Thermodynamics and Phase Diagram of the Fe-C System

JOHN CHIPMAN

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 \( \alpha \rightarrow \gamma \) equilibrium are shown to agree with measured values of the activity of iron in the solid and liquid solutions and the thermodynamic properties of pure iron. Of all the reported carbides of iron only two may be studied under equilibrium conditions. The solubilities of cementite and of \( \chi \)-carbide in \( \alpha \)-Fe are deduced from measured equilibria. Both are metastable at all temperatures with respect to graphite and its saturated solution in iron. The \( \chi \)-carbide becomes more stable than cementite below about 230°C. Certain published data on \( \epsilon \)-carbide permit an estimate of its free energy as a precipitate during the aging process.

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 Fe-C 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 \( \gamma \)-solubilities by Benz and Elliott\(^3\) but omitted the nearly simultaneous publication of data on the liquidus by Buckley and Hum-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 Wünnning\(^7\) 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 \( \alpha \)-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 pct by recent studies of Ferrier and Olette\(^10\) and of Morris, Foerster, Schulz, and Zellars.\(^11\) The heat capacity of the solid, particularly in the \( \gamma \)-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°C 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.

I) THE AUSTENITE FIELD

The fcc 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

\[
C + 2H_2 = CH_4 \quad [1]
\]

\[
C + CO_2 = 2CO \quad [2]
\]

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\(^1\) et al.: ex-

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cept at the highest carbon concentrations) and of Ban-ya 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[28] 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[27] and of Schürmann, Schmidt, and Wegener. [28] 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

\[ a_c = \frac{n_C}{n_{Fe} - n_C} = \frac{y_C}{1 - y_C} = z_C \]  

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

\[ \ln \psi_C = \ln \psi_C^0 + \theta_C y_C \]  

where \( \psi_C^0 \) is its value at infinite dilution and \( \theta_C \) is an interaction coefficient, both being functions of temperature.

In their plot of \( \log K \) vs \( 1/T \) they found that a straight line based on data at 900° to 1150°C fell outside the 2σ limits at 1300°C. 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°C data. For this reason a simpler equation closely approximating line A of Ref. 8 will be used here for all compositions and temperatures (1968 scale) within the austenite field:

\[ \log a_C^\gamma = -(1930/T)y_C^2 + \log (1 - y_C) \]  

The solubility of graphite in austenite is readily calculated from Eq. [5] by setting \( a_C^\gamma \) equal to unity. Two other kinds of data are also available: the direct measurements of Wells[28] and of Gurry[24] and a downward extrapolation of the solidus line of Benz and Elliott[7] to the eutectic temperature. All of these data are in rather good agreement and average values are shown in Table 1. 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 Fig. 1.

**Table 1. Solubility of Graphite and Cementite in Austenite**

<table>
<thead>
<tr>
<th>Temp, °C</th>
<th>Graphite</th>
<th>Cementite</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( y_C )</td>
<td>Pct C</td>
</tr>
<tr>
<td>727*</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>738t</td>
<td>0.0320</td>
<td>0.56</td>
</tr>
<tr>
<td>800</td>
<td>0.0408</td>
<td>0.87</td>
</tr>
<tr>
<td>900</td>
<td>0.0561</td>
<td>1.19</td>
</tr>
<tr>
<td>1000</td>
<td>0.0725</td>
<td>1.53</td>
</tr>
<tr>
<td>1100</td>
<td>0.0896</td>
<td>1.89</td>
</tr>
<tr>
<td>1148t</td>
<td>0.0996</td>
<td>2.08</td>
</tr>
<tr>
<td>1154t</td>
<td>0.0990</td>
<td>2.08</td>
</tr>
</tbody>
</table>

* Cementite eutectoid.
† Graphite eutectoid.
‡ Cementite eutectic.
§ Graphite eutectic.

Fig. 1—Portion of the phase diagram Fe-C. Metastable γ-range and system Fe-Fe₃C shown by dashed lines. Curie temperature dotted.

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**II) THE γ-LIQUID EQUILIBRIUM**

The solidus line of Benz and Elliott[7] and a portion of the liquidus line of Buckley and Hume-Rothery[4] corrected to the 1968 scale are shown in Fig. 1. The solidus has been given a slight inflection with downward curvature near its lower end to conform to the data of Ban-ya et al. Both lines are superior in accuracy to those of earlier investigators but are strongly supported by the earlier work of Adcock.[28] The liquidus line includes a dotted extension to the calculated[27] melting point of γ-Fe. Interpolated values are listed in Table II and the entire liquidus line appears in Fig. 4. The activity of carbon at any temperature is the same at the liquidus and solidus compositions. Values calculated from Eq. [5] are included in the table.

\[ \log a_C^\gamma = 2300/T - 0.920 + (3860/T)y_C \]  

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