A Thermodynamic Analysis of the Fe-C and Fe-N Phase Diagrams

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The experimental information on the Fe-C and Fe-N phase diagrams is evaluated in order to be able to recalculate the phase diagrams in close agreement with the experimental information available. Analytical expressions for the Gibbs energy of pure iron in the bcc and liquid states relative to the fcc state have been obtained by means of power series expansions. A set of parameters describing the Gibbs energy of the individual phases is presented.

The classical way to construct a phase diagram is by connecting the experimental points by hand. However, the equilibrium phase diagram of a system may be regarded as a manifestation of the thermodynamic properties of the system. A much more powerful way to construct the diagram is thus to analyze the experimental data in thermodynamic terms and, if possible, to combine the phase equilibrium information with thermochemical data. This method has been applied to the Fe-C system many times. The work by Darken and Gurry\(^1\) and by Benz and Elliott\(^1\) deserve mentioning. More recently, Harvig\(^2\) made a detailed evaluation of the solid equilibria and Chipman\(^3\) considered all the equilibria in the Fe-C system. However, the equations given by Chipman for the Gibbs energy functions of the individual phases do not quite reproduce the diagram he presents. Examples are given in Table I. The present work was started in order to obtain a self-consistent description of the Fe-C system.

Both Harvig and Chipman based their analyses on thermodynamic functions for pure iron tabulated by Orr and Chipman.\(^4\) Quite recently, Hillert and Jarl\(^6\) proposed the use of truncated power series expansions to obtain analytical expressions for the magnetic contribution to the Gibbs energy. Hillert and Jarl also evaluated an expression for the nonmagnetic contribution to the Gibbs energy of ferrite relative austenite in pure iron. When their expression was applied to the Fe-C system and combined with various carbon activity data, it was found to predict a two-phase region, \(\alpha + \gamma\), which is narrower than the experimental one by about 10 pct. The same type of examination was then made of the Fe-N system and a similar result was obtained.

The experimental information on the \(\alpha + \gamma\) two-phase field in these systems seems to be so well established that it is justified to adjust the description of the Gibbs energy for pure iron in order to obtain better agreement. It should be noticed that Hillert and Jarl evaluated their parameters to give agreement with the heat of transformation at the two \(\alpha/\gamma\) transition points in pure iron and that information is subject to some experimental uncertainty.

An analysis of the Fe-C system will now be presented which is based on the description of the magnetic contribution to the Gibbs energy of bcc-iron, given by Hillert and Jarl and on the experimental width of the \(\alpha + \gamma\) two-phase region. The evaluations will be similar to Harvig's but Chipman's choice of experimental data for the nonvariant solid-liquid phase equilibria will be used. An analysis of the Fe-N system will also be presented which follows closely the recent analysis of Hillert and Jarl.\(^7\) The 1968 temperature scale will be used.

GIBBS ENERGY OF PURE IRON

Inden\(^8\) has shown that the following types of expressions can describe the magnetic contribution to the specific heat of a ferromagnetic metal \(A\) with a rather good accuracy:

\[
\begin{align*}
c_A^\alpha & = K_A^\alpha R \ln \frac{1 + \tau^2}{1 - \tau^2} & \text{for } \tau < 1 \\
c_A^\beta & = K_A^\beta R \ln \frac{\tau^2 + 1}{\tau^2 - 1} & \text{for } \tau > 1
\end{align*}
\]

where \(\tau = T/T_C\), \(T_C\) being the Curie temperature, and \(K_A^\alpha\) and \(K_A^\beta\) are two constants characteristic of the element \(A\) in its ferromagnetic and paramagnetic states which are here denoted by \(\alpha\) and \(\beta\), respectively. The Gibbs energy will then be obtained by integrating Eqs.

\[
\begin{align*}
W_{\text{Pct Carbon in Ferrite}} & \quad W_{\text{Pct Carbon in Liquid}} \\
\text{Equilibrium} & \quad \text{Temperature, } ^\circ\text{C} & \quad \text{Temperature, } ^\circ\text{C} \\
\text{Metastable Eutectic} & \quad 1148 & \quad 4.30 & \quad 2.11 \\
\text{Chipman, reported} & \quad 1137 & \quad 4.21 & \quad 2.07 \\
\text{Chipman, recalculated} & \quad 1148 & \quad 4.31 & \quad 2.12 \\
\text{Present evaluation} & \quad 1154 & \quad 4.26 & \quad 2.09 \\
\text{Stable Eutectic} & \quad 1154 & \quad 4.26 & \quad 2.08 \\
\text{Chipman, reported} & \quad 1143 & \quad 4.17 & \quad 2.24 \\
\text{Chipman, recalculated} & \quad 1154 & \quad 4.26 & \quad 2.09 \\
\text{Present evaluation} & \quad 1149 & \quad 0.53 & \quad 0.17 & \quad 0.09 \\
\text{Present evaluation} & \quad 1488 & \quad 0.569 & \quad 0.172 & \quad 0.096 \\
\text{Present evaluation} & \quad 1495 & \quad 0.517 & \quad 0.167 & \quad 0.090 \\
\text{Metastable Eutectoid} & \quad 727 & \quad 0.77 & \quad 0.0218 \\
\text{Chipman, reported} & \quad 729 & \quad 0.742 & \quad 0.0223 \\
\text{Chipman, recalculated} & \quad 727 & \quad 0.766 & \quad 0.0210 \\
\text{Present evaluation} & \quad 738 & \quad 0.68 & \quad 0.0206 \\
\text{Present evaluation} & \quad 737 & \quad 0.689 & \quad 0.0214 \\
\text{Present evaluation} & \quad 739 & \quad 0.676 & \quad 0.0196
\end{align*}
\]

Table I. Nonvariant Equilibria in the Fe-C System According to Various Evaluations Using the 1968 Temperature Scale

Hillert and Jarl approximated Eqs. [1] and [2] with the first three terms in the MacLaurin series expansions:

\[
G = G_0 + \int_{T_0}^{T} cp\,dT - T \int_{T_0}^{T} (cp/T)\,dT.
\]

Since it is not possible to formulate the entropy part of the Gibbs energy in terms of elementary functions, it was approximated by using a different expression for the magnetic contribution to the Gibbs energy, above and below the Curie temperature respectively. The magnetic contribution thus approaches zero at high temperatures. The following relations then hold:

\[
c^A_{m}\beta = 2K^A_{Fe}R(T^2 + r^3/3 + r^{15}/5) \quad \text{for } r < 1 \quad [3]
c^A_{m}\beta = 2K^A_{Fe}R(r^6 + r^{15}/3 + r^{25}/5) \quad \text{for } r > 1. \quad [4]
\]

For the case of bcc-iron they thus obtained using \( T_C = 1043 \) K: \( K^A_{Fe} = 0.7504 \) and \( K^A_{Fe} = 1.073 \), yielding:

\[
\Delta G^m_{Fe} = -6507.4[(T/1043)^3/10 + (T/1043)^{15}/315 + (T/1043)^{24}/1500] \quad \text{(J/mol) for } T > 1043 \, \text{K} \quad [5]
\]

and

\[
\Delta G^m_{Fe} = -9177.4 + 9.719T - 3934.9[(T/1043)^3/6 + (T/1043)^{10}/135 + (T/1043)^{15}/600] \quad \text{(J/mol) for } T < 1043 \, \text{K} \quad [6]
\]

where \( \Delta G^m_{Fe} \) and \( \Delta G^m_{Fe} \) denote the magnetic contributions to the Gibbs energy above and below the Curie temperature respectively. The magnetic contribution thus approaches zero at high temperatures. The nonmagnetic part of the specific heat is often found to vary linearly with the temperature, provided that the temperature is sufficiently high above the Debye temperature:

\[c = \alpha + \beta T\]

The following relations then hold:

\[
G = A + BT - \alpha T \ln T - \beta/2T^2 \quad [7]
\]

\[
H = A + \alpha T + \beta/2T^2 \quad [8]
\]

where \( A \) and \( B \) are integration constants.

For the difference in Gibbs energy between the ferritic (bcc) and the austenitic (fcc) states we thus obtain:

\[
\Delta G^m_{Fe} - \Delta G^m_{Fe} = \Delta A + \Delta BT - \Delta \alpha T \ln T - \Delta \beta/2T^2 + \Delta G^m_{Fe}
\]

where the last term is calculated according to Eqs. [5] or [6]. The four adjustable parameters will now be evaluated in the following way. The transformation temperatures taken from Orr and Chipman and corrected to the 1968 temperature scale are 1185 and 1667 K. The condition that the difference in Gibbs energy between the two phases must vanish at the transformation temperatures gives two equations. The value at 1000 K of \( \Delta G^m_{Fe} - \Delta G^m_{Fe} = 338 \) J/mol proposed by Orr and Chipman has previously been successfully applied to describe the width of the \( \alpha + \gamma \) phase field in the Fe-C system. It was thus accepted in the present evaluation. The remaining condition, necessary in order to evaluate the parameters, was a least square fit to the enthalpies of transformation reported by Braun and Kohlhaas,\(^6\) 910 J/mol at 1185 K and 850 J/mol at 1667 K.

The following values were obtained:

\[
\Delta A = 1462.4 \quad (\text{J/mol})
\]

\[
\Delta B = -8.282 \quad (\text{J/mol})
\]

\[
-\Delta \alpha = 1.15 \quad (\text{J/mol})
\]

\[
-\Delta \beta/2 = -0.0064 \quad (\text{J/mol})
\]

The recalculated transformation enthalpies are 1011 J/mol at 1185 K and 825 J/mol at 1667 K. The value at 1667 K is in satisfactory agreement with the value of 836 J/mol chosen by Orr and Chipman, and 824 J/mol extrapolated from data by Morris, Foerster, Schultz and Zellars,\(^9\) and it is within the error limits of the experimental data by Braun and Kohlhaas. The value at 1185 K seems somewhat too high and it is outside the error limits of Braun and Kohlhaas. They reported 910 ± 20 J/mol. The value from Darken and Smith\(^9\) which was accepted by Orr and Chipman is 900 J/mol. On the other hand, the value falls inside the error limits for the value reported by Anderson and Hultgren,\(^10\) 941 ± 84 J/mol. Anyway, the high value was accepted for the present purpose.

The difference in Gibbs energy between the two crystalline phases of iron can now be calculated at all temperatures. The calculated values fall very close to those of Orr and Chipman. In the temperature range 500 to 1000 K the discrepancy is always less than 30 J/mol and in the range 1000 to 1800 K it is always less than 10 J/mol. The agreement with the results from Kaufman and Nesor\(^1\) is very good in the medium temperature range (i.e., 1100 to 1700 K). At lower temperatures both the present evaluation and the one presented by Orr and Chipman differ considerably from the results of Kaufman and Nesor. At \( T = 500 \) K the different authors give: (J/mol and J/mol K)

\[
\begin{align*}
\text{Orr and Chipman} & : & 3639 & \quad \text{8.24} \\
\text{Kaufman and Nesor} & : & 3150 & \quad \text{7.09}
\end{align*}
\]

For the entropy the following values were obtained:

\[
\begin{align*}
\Delta S^m_{Fe} & = 19.5 \quad (\text{J/mol K}) \\
\Delta S^m_{Fe} & = 16.6 \quad (\text{J/mol K})
\end{align*}
\]

The values from the present analysis fall rather close to those of Orr and Chipman. Below this temperature no values are available from Orr and Chipman. For the entropy difference Kaufman and Nesor give at \( T = 300 \) K: \( \Delta S^m_{Fe} = 6.56 \) J/mol K whereas the present evaluation gives 8.62 J/mol K. The discrepancy in entropy is closely connected to the discrepancies in transformation enthalpies mentioned above. It is possible that a better agreement with the experimental enthalpy of transformation at 1667 K and 1185 K could be obtained by using a different expression for the magnetic contribution to the difference in specific heat. In this connection it should be emphasized that the present author has made no attempt to account for the two different spin-states in the fcc form of iron. This special effect will yield a more complicated temperature dependency for the specific heat of \( \gamma \)-iron and was taken into account by Kaufman and Bernstein\(^1\) who treated it in terms of a so-called Schottky anomaly.