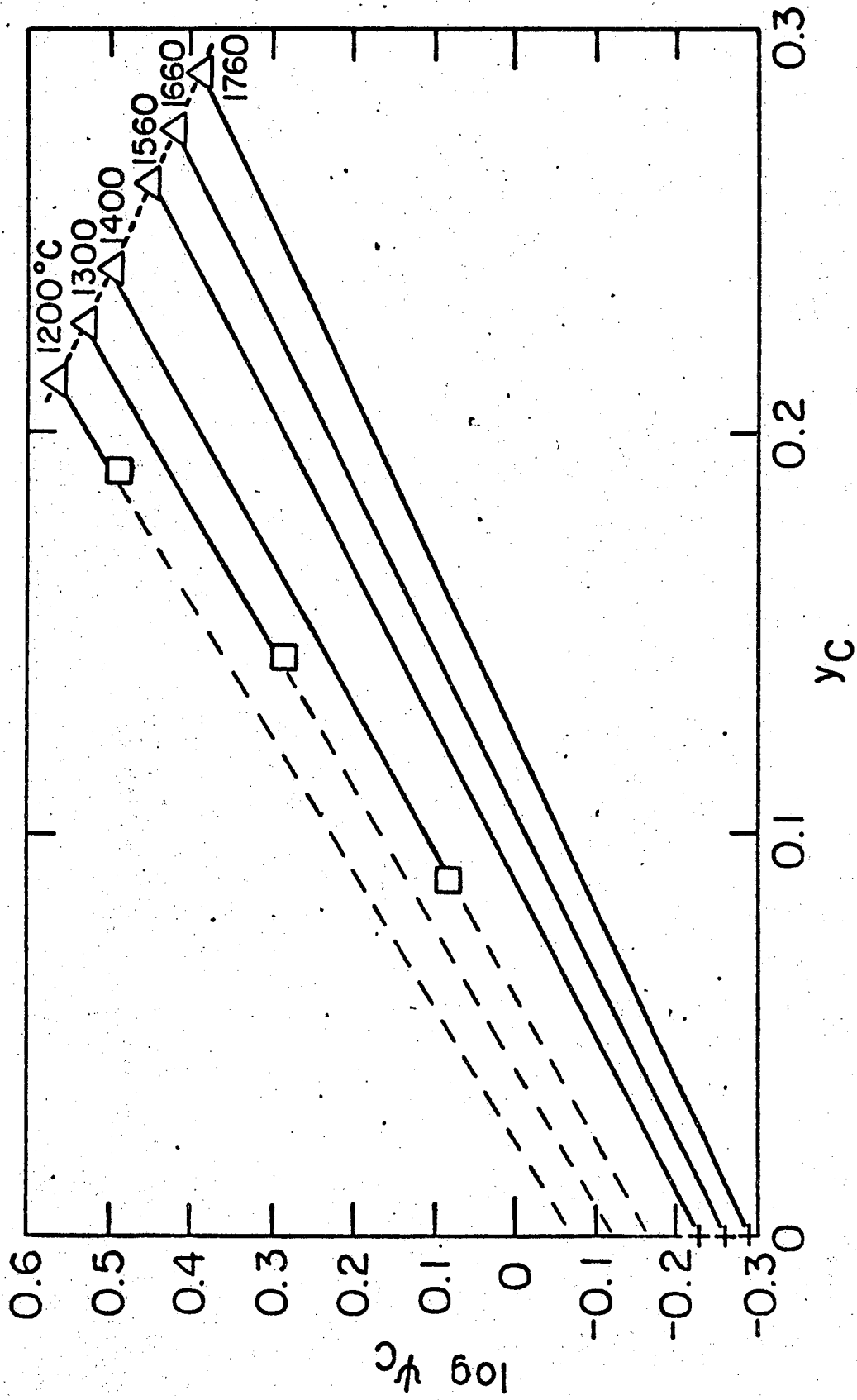
Fig. 2 Activity coefficient of Carbon in Liquid Iron.

XBL713-6589
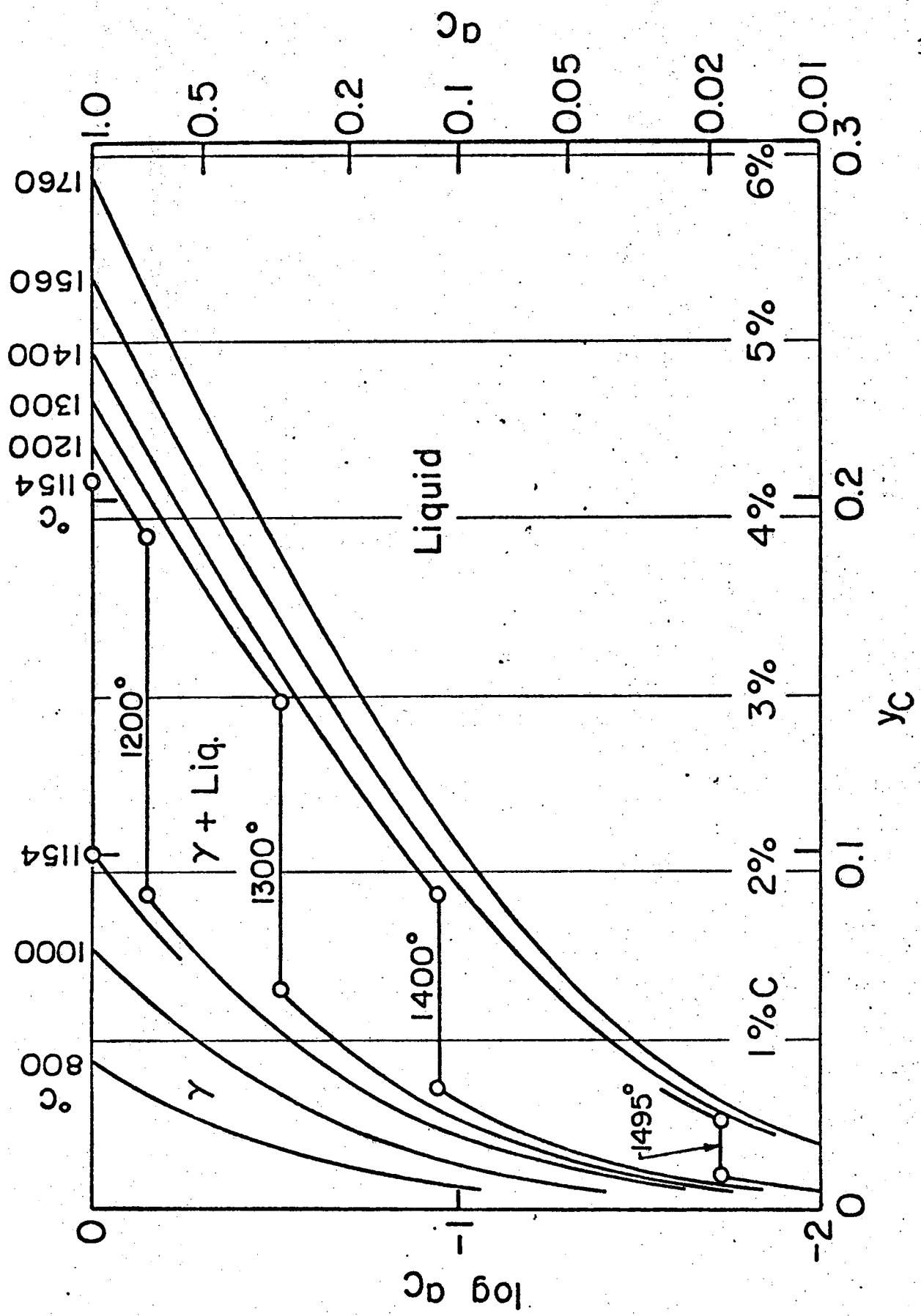
Fig.3—Activity of Carbon in Y and Liquid Iron.
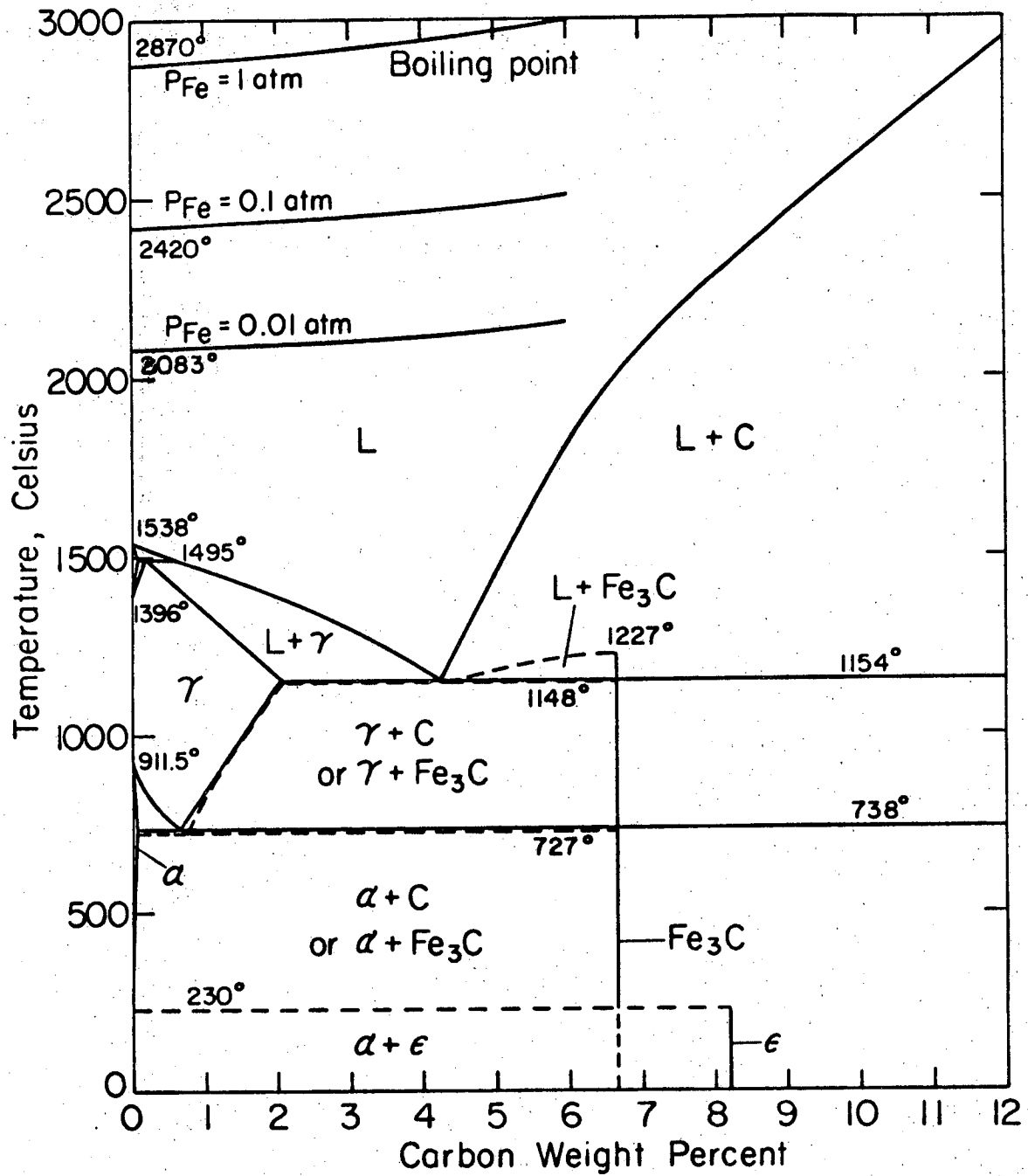
XBL 713-6590

Fig. 4 The iron-carbon phase diagram.

XBL713-6591
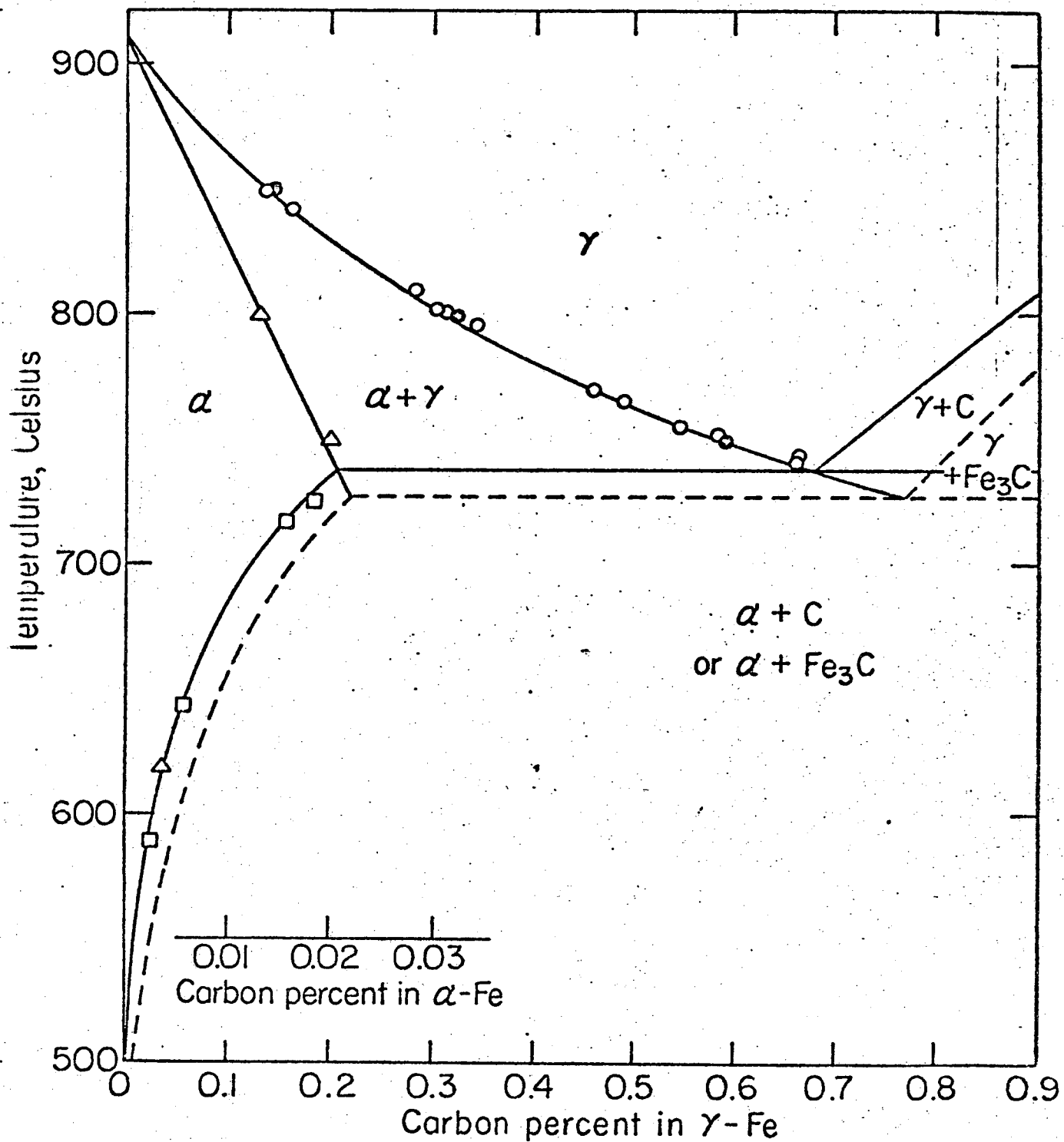
Fig. 5 Equilibria involving α-Ferrite.
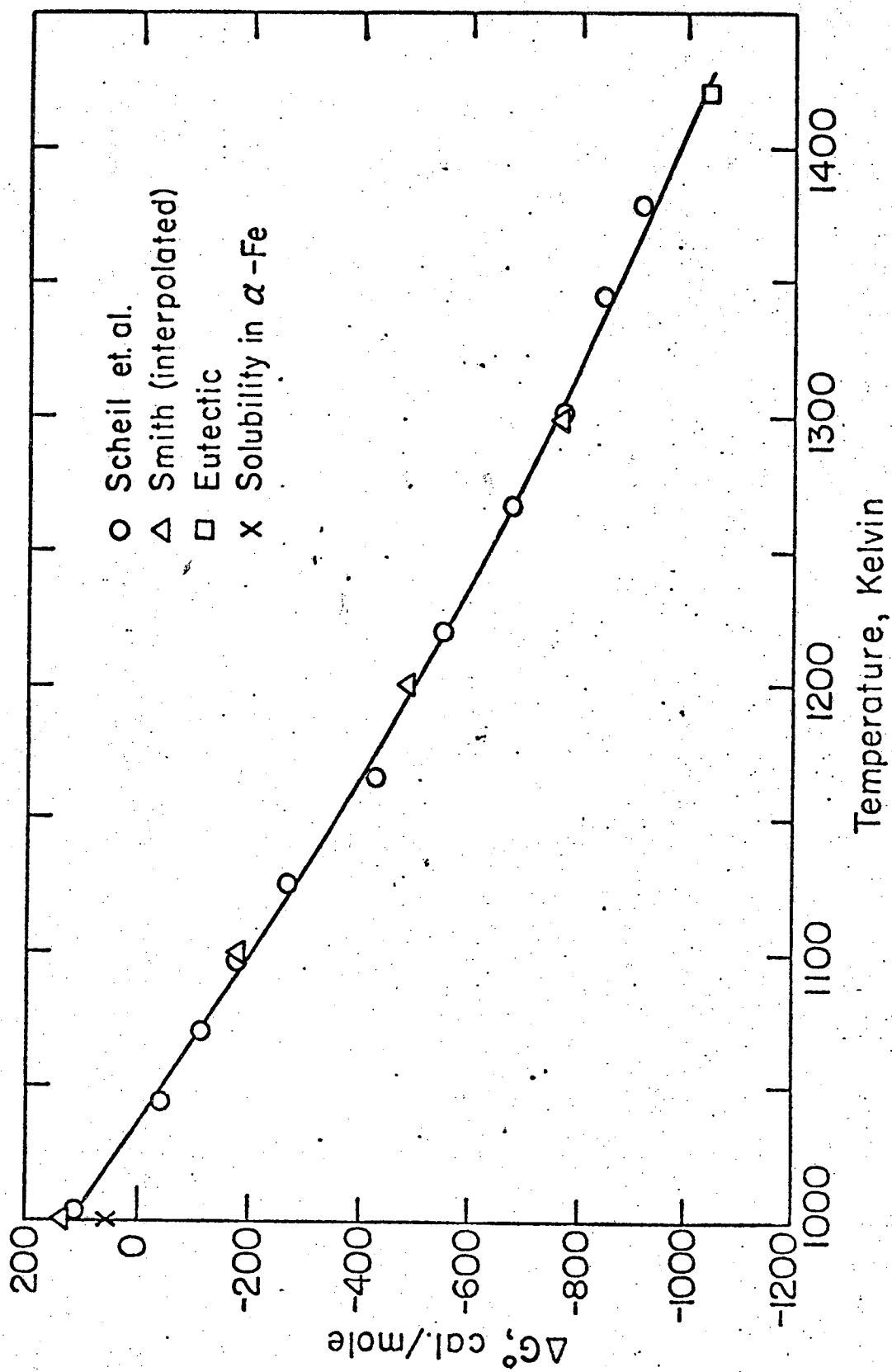
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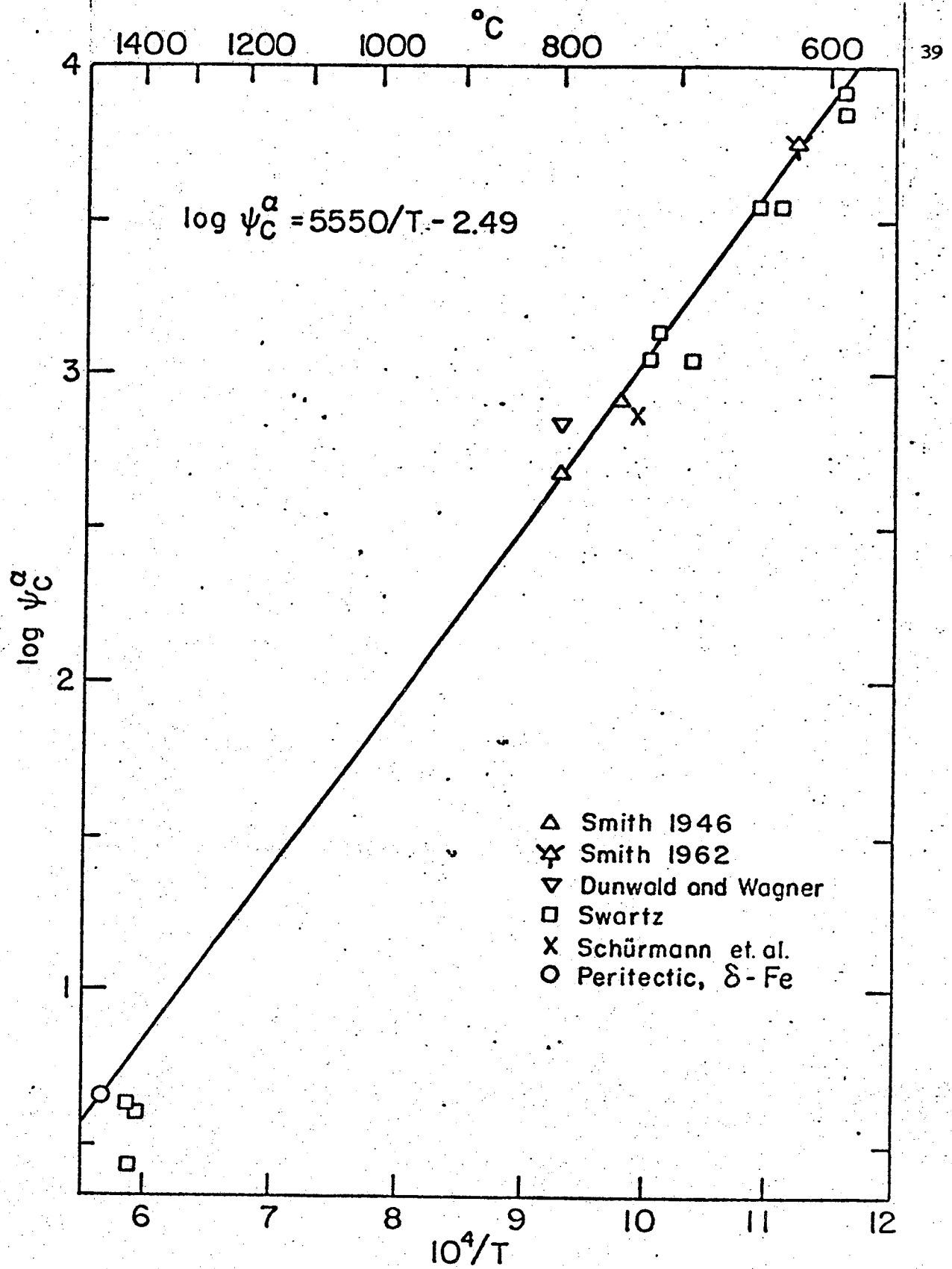
Fig. 6 Activity coefficient of Carbon in α-δ Iron.

XBL713-6593

Fig. 7 Free energy of the reaction $3Fe(\gamma) + C(graph) = Fe_3C$.
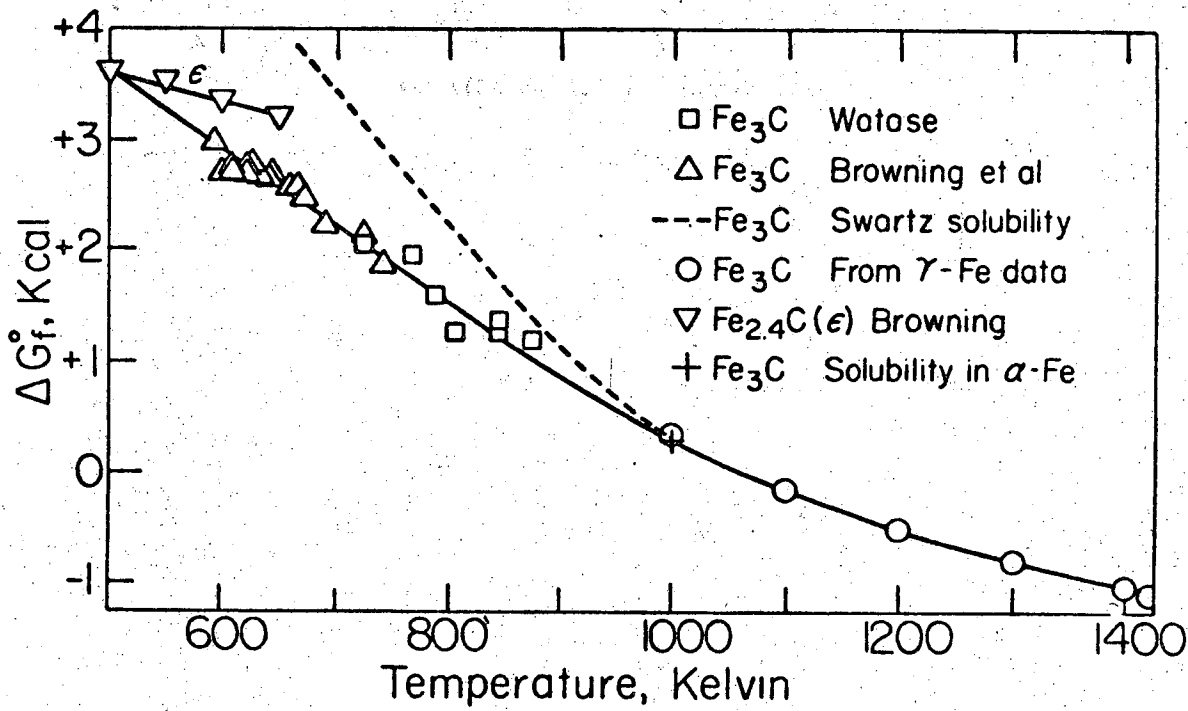
XBl 713-6594

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

XBL713-6595
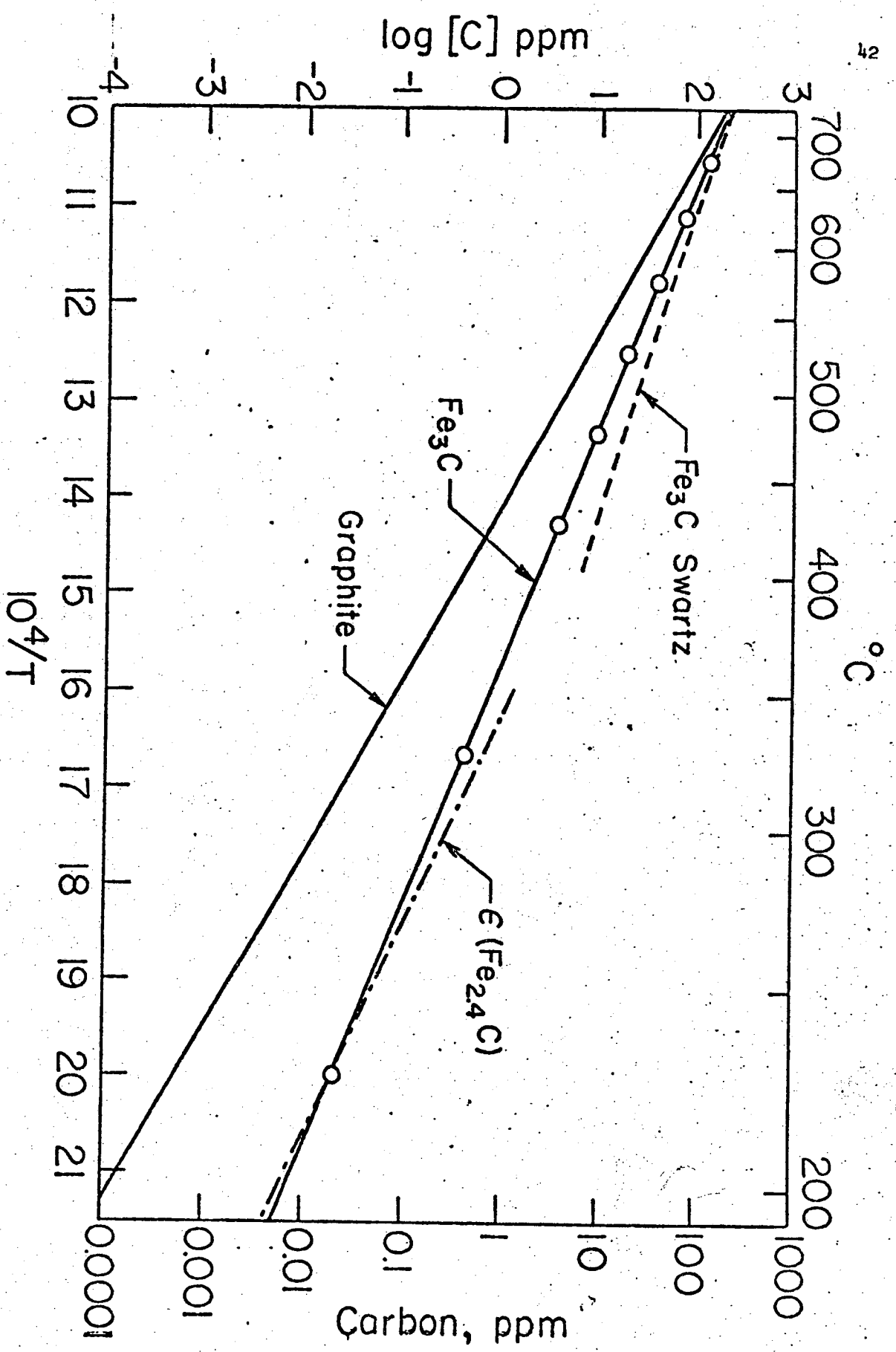
Fig.9 Solubilities in α-Fe.

Fig. 10 Activities in Cementite - saturated Austenite.

XBL713-6602