A Re-examination of the Thermodynamics of the Proeutectoid Ferrite Transformation in Fe-C Alloys

G. J. SHIFLET, J. R. BRADLEY, AND H. I. AARONSON

Three models of the statistical thermodynamics of interstitial solid solutions have been used to reevaluate the thermodynamics of the proeutectoid ferrite reaction. The models of Kaufman, Radcliffe and Cohen and of Lacher, Fowler and Guggenheim, which were employed in a previous study of this type, together with the model recently developed by McLellan and Dunn are used in conjunction with the extensive experimental data of Ban-ya, Elliott and Chipman, of Lobo and Geiger and of Dunn and McLellan on the activities of carbon in austenite and ferrite. Application of the McLellan and Dunn model and that of Lacher, Fowler and Guggenheim to carbon in austenite yields activities of carbon which are numerically indistinguishable and activities of iron which are mathematically identical. However, the new activity data have revealed important differences between the present calculations and those of Aaronson, Domian and Pound. An average carbon-carbon repulsion energy in austenite of 1925 cal/mole (8054 J/mole) was determined from the CO/CO_2 data of Ban-ya *et al.* However, the C-C interaction energy in ferrite was found to be opposite in sign but exhibited erratic variations with temperature despite the large amount of activity data available. The $\gamma/(\alpha + \gamma)$ phase boundary calculated from the new data differs significantly, at lower temperatures, from the best curves reported by Aaronson *et al.* The calculated $\alpha/(\alpha + \gamma)$ phase boundary also differs appreciably from the previous results and exhibits only limited agreement with the experimentally determined phase boundary. Calculation of the free energy change associated with the proeutectoid ferrite reaction and T_0-composition curves differs little from previous results; internal agreement among the new sets of curves, however, is much improved.

It has been over a decade since Aaronson, Domian and Pound (ADP)[1] employed several models of interstitial solid solutions in their study of the thermodynamics of the proeutectoid ferrite reaction in Fe-C alloys. At that time formalisms due to Zener,[2] Kaufman, Radcliffe and Cohen (KRC),[3,4] Darken and Smith,[5] and Lacher[6] and Fowler and Guggenheim (LFG)[7] were analyzed comparatively; the experimental data for the activities of carbon in austenite and in ferrite were limited to the exceptionally well regarded CO/CO_2 data of R. P. Smith.[8] These data, however, are adequately complete at only three temperatures. The present investigation, like that of ADP, was motivated in part by the need to predict thermodynamic properties of the proeutectoid ferrite reaction in ranges of composition and temperature where equilibrium data cannot be obtained. Such thermodynamic information constitutes a fundamental requirement for the interpretation of transformation kinetics studies performed in these temperature-composition ranges. It is also intended to establish a basis for future studies of the thermodynamics and kinetics of the proeutectoid ferrite reaction in Fe-C-*X* systems.

The statistical thermodynamics of interstitial solid solutions has been an area of much theoretical activity since the work of ADP, particularly on the part of R. B. McLellan and coworkers.[9-18] Of the many models considered by MeLellan for binary interstitial solid solutions, the widely used first order quasichemical treatment developed by McLellan and Dunn (MD)[11] is the most rigorous approach which they subsequently extended to encompass the statistical thermodynamics of Fe-C-*X* alloys and hence is the one which will be employed here. Concurrently with these theoretical studies, the base of data on the activity of C in γ and in α has been markedly expanded in the last decade. The data of Ban-ya, Elliott and Chipman (BEC)[19,20] on the activity of carbon in austenite, a_γ, of Dunn and McLellan[15] on the activity of carbon in ferrite, a_α, and of Lobo and Geiger[21,22] on both a_γ and a_α now provide extensive coverage of both the γ and the α regions of Fe-C alloys. This confluence of new theoretical and experimental studies both invites and requires a reexamination of the thermodynamics of the proeutectoid ferrite reaction in Fe-C alloys at this time. The quasichemical treatment of MD will be compared with the two most useful thermodynamic analyses previously employed by ADP, namely KRC and LFG, making full use of the activity data which has recently become available.

The KRC approach[13] considers an interstitial atom to exclude from occupancy by other interstitial atoms a number of nearest neighboring interstitial sites. This model was selected for reconsideration here primarily because of the algebraically simple form taken by the thermodynamic relationships of interest. The LFG treatment[6,7] represents a more refined approach aimed at resolving the problem of overlapping exclusion regions of nearby interstitials. Although the thermodynamic relationships derived from this model

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are considerably more complex and must often be analyzed by a trial and error procedure, the LFG formalism was concluded by ADP to be the best available at that time.

Aaronson, Domian and Pound[1] pointed out that the LFG treatment does not give the correct expression in the limit of infinite pairwise interaction energy between carbon atoms in austenite (w_γ). An improvement over the LFG model offered by the quasichemical model of McLellan and Dunn is that the resultant expression for the relative partial molar free energy of the solution corresponds correctly to that for complete blocking of neighboring interstitial sites at infinite C-C interaction energies.[11] As will be demonstrated, despite this significant theoretical refinement, application of the MD model to Fe-C alloys, where w_γ is relatively small, yields results identical to those for the LFG model. This is an unexpected outcome, particularly in view of the mathematically dissimilar forms of the interstitial (carbon) activity expressions of the two models. Accordingly, the main thrust of the present investigation cannot be directed toward a comparative examination of the LFG and MD models. Instead, emphasis will be placed upon making full use of the expanded base of activity data to compare present results with the best of those from ADP's work based upon the activity data of R. P. Smith.[8]

SUMMARY OF THE STATISTICAL THERMODYNAMIC MODELS

KRC considered the composition and temperature dependence of the activity of carbon in austenite, a_γ, in terms of a temperature independent number of excluded sites.[3] Darken and Smith[5] on the other hand, allowed the number of excluded sites to vary with temperature, yielding the following relationship:

$$\ln a_\gamma = \ln \frac{x_\gamma}{1-(14-12e^{-w_\gamma/RT})x_\gamma} + \frac{\Delta\bar{H}_\gamma - \Delta\bar{S}_\gamma^{xs}T}{RT} \qquad [1]$$

where x_γ = mole fraction of carbon in austenite, w_γ = pairwise interaction energy between adjacent carbon atoms in austenite, R = the gas constant, T = absolute temperature, and $\Delta\bar{H}_\gamma$ and $\Delta\bar{S}_\gamma^{xs}$ = the partial molar enthalpy and the partial molar nonconfigurational entropy of solution in austenite, respectively. The quantity $(14 - 12\exp(-w_\gamma/RT))$ represents the temperature dependence of the number of excluded sites.

A similar expression can be obtained for the activity of carbon in ferrite, a_α:

$$\ln a_\alpha = \ln \frac{x_\alpha}{3-(12-8e^{-w_\alpha/RT})x_\alpha} + \frac{\Delta\bar{H}_\alpha - \Delta\bar{S}_\alpha^{xs}T}{RT} \qquad [2]$$

where x_α, w_α, $\Delta\bar{H}_\alpha$ and $\Delta\bar{S}_\alpha^{xs}$ are as defined above, but now for ferrite.

The expression for the activity of carbon in austenite obtained from the LFG formalism was presented by ADP as:

$$\ln a_\gamma = 5\ln\frac{1-2x_\gamma}{x_\gamma} + \frac{6w_\gamma}{RT} + 6\ln\left\{\frac{[1-2(1+2J_\gamma)x_\gamma+(1+8J_\gamma)x_\gamma^2]^{1/2}-1+3x_\gamma}{[1-2(1+2J_\gamma)x_\gamma+(1+8J_\gamma)x_\gamma^2]^{1/2}+1-3x_\gamma}\right\} + \frac{\Delta\bar{H}_\gamma - \Delta\bar{S}_\gamma^{xs}T}{RT} \qquad [3]$$

where $J_\gamma = 1 - e^{-w_\gamma/RT}$. The corresponding equation for the activity of carbon in ferrite is:

$$\ln a_\alpha = 3\ln\frac{3-4x_\alpha}{x_\alpha} + \frac{4w_\alpha}{RT} + 4\ln\left\{\frac{[9-6x_\alpha(2J_\alpha+3)+(9+16J_\alpha)x_\alpha^2]^{1/2}-3+5x_\alpha}{[9-6x_\alpha(2J_\alpha+3)+(9+16J_\alpha)x_\alpha^2]^{1/2}+3-5x_\alpha}\right\} + \frac{\Delta\bar{H}_\alpha - \Delta\bar{S}_\alpha^{xs}T}{RT} \qquad [4]$$

where $J_\alpha = 1 - e^{-w_\alpha/RT}$.

McLellan and Dunn (MD) have developed a further refined model[11] based upon the first order formalism of Guggenheim[23] in which the partial molar free energy of solution is related to the pairwise interaction energy, w, between nearest neighbor interstitials. For the activity of the interstitial solute they write:

$$a = \frac{\theta/\beta}{1-\theta/\beta}\, e^{(\Delta\bar{H}-\Delta\bar{S}^{xs}T)/RT} \times\left\{\left(\frac{\theta/\beta}{1-\theta/\beta}\right)^2\left(\frac{1-\theta/\beta-\phi}{\theta/\beta-\phi}\right)\right\}^{-z/2} e^{zw/2RT} \qquad [5]$$

where

$$\phi = \frac{1-\{1-4(1-e^{-w/RT})\theta/\beta(1-\theta/\beta\}^{1/2}}{2(1-e^{-w/RT})}$$

and θ is the ratio of the number of moles of solute atoms to solvent atoms. In this equation β is the ratio of the number of interstitial to substitutional sites and z is the coordination number of the solvent lattice. Here, Eq. [7] of Ref. 11 has been altered to incorporate molar quantities and $(\Delta\bar{H} - \Delta\bar{S}^{xs}T)$ has been substituted for $\Delta\bar{G}_u$, the relative partial molar free energy of a solute atom in solution with respect to the pure solute.

Making the substitution $\theta = x/(1-x)$ and noting for a fcc lattice that $\beta = 1$ and $z = 12$, Eq. [5] can be rearranged to express the activity of carbon in austenite in a form similar to that of Eq. [3]:

$$\ln a_\gamma = 11\ln\frac{1-2x_\gamma}{x_\gamma} + \frac{6w_\gamma}{RT} + 6\ln\left\{\frac{[1-2(1+2J_\gamma)x_\gamma+(1+8J_\gamma)x_\gamma^2]^{1/2}-1+(1+2J_\gamma)x_\gamma}{[1-2(1+2J_\gamma)x_\gamma+(1+8J_\gamma)x_\gamma^2]^{1/2}-1+2J_\gamma+(1-4J_\gamma)x_\gamma}\right\} + \frac{\Delta\bar{H}_\gamma - \Delta\bar{S}_\gamma^{xs}T}{RT}. \qquad [6]$$

Similarly, for the activity of carbon in ferrite ($\beta = 3$, $z = 8$):

$$\ln a_\alpha = 7\ln\frac{3-4x_\alpha}{x_\alpha} + \frac{4w_\alpha}{RT} + 4\ln\left\{\frac{[9-6x_\alpha(3+2J_\alpha)+x_\alpha^2(9+16J_\alpha)]^{1/2}-3+x_\alpha(3+2J_\alpha)}{[9-6x_\alpha(3+2J_\alpha)+x_\alpha^2(9+16J_\alpha)]^{1/2}-3+6J_\alpha+x_\alpha(3-8J_\alpha)}\right\} + \frac{\Delta\bar{H}_\alpha - \Delta\bar{S}_\alpha^{xs}T}{RT}. \qquad [7]$$

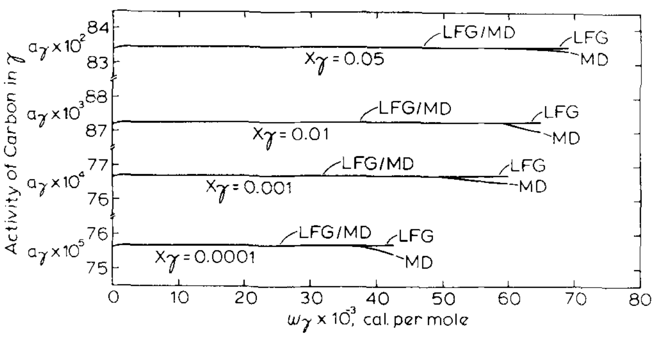

Fig. 1—w_γ *vs* a_γ. Comparison of Eq. [3]-LFG and Eq. [6]-MD for various values of x_γ.

Figure 1 compares the activities calculated from the expressions of LFG and MD (Eqs. [3] and [6]) as a function of w_γ. Although this is surely not apparent from a visual comparison of Eqs. [3] and [6], these relationships are found to be numerically the same for small values of w_γ. At large values, *e.g.*, w_γ = 30,000 cal/mole when x_γ = 0.0001, the activity calculated from the MD expressions begins to fall while that of LFG remains essentially constant. The value of w_γ at which the two relationships initially diverge increases with increasing solute concentration. However, the carbon-carbon interaction energy in Fe-C austenite is more than an order of magnitude smaller than this value. Hence the LFG and MD models should yield identical results.

INTERACTION ENERGIES IN AUSTENITE

The procedure for determining the interaction energies of carbon in austenite entails plotting ln a_γ *vs* the x_γ and w_γ dependent portions of the right hand side of Eqs. [1], [3] or [6]. The best estimate of this energy is arrived at by changing w_γ in small increments until a least squares slope of unity is obtained. Values of w_γ were secured in this manner for each temperature at which sufficient activity data were available. Figures 2(*a*) and (*b*) show typical plots constructed from the data of Ban-ya, Elliott and Chipman[20] at 1000°C and from that of Lobo and Geiger[22] at 800°C for each of the three models. Interaction energies, temperatures and the sources of the data are summarized in Table I for the KRC model and in Table II for the LFG and MD models. All values of w_γ are seen to be positive, indicating a repulsion energy between carbon atoms in austenite, in agreement with previous results.[1,5] From Tables I and II two important features should be noted concerning inconsistencies in the results obtained from the two data sources: the data of Ban-ya, Elliott and Chipman, established by equilibrium with CO/CO_2 mixtures, yield values of w_γ and w_γ/T significantly greater than those calculated from Lobo and Geiger's CH_4/H_2 data; and while w_γ and w_γ/T do not seem to be independent of temperature they do not show any systematic temperature dependence. ADP noted similar though smaller differences separating the w_γ's determined from the two different gas equilibria and concluded that the CO/CO_2 data may be more accurate. The present results from the CO/CO_2 data are significantly higher than the values determined by ADP from the CO/CO_2 data of R. P. Smith.[8] The average values of w_γ for the KRC and LFG/MD models are 1405 and 1925 cal/mole (5878 and 8054 J/mole) respectively for the CO/CO_2 data compared with 375 and 415 cal/mole (1569 and 1736 J/mole) for the CH_4/H_2 data. These values are so clearly incompatible that the results from each body of data must hereafter be analyzed separately.

DETERMINATION OF $\Delta\bar{H}_\gamma$ AND $\Delta\bar{S}_\gamma^{xs}$

The intersection of the least squares lines (*e.g.*, Fig. 2) with the ln a_γ axis represents the last term in Eqs. [1], [3] and [6] and thus values of $\Delta\bar{H}_\gamma$ and $\Delta\bar{S}_\gamma^{xs}$

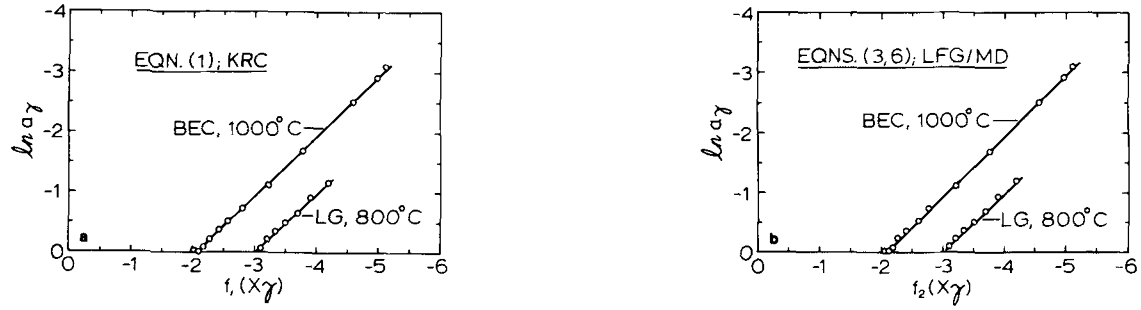

Fig. 2—Variation of activity of carbon in austenite with carbon content at 1000 and 800°C. Experimental data taken from Ban-ya, Elliott and Chipman (BEC)[20] at 1000°C and Lobo and Geiger (LG)[22] at 800°C.

(*a*) $f_1(x_\gamma) = \ln\{x_\gamma/[1 - (14 - 12e^{-w_\gamma/RT})x_\gamma]\}$,

$$(b)\, f_2(x_\gamma) = \ln\left\{\frac{([1-2(1+2J_\gamma)x_\gamma + (1+8J_\gamma)x_\gamma^2]^{1/2} - (1+3x_\gamma)^6(1-2x_\gamma)^5 e^{6w_\gamma/RT}}{([1-2(1+2J_\gamma)x_\gamma + (1+8J_\gamma)x_\gamma^2]^{1/2} + 1 - 3x_\gamma)^6 x_\gamma^5}\right\}$$

for LFG, and

$$f_2(x_\gamma) = \ln\left\{\frac{([1-2(1+2J_\gamma)x_\gamma + (1+8J_\gamma)x_\gamma^2]^{1/2} - 1 + (1+2J_\gamma)x_\gamma)^6(1-2x_\gamma)^{11} e^{6w_\gamma/RT}}{([1-2(1+2J_\gamma)x_\gamma + (1+8J_\gamma)x^2]^{1/2} - 1 + 2J_\gamma + (1-4J_\gamma)x_\gamma)^6 x_\gamma^{11}}\right\}$$

for MD, where $J_\gamma = 1 - e^{-w_\gamma/RT}$.

Table I. Evaluation of w_γ From Eq. [1] (KRC)

Source of a_γ Data, Ref. No.	Temp, °C	Gas Mixture	w_γ	$w_\gamma - \sigma$	$w_\gamma + \sigma$	w_γ/T	Source of Constants
20	1300	CO/CO_2	1565	1320	1825	0.995	Present Investigation
19	1150	CO/CO_2	1310	1210	1410	0.920	Present Investigation
20	1000	CO/CO_2	1355	1240	1475	1.064	Present Investigation
20	900	CO/CO_2	1395	1245	1560	1.189	Present Investigation
8	800	CO/CO_2	1060	1000	1120	0.988	ADP
8	1000	CO/CO_2	1250	1200	1300	0.982	ADP
8	1200	CO/CO_2	1405	1040	1770	0.954	ADP
22	848	CH_4/H_2	302	265	350	0.272	Present Investigation
22	813	CH_4/H_2	390	355	425	0.359	Present Investigation
22	800	CH_4/H_2	345	325	365	0.322	Present Investigation
22	783	CH_4/H_2	455	425	485	0.432	Present Investigation
8	800	CH_4/H_2	960	905	1020	0.363	ADP
8	1000	CH_4/H_2	1370	1335	1405	0.418	ADP

Table II. Evaluation of w_γ From Eqs. [3, 6] (LFG/MD)

Source of a_γ Data, Ref. No.	Temp, °C	Gas Mixture	w_γ	$w_\gamma - \sigma$	$w_\gamma + \sigma$	w_γ/T	Source of Constants
20	1300	CO/CO_2	1960	1600	2375	1.246	Present Investigation
19	1150	CO/CO_2	1965	1825	2110	1.381	Present Investigation
20	1000	CO/CO_2	1915	1735	2110	1.504	Present Investigation
20	900	CO/CO_2	1860	1635	2120	1.586	Present Investigation
8	800	CO/CO_2	1310	1215	1410	1.221	ADP
8	1000	CO/CO_2	1695	1590	1805	1.332	ADP
8	1200	CO/CO_2	1615	1195	2030	1.096	ADP
22	848	CH_4/H_2	335	285	385	0.299	Present Investigation
22	813	CH_4/H_2	430	390	475	0.396	Present Investigation
22	800	CH_4/H_2	380	355	405	0.354	Present Investigation
22	783	CH_4/H_2	515	480	555	0.488	Present Investigation
8	800	CH_4/H_2	960	905	1020	0.895	ADP
8	1000	CH_4/H_2	1370	1335	1405	1.076	ADP

Table III. Evaluation of $\Delta\bar{H}$ and $\Delta\bar{S}^{xs}$

Equation Defining a_γ vs x_γ Relationship	Gas Mixtures	$\Delta\bar{H}_\gamma$	$\Delta\bar{S}^{xs}_\gamma$	Source of a_γ Data, Ref. No.	Source of Constants
[3] LFG	CO/CO_2	10525	-2.34	8	ADP
[3, 6] LFG/MD	CO/CO_2	9213	3.22	19, 20	Present Investigation
[1] KRC	CO/CO_2	10630	4.12	8	ADP
[1] KRC	CO/CO_2	9228	3.19	19, 20	Present Investigation
[3, 6] LFG/MD	CH_4/H_2	8465	1.89	22	Present Investigation
[1] KRC	CH_4/H_2	8535	1.90	8	ADP
[1] KRC	CH_4/H_2	8365	1.79	22	Present Investigation

Table IV. Evaluation of w_α From Eq. [2] (KRC)

Source of a_γ Data, Ref. No.	Temp, °C	w_α	w_α/T	Source of Constants
15	825	-16130	14.69	Present Investigation
15	800	-11245	10.48	Present Investigation
8	800	-9605	8.95	ADP
21	797	-8255	7.71	Present Investigation
8	750	-7650	7.48	ADP
15	735	-13090	12.99	Present Investigation
21	727	-6465	6.47	Present Investigation
21	702	-14235	14.60	Present Investigation

can be solved for simultaneously from the intercept at any two temperatures. Average values are included in Table III together with previous results. In most cases, the values of $\Delta\bar{H}_\gamma$ and $\Delta\bar{S}^{xs}_\gamma$ from the present investigation for each model and gas mixture are in good agreement with their counterparts reported by ADP. Both studies indicate higher values of $\Delta\bar{H}_\gamma$ and $\Delta\bar{S}^{xs}_\gamma$ for the CO/CO_2 data than for the CH_4/H_4 data. Also, application of the new activity data in the present investigation yields values nearly identical to those previously obtained for a given type of gas mixture, particularly CO/CO_2.

INTERACTION ENERGIES IN FERRITE

Equations [2], [4] and [7] have been applied to the experimental data of Dunn and McLellan[15] and Lobo and Geiger[21] on the activity of carbon in ferrite at a total of fourteen temperatures ranging from 575 to 848°C to determine w_α in the same manner used to establish w_γ. Negative values of w_α, indicating an attractive interaction energy between nearest neighboring carbon atoms in ferrite resulted at each temperature for which a least squares slope of unity was attained. The inability to obtain the correct theoretical slope at some temperatures may be due to the "intercept effect" investigated by Smith.*[8] Table IV lists values of w_α at seven temperatures including those determined by ADP using the KRC model (Eq. [2]). Similar results were obtained for the LFG/MD formalisms. Due to the very wide range and irregular variation with temperature of the w_α values, a single plausible one which could be incorporated in Eqs. [2], [4] and [7] for subsequent use cannot presently be suggested. Using the data of Smith[8] for a_α at two temperatures ADP were also unable to arrive at a single value of w_α. To circumvent the problem of determining w_α, the following approximation for the activity of carbon in ferrite is used:

$$\ln a_\alpha = \ln x_\alpha + \frac{26{,}800 - 12.29\,T}{RT}. \qquad [8]$$

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*This effect results from plots of CH_4/H_2 ratio against chemically analyzed weight percent carbon which are straight lines that intersect the abcissa at some positive rather than zero wt pct C. The intercept is then subtracted from each measured pct C. The ratio of the intercept to the measured pct carbon is often substantial as a result of the greatly limited solubility of carbon in ferrite.

The constants now used in this equation are the $\Delta\overline{H}_\alpha$ and $\Delta\overline{S}_\alpha^{xs}$ values obtained by Lobo and Geiger[21] from their a_α data at eight temperatures.*

DETERMINATION OF a_{Fe_γ}

KRC[3] derived the following expression for the activity of iron in austenite, a_{Fe_γ}:

$$\ln a_{\mathrm{Fe}_\gamma} = \frac{1}{z_\gamma - 1} \ln\left(\frac{1 - z_\gamma x_\gamma}{1 - x_\gamma}\right) \qquad [9]$$

where $z_\gamma = 14 - 12e^{-w_\gamma/RT}$. [9a]

By applying the Gibbs-Duhem relationship to the LFG model, Eq. [3], ADP obtained:

$$\ln a_{\mathrm{Fe}_\gamma} = 5\ln\left(\frac{1 - x_\gamma}{1 - 2x_\gamma}\right) + 6\ln\left\{\frac{1 - 2J_\gamma + (4J_\gamma - 1)x_\gamma - [1 - 2(1 + 2J_\gamma)x_\gamma + (1 + 8J_\gamma)x_\gamma^2]^{1/2}}{2J_\gamma(2x_\gamma - 1)}\right\}. \qquad [10]$$

In the Appendix, the Gibbs-Duhem equation is applied to the MD model. Unexpectedly, the result obtained is identical in all respects to Eq. [10], further illustrating the similarity of the LFG and the MD models.

THE $\gamma/\alpha + \gamma$ OR Ae3 PHASE BOUNDARY

The $\gamma/(\alpha + \gamma)$ or Ae3 phase boundary may now be calculated for the KRC and LFG/MD models based upon the equality of the partial molar free energy of Fe at the $\alpha/(\alpha + \gamma)$ and $\gamma/(\alpha + \gamma)$ phase boundaries, *i.e.*, $F_{\mathrm{Fe}_\alpha}^{\alpha\gamma} = F_{\mathrm{Fe}_\gamma}^{\gamma\alpha}$. Writing the partial molar free energies in terms of activities and setting $a_{\mathrm{Fe}_\alpha}^{\alpha\gamma} = 1$ gives:[3]

$$\Delta F_{\mathrm{Fe}}^{\gamma\rightarrow\alpha} = RT\ln a_{\mathrm{Fe}_\gamma}^{\gamma\alpha} \qquad [11]$$

Replacing x_γ in Eqs. [9] and [10] by $x_\gamma^{\gamma\alpha}$, the Ae3 composition, and substituting these expressions for $\ln a_{\mathrm{Fe}_\gamma}^{\gamma\alpha}$ in Eq. [11], $x_\gamma^{\gamma\alpha}$ may be calculated as a function of temperature for each of the models.

For the KRC model (Eq. [9]):

$$x_\gamma^{\gamma\alpha} = \frac{1 - e^\phi}{z_\gamma - e^\phi} \qquad [12]$$

where

$$\phi = \frac{(z_\gamma - 1)\Delta F_{\mathrm{Fe}}^{\gamma\rightarrow\alpha}}{RT} \qquad [12a]$$

and z_γ is defined in Eq. [9a].

ADP applied the same approach to the LFG formalism, deriving the following equation which they solved for $x_\gamma^{\gamma\alpha}$ by trial and error:

$$\Delta F_{\mathrm{Fe}}^{\gamma\rightarrow\alpha} = RT\left[5\ln\left(\frac{1 - x_\gamma^{\gamma\alpha}}{1 - 2x_\gamma^{\gamma\alpha}}\right) + 6\ln\left\{\frac{1 - 2J_\gamma + (4J_\gamma - 1)x_\gamma - [1 - 2(1 + 2J_\gamma)x_\gamma + (1 + 8J_\gamma)x_\gamma^2]^{1/2}}{2J_\gamma(2x_\gamma - 1)}\right\}\right]. \qquad [13]$$

Equation [13] also applies to the MD model as the a_{Fe_γ} expressions for the LFG and MD approaches are identical. The values of $\Delta F_{\mathrm{Fe}}^{\gamma\rightarrow\alpha}$ used in Eqs. [12] and [13] are calculated from an empirical relationship[24] based upon data tabulated by Fisher.[25]

Equations [12] and [13] have been used to calculate Ae3 curves for the KRC and LFG/MD models using the average values of w_γ from each source of activity data. These phase boundaries, labeled accordingly, are shown in Fig. 3. Also included in Fig. 3 is the experimental Ae3 from Hansen.[26] Nearly all of the calculated curves are in good agreement with the experimental Ae3. At lower temperatures, where a direct comparison with experiment is not presently feasible, however, the calculated curves increasingly diverge from one another, exhibiting differences greater than a factor of three at 200°C. Because the LFG/MD analysis can accommodate overlap of carbon repulsion shells, which becomes important at the high carbon concentrations of the Ae3 when extrapolated to low temperatures, whereas that of KRC cannot, the former is preferred. As previously indicated, the w_γ obtained from the CO/CO₂ data of Ban-ya *et al* appears more accurate than the much lower value calculated from that of Lobo and Geiger, hence the BEC-based LFG/MD Ae3 should be more nearly correct. Note that the increase in w_γ from the 1500 cal/mole computed by ADP from the activity data of R. P. Smith[8] to the 1925 cal/mole which characterizes the considerably more extensive activity data of BEC decreases the value of the extrapolated Ae3 at 200°C by ca. 4.5 at. pct C. In view of the exponential dependence of the diffusivity of carbon in austenite upon carbon content, such a difference will clearly result in a major effect upon calculations of the growth kinetics of bainite.

THE $\alpha/\alpha + \gamma$ PHASE BOUNDARY

Of particular importance to studies of the mechanism of the bainite reaction is the estimation of the maximum metastable equilibrium proportion of carbon in ferrite formed at temperatures below the eutectoid temperature. At equilibrium the partial molar free energies of carbon in ferrite at the $\alpha:\gamma$ boundary and of austenite at the $\gamma:\alpha$ boundary are equal, *i.e.*, $\overline{F}_{C_\gamma}^{\gamma\alpha} = \overline{F}_{C_\alpha}^{\alpha\gamma}$. Therefore the $\alpha/(\alpha + \gamma)$ phase boundary composition, $x_\alpha^{\alpha\gamma}$, may be calculated for each model by equating Eq. [8] to the appropriate expression for $\ln a_\gamma$ (Eq. [1], [3] or [6]) into which the correct value of $x_\gamma^{\gamma\alpha}$ has been substituted for x_γ. Based upon the Darken and Smith[5] form of the KRC relationship for a_γ, Eq. [1],

$$\ln x_\alpha^{\alpha\gamma} = \frac{1 - e^\phi}{e^\phi(z_\gamma - 1)} + \frac{(\Delta\overline{H}_\gamma - 26{,}800) - T(\Delta\overline{S}_\gamma^{xs} - 12.29)}{RT} \qquad [14]$$

where z_γ and ϕ are defined by Eqs. [9a] and [12a]. From the LFG activity expression, Eq. [3],

$$\ln x_\alpha^{\alpha\gamma} = 5\ln\frac{1 - 2x_\gamma^{\gamma\alpha}}{x_\gamma^{\gamma\alpha}} + 6\ln\left(\frac{\delta - 1 + 3x_\gamma^{\gamma\alpha}}{\delta + 1 - 3x_\gamma^{\gamma\alpha}}\right)$$

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*The authors wish to thank Dr. T. Wada of Climax Molybdenum Co. for bringing to their attention an error in the original version of equation [8].

$$+\frac{(\Delta\bar{H}_\gamma - 26{,}800) - T(\Delta\bar{S}^{xs}_\gamma - 12.29) + 6w_\gamma}{RT} \qquad [15]$$

where $\delta = [1 - 2(1 - 2J_\gamma)x^{\gamma\alpha}_\gamma + (1 + 8J_\gamma)x^{\gamma\alpha^2}_\gamma]^{1/2}$. [16]

Similarly, from the MD equation for a_γ, Eq. [6],

$$\ln x^{\alpha\gamma}_\alpha = 11\ \ln\frac{1 - 2x^{\gamma\alpha}_\gamma}{x^{\gamma\alpha}_\gamma} + 6\ln\left\{\frac{\delta - 1 + (1 + 2J_\gamma)x^{\gamma\alpha}_\gamma}{\delta - 1 + 2J_\gamma + (1 - 4J_\gamma)x^{\gamma\alpha}_\gamma}\right\} + \frac{(\Delta\bar{H}_\gamma - 26{,}800) - T(\Delta\bar{S}^{xs}_\gamma - 12.29) + 6w_\gamma}{RT}. \qquad [17]$$

Values of $\Delta\bar{H}_\gamma$ and $\Delta\bar{S}^{xs}_\gamma$ listed in Table III for the present investigation and average values of w_γ for Lobo and Geiger and BEC data from Tables I and II have been used in Eqs. [14], [15] and [17] to calculate $x^{\alpha\gamma}_\alpha$ over the same range of temperature as was used for $x^{\gamma\alpha}_\gamma$ (Fig. 4). Also included in Fig. 4 are the experimentally determined $\alpha/(\alpha + \gamma)$ phase boundary from Hansen[26] and the curve calculated by ADP from the LFG formalism using a constant value of $J_\gamma = 0.474$. Over much of the temperature range all four of the curves for the present investigation are found to lie at lower carbon contents than the experimental curve and also that calculated by ADP. The curves computed using the constants derived from the activity activity data of BEC are shifted downward relative to the other two curves, in only slightly poorer agreement with the experimental results. The maximum value of x for each of the phase boundaries is seen to fall in the range of 600 to 650°C. The curve calculated by ADP is in very good agreement with the experimental results. However, the choice of an averaged, temperature independent value of J_γ ($J_\gamma = 1 - \exp(-w_\gamma/RT)$) for this calculation, while necessary when sufficient reliable data on the activity of carbon in austenite were unavailable, no longer seems appropriate. Hence the acquisition of better data appears to have exposed the limited accuracy of the available theories.

THE FREE ENERGY CHANGE OF THE PROEUTECTOID FERRITE REACTION, $\Delta F^{\gamma\rightarrow\alpha+\gamma_1}$

This approach is based upon the standard chemical thermodynamic expression:

$$\Delta F = RT\left[x_\gamma \ln\frac{a^{\gamma\alpha}_\gamma}{a_\gamma} + (1 - x_\gamma)\ln\frac{a^{\gamma\alpha}_{\text{Fe}_\gamma}}{a_{\text{Fe}_\gamma}}\right] \qquad [18]$$

Appropriate $\ln a$ expressions are now substituted into this relationship. For KRC the free energy expression obtained by ADP is:

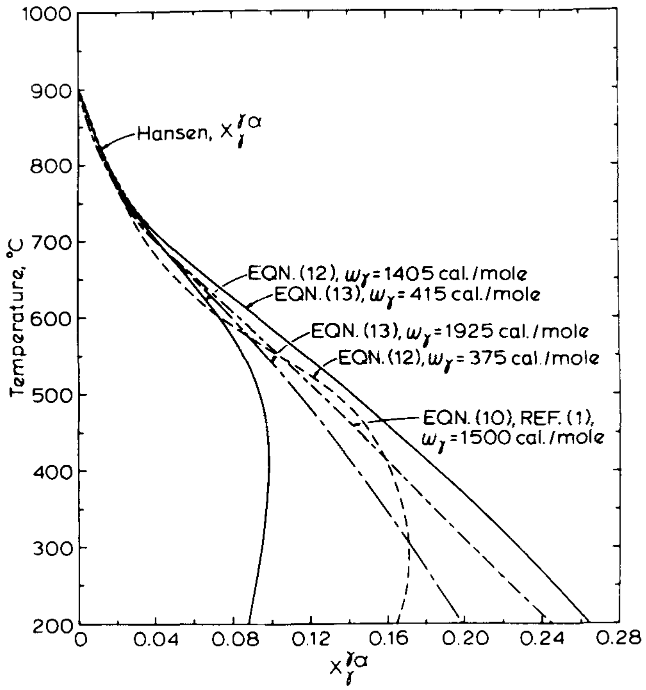

Fig. 3—$x^{\gamma\alpha}_\gamma$ *vs* temperature from Eq. [12]-KRC or Darken-Smith statistics and Eq. [13]-LFG/MD statistics with optimum LFG curve of ADP for comparison.

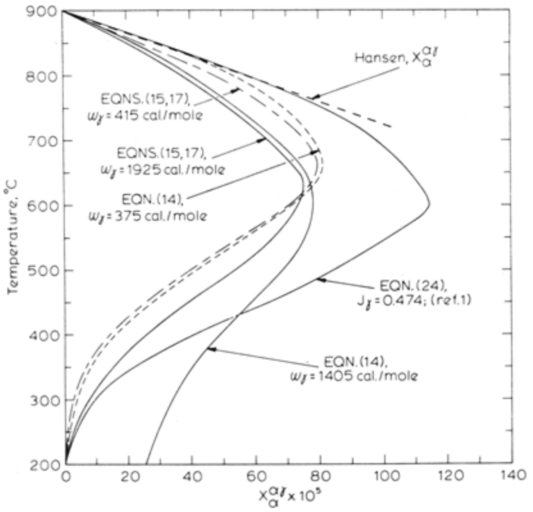

Fig. 4—$x^{\alpha\gamma}_\alpha$ *vs* temperature. Equation [14]-KRC or Darken-Smith statistics, and Eqs. [15, 17]-LFG/MD statistics with optimum LFG curve of ADP for comparison.

$$\Delta F^{\gamma\rightarrow\alpha+\gamma_1} = RT\left\{x_\gamma\left[\ln\frac{(1 - e^\phi)(1 - z_\gamma x_\gamma)}{(z_\gamma - 1)(x_\gamma e^\phi)}\right] + \frac{(1 - x_\gamma)}{(z_\gamma - 1)}\ln\left[\frac{(1 - x_\gamma)e^\phi}{1 - z_\gamma x_\gamma}\right]\right\} \qquad [19]$$

where ϕ and z_γ are as defined for Eq. [14]. For LFG the corrected version of the equation written by ADP is:

$$\Delta F^{\gamma\rightarrow\alpha+\gamma_1} = RT\left\{x_\gamma\left(5\ \ln\left[\frac{(1 - 2x^{\gamma\alpha}_\gamma)x_\gamma}{(1 - 2x_\gamma)x^{\gamma\alpha}_\gamma}\right] + 6\ \ln\left[\frac{(\delta^{\gamma\alpha}_\gamma - 1 + 3x^{\gamma\alpha}_\gamma)(\delta_\gamma + 1 - 3x_\gamma)}{(\delta_\gamma - 1 + 3x_\gamma)(\delta^{\gamma\alpha}_\gamma + 1 - 3x^{\gamma\alpha}_\gamma)}\right]\right) + (1 - x_\gamma)\left(5\ln\left[\frac{(1 - x^{\gamma\alpha}_\gamma)(1 - 2x_\gamma)}{(1 - x_\gamma)(1 - 2x^{\gamma\alpha}_\gamma)}\right] + 6\ln\left[\frac{(1 - 2J_\gamma + (4J_\gamma - 1)x^{\gamma\alpha}_\gamma - \delta^{\gamma\alpha}_\gamma)(2J_\gamma(2x_\gamma - 1))}{(1 - 2J_\gamma + (4J_\gamma - 1)x_\gamma - \delta_\gamma)(2J_\gamma(2x^{\gamma\alpha}_\gamma - 1))}\right]\right)\right\}. \qquad [20]$$

Likewise for MD the free energy of the proeutectoid reaction can be written as:

$$\Delta F^{\gamma\rightarrow\alpha+\gamma_1} = RT\left\{x_\gamma\left(11\ln\left[\frac{(1-2x_\gamma^{\gamma\alpha})x_\gamma}{(1-2x_\gamma)x_\gamma^{\gamma\alpha}}\right] + 6\ln\left[\frac{(-1+x_\gamma^{\gamma\alpha}(1+2J_\gamma)+\delta_\gamma^{\gamma\alpha})(2J_\gamma-1+x_\gamma(1-4J_\gamma)+\delta_\gamma)}{(-1+x_\gamma(1+2J_\gamma)+\delta_\gamma)(2J_\gamma-1+x_\gamma^{\gamma\alpha}(1-4J_\gamma)+\delta_\gamma^{\gamma\alpha})}\right]\right)\right.$$
$$\left.+(1-x_\gamma)\left(5\ln\left[\frac{(1-x_\gamma^{\gamma\alpha})(1-2x_\gamma)}{(1-x_\gamma)(1-2x_\gamma^{\gamma\alpha})}\right] + 6\ln\left[\frac{(1-2J_\gamma+(4J_\gamma-1)x_\gamma^{\gamma\alpha}-\delta_\gamma^{\gamma\alpha})(2J_\gamma(2x_\gamma-1))}{(1-2J_\gamma+(4J_\gamma-1)x_\gamma-\delta_\gamma)(2J_\gamma(2x_\gamma^{\gamma\alpha}-1))}\right]\right)\right\}. \quad [21]$$

Here $\delta_\gamma^{\gamma\alpha}$ is given by Eq. [16] and δ_γ is obtained from the same equation by substituting x_γ for $x_\gamma^{\gamma\alpha}$.

The free energy changes calculated from Eqs. [19] to [21] at $x_\gamma = 0.02$, a representative carbon content, are shown as a function of temperature in Fig. 5. Note that the ΔF values calculated during this investigation fall largely below those reported by ADP, at the lower temperatures, by amounts which increase with decreasing temperature. These differences become appreciable despite the fact that the presence of the solute concentration terms in logarithmic form considerably reduces effects from any source upon ΔF. In the concentrations of phase boundaries, on the other hand, the presence of exponentials in the controlling equations considerably magnifies the influence of any differences.

$\Delta F^{\gamma\rightarrow\alpha}$ AND THE T_0 TEMPERATURE

Following the procedure of KRC and ADP the free energy of the ferrite phase of composition x_γ can be written as:

$$F^\alpha = RT[x_\alpha \ln x_\alpha + (1-x_\alpha)\ln(1-x_\alpha)] + x_\alpha(F_c^G + 26{,}800 - 12.29T) + (1-x_\alpha)F_{\text{Fe}}^\alpha \quad [22]$$

where F_c^G = free energy of pure graphite and F_{Fe}^α = free energy of pure α-iron at temperature T. For

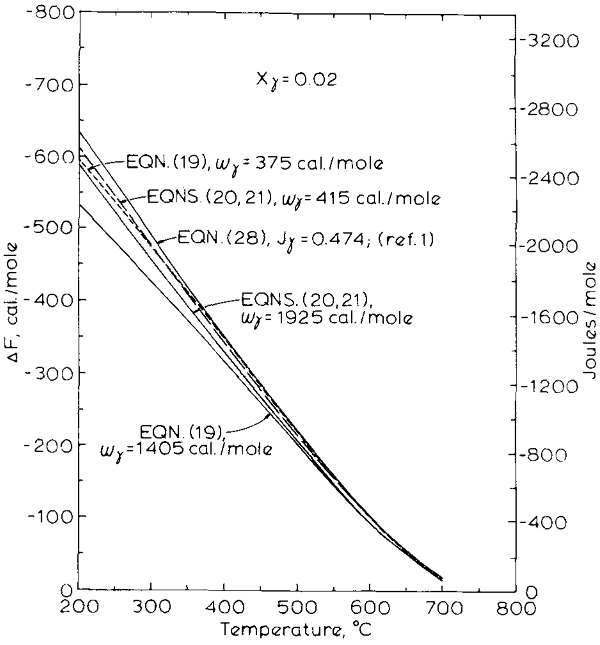

Fig. 5—$\Delta F^{\gamma\rightarrow\alpha+\gamma_1}$ from 700 to 200°C from Eq. [19]-KRC, Eq. [20]-LFG, Eq. [21]-MD and Eq. [28] of ADP (based on LFG) for comparison.

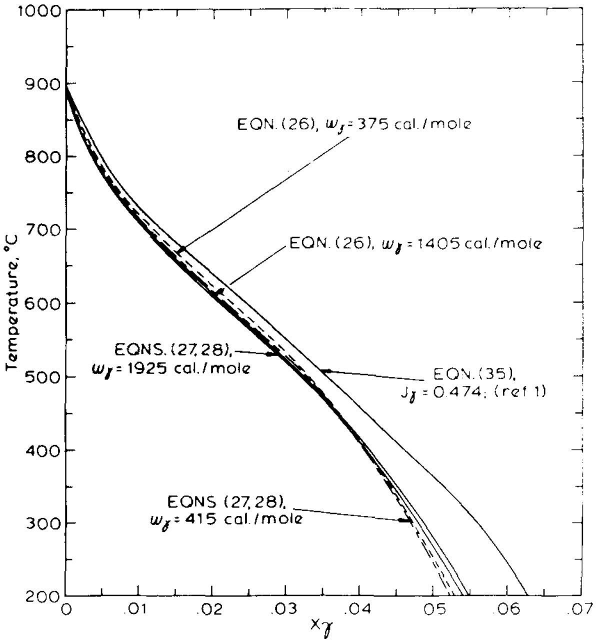

Fig. 6—T_0 for transformation of austenite to ferrite of the same composition as a function of mole fraction of carbon. Equation [35] of ADP, via LFG, included for comparison.

the Darken and Smith form of the KRC model the free energy of austenite of composition x_γ is given by:

$$F^\gamma = \frac{RT}{z_\gamma - 1}[(1-z_\gamma x_\gamma)\ln(1-z_\gamma x_\gamma) - (1-x_\gamma) \times \ln(1-x_\gamma) + x_\gamma(z_\gamma-1)\ln x_\gamma] + x_\gamma(\Delta\bar{H}_\gamma - \Delta\bar{S}_\gamma^{xs}T + F_c^G) + (1-x_\gamma)F_{\text{Fe}}^\gamma \quad [23]$$

where F_{Fe}^γ = free energy of pure γ-iron at temperature T and $\Delta\bar{H}_\gamma$ and ΔS_γ^{xs} are taken from Table III. For the LFG formalism:

$$F^\gamma = 5RT[(1-x_\gamma)\ln(1-x_\gamma) - (1-2x_\gamma)\ln(1-2x_\gamma) - x_\gamma \ln x_\gamma] + 6RT\left[x_\gamma \ln\left(\frac{\delta_\gamma - 1 + 3x_\gamma}{\delta_\gamma + 1 - 3x_\gamma}\right) + (1-x_\gamma)\ln\left(\frac{1-2J_\gamma+(4J_\gamma-1)x_\gamma-\delta_\gamma}{2J_\gamma(2x_\gamma-1)}\right)\right] + x_\gamma(\Delta\bar{H}_\gamma - \Delta\bar{S}_\gamma^{xs}T + 6w_\gamma + F_c^G) + (1-x_\gamma)F_{\text{Fe}}^\gamma \quad [24]$$

and for the MD model:

$$F^\gamma = RT\Big[-11x_\gamma \ln x_\gamma + (16x_\gamma - 5)\ln(1-2x_\gamma)$$

$$
- 6x_\gamma \ln\left(\frac{2J_\gamma - 1 + x_\gamma(1 - 4J_\gamma) + \delta_\gamma}{-1 + x_\gamma(1 + 2J_\gamma) + \delta_\gamma}\right) + 5(1 - x_\gamma)
$$

$$
\times \ln(1 - x_\gamma) + 6(1 - x_\gamma)
$$

$$
\times \ln\left(\frac{1 - 2J_\gamma + (4J_\gamma - 1)x_\gamma - \delta_\gamma}{2J_\gamma(2x_\gamma - 1)}\right)\Bigg]
$$

$$
+ x_\gamma(\Delta\bar{H}_\gamma - \Delta\bar{S}_\gamma^{xs}T + 6w_\gamma + F_C^G) + (1 - x_\gamma)F_{\mathrm{Fe}}^\gamma . \quad [25]
$$

The T_o temperature is that temperature at which ferrite and austenite of the same composition, x, are in unstable equilibrium *i.e.* $\Delta F^{\gamma\rightarrow\alpha} = F^\alpha - F^\gamma = 0$. From the KRC approach, this free energy change is:

$$
\Delta F^{\gamma\rightarrow\alpha} = \frac{RT}{z_\gamma - 1}[z_\gamma(1 - x)\ln(1 - x) - (1 - 2x)
$$

$$
\times \ln(1 - 2x)] + x[(26{,}800 - \Delta\bar{H}_\gamma)
$$

$$
- (12.29 - \Delta\bar{S}_\gamma^{xs})T\,] + (1 - x)\Delta F_{\mathrm{Fe}}^{\gamma\rightarrow\alpha}. \quad [26]
$$

For LFG the corrected free energy equation given by ADP is:

$$
\Delta F^{\gamma\rightarrow\alpha} = RT\Bigg\{6\ln\left[\frac{x(\delta + 1 - 3x)}{(\delta - 1 + 3x)}\right]
$$

$$
- 6(1 - x)\ln\left[\frac{1 - 2J_\gamma + (4J_\gamma - 1)x - \delta}{2J_\gamma(2x - 1)}\right]
$$

$$
-4(1-x)
$$

$$
\times \ln(1 - x) + 5(1 - 2x)\ln(1 - 2x)\Bigg\}
$$

$$
+ x[(26{,}800 - \Delta\bar{H}_\gamma) - (12.29 - \Delta\bar{S}_\gamma^{xs})T
$$

$$
- 6w_\gamma\,] + (1 - x)\Delta F_{\mathrm{Fe}}^{\gamma\rightarrow\alpha}. \quad [27]
$$

And for the MD model:

$$
\Delta F^{\gamma\rightarrow\alpha} = RT\Bigg\{12x\ln x - 4(1 - x)\ln(1 - x)
$$

$$
- 6(1 - x)\ln\left[\frac{1 - 2J_\gamma + (4J_\gamma - 1)x - \delta}{2J_\gamma(2x - 1)}\right]
$$

$$
+ 6x\ln\left[\frac{2J_\gamma - 1 + x(1 - 4J_\gamma) + \delta}{-1 + x(1 + 2J_\gamma) + \delta}\right]
$$

$$
- (16x - 5)\ln(1 - 2x)\Bigg\} + x[(26{,}800 - \Delta\bar{H}_\gamma)
$$

$$
- (12.29 - \Delta\bar{S}_\gamma^{xs})T - 6w_\gamma\,]
$$

$$
+ (1 - x)\Delta F_{\mathrm{Fe}}^{\gamma\rightarrow\alpha}. \quad [28]
$$

$T_o - x$ curves were obtained for each model by setting Eqs. [26] to [28] equal to zero and solving for x as a function of temperature by trial and error. All four of these curves, plotted in Fig. 6, follow similar paths, but lie somewhat below that of ADP. At a composition of about $x_\gamma = 0.035$ this difference becomes more pronounced with further increases in carbon content.

DISCUSSION

The distinguishing feature of the quasichemical statistical thermodynamic description of interstitial solid solutions developed by McLellan and Dunn[11] relative to that of Lacher[6] and Fowler and Guggenheim[7] is that it produces the correct expression, corresponding to complete blocking of all nearest neighbor interstitial sites, in the limit of an infinite pairwise repulsion energy between solute atoms. However, it has been shown here that application of these two models to solutions of carbon in iron, where the interaction energies are relatively small, yields numerically identical results. An appreciable difference between the values of the activity of carbon in austenite calculated from these two models is found only for values of the interaction energy, w_γ, orders of magnitude greater than the best available estimate.

It must be mentioned that Alex and McLellan have extended the first-order approach to include the effects of second[17] and third[18] nearest neighbor solute interactions. They have shown that at high temperatures even strong interactions of these types have negligible effect on the partial configurational entropy and only a somewhat larger influence upon the partial enthalpy. On this basis, consideration of second and third order solute interactions is expected to have no significant effect upon the present results.

The a_γ *vs* x_γ data of Ban-ya, Elliott and Chipman[19,20] obtained by means of CO/CO_2 equilibria and those of Lobo and Geiger[22] determined from CH_4/H_2 gas mixtures were applied to the LFG/MD model to secure essentially temperature-independent average values of w_γ of 1925 and 415 cal/mole. The 1925 cal/mole result is in very good agreement with that of 1970 cal/mole (8242 J/mole) obtained by Dunn and McLellan[13] from the Ban-ya *et al*[19,20] data using a different technique. Their w_γ was also found to be effectively temperature independent. Both results are in reasonable agreement with, though surely an improvement upon, the $w_\gamma = 1500$ cal/mole (6276 J/mole) reported by ADP from application of the LFG treatment to the more limited CO/CO_2 data of R. P. Smith.[8] The much lower w_γ obtained from the CH_4/H_2 data of Lobo and Geiger[22] again supports the view[1,3] that results obtained from this gas mixture are subject to greater inaccuracies than those derived from CO/CO_2 mixtures.

Comparison of the calculated Ae3 using $w_\gamma = 1925$ cal/mole with that reported by ADP for the LFG model demonstrates clearly the importance of the *ca.* 400 calories per mole (1674 J/mole) difference in w_γ, particularly at lower temperatures, where the carbon concentration of the Ae3 is lowered as much as 4.5 at. pct at 200°C. This change will markedly affect the interpretation of growth kinetics studies performed at such temperatures.

Efforts to determine a temperature independent interaction energy between carbon atoms in ferrite, w_α, were unsuccessful, thereby paralleling the experience of ADP despite the markedly increased amount of data on the activity of carbon in ferrite now available. However, the conclusions that w_α is a binding energy[1,27,28] was strongly supported. The difficulty may now be tentatively suggested to be in the inability of the various models employed to cope with an attractive interaction between adjacent interstitial atoms. The inability to arrive at a satisfactory estimate of w_α may be responsible to a large extent for the disturbing lack of agreement between the calculated and experimental $\alpha/(\alpha + \gamma)$ phase boundaries which the present investigation has demonstrated.

An improved estimate of the free energy change attending the proeutectoid ferrite reaction as a function of temperature has been obtained and compared with the values reported by ADP. The free energy change calculated during this study has been shown to fall increasingly below that of ADP with decreasing temperature.

Good agreement has been demonstrated among the four T_o-composition curves calculated during this investigation. The compatability of these results based upon differing models and a broad range of interaction energies firmly establishes a quite accurate T_o-composition curve. Differences between these and the previous results of ADP may be due largely to their need to use a temperature independent optimum value of $J = 1 - e^{-w/RT} = 0.474$ as a consequence of the limited amounts of reliable activity data then available.

CONCLUSIONS

The thermodynamics of the proeutectoid ferrite reaction have been reevaluated as a result of the recent availability of new data on the activity of carbon in austenite and ferrite and more sophisticated thermodynamic models of interstitial solid solutions. In particular the McLellan and Dunn (MD) quasichemical model is compared with the results from the Lacher and Fowler and Guggenheim (LFG) treatment reported in a parallel study in 1966 by Aaronson, Domian and Pound (ADP).

1) Although the activity expressions for the LFG and MD models are quite different in appearance, the activity of carbon in austenite evaluated in either approach is numerically the same until w_γ exceeds an unreasonably high value, *e.g.* at $w_\gamma = 30{,}000$ cal/mole (125,520 J/mole) when $x_\gamma = 0.0001$. In austenite w_γ is less than 2000 cal/mole (8368 J/mole), hence in its present application the new model of McLellan and Dunn becomes numerically indistinguishable from the older LFG formalism.

2) Application of the Gibbs-Duhem relationship to the MD expression for the activity of carbon in austenite yields an equation for the activity of iron in austenite mathematically identical to that derived by ADP for the LFG model.

3) For determination of the interaction energy in austenite, the CO/CO_2 data of BEC were concluded to be the more reliable of those which have been recently reported; from these data a value of $w_\gamma = 1925$ cal/mole (8054 J/mole) was secured, significantly different from the 1500 cal/mole (6276 J/mole) ADP obtained using the more limited CO/CO_2 data of R. P. Smith.

4) Despite the availability of much more data on the activity of carbon in ferrite, values of the interaction energy between C atoms in ferrite, w_α, were obtained which varied markedly and irregularly with temperature. As ADP previously reported this is an attractive energy; however, it is now suspected that this erratic behavior may be due more to the inadequacies of the models when applied to an attractive interaction energy than to deficiencies in the activity data.

5) Calculated values of the $\gamma/(\alpha + \gamma)$ phase boundary compositions using the LFG/MD formalisms and $w_\gamma = 1925$ cal/mole were found to differ significantly from the best results of ADP, particularly at lower temperatures. In the case of the $\alpha/(\alpha + \gamma)$ boundary different results were also obtained but these were due primarily to a more accurate method of calculation allowed by the greater amount of experimental data now available. Agreement between the calculated and measured Ae3 curves continues to be very good; in the case of the $\alpha/(\alpha + \gamma)$ curve, agreement has become slightly worse.

6) The free energy change associated with the proeutectoid ferrite reaction and the T_o-composition curves calculated in the present analysis differed little with respect to those obtained by ADP. However, internal agreement among the present results is better than that obtained in the earlier investigation.

APPENDIX

The Gibbs-Duhem relationship between the activities of iron and of carbon in austenite is written:

$$\ln a_{Fe_\gamma} = -\int \frac{x_\gamma}{1 - x_\gamma}\, d\ln a_\gamma \qquad [A1]$$

where $\ln a_\gamma$ for the McLellan and Dunn[11] model is given by Eq. [6]. After considerable manipulation $d\ln a_\gamma$ for this model can be expressed as

$$d\ln a_\gamma = -11\left(\frac{1}{x_\gamma(1 - 2x_\gamma)}\right) dx_\gamma$$

$$+ 6\left\{\frac{\delta + 2J_\gamma\delta - 1 - 2J_\gamma + x_\gamma + 8x_\gamma J_\gamma}{\delta(-1 + x_\gamma + 2x_\gamma J_\gamma + \delta)}\right\} dx_\gamma - 6\left\{\frac{\delta - 4\delta J_\gamma - 1 - 2J_\gamma + x_\gamma + 8J_\gamma x_\gamma}{\delta(2J_\gamma - 1 + x_\gamma - 4x_\gamma J_\gamma + \delta)}\right\} dx_\gamma \qquad [A2]$$

where $J_\gamma = 1 - e^{-w/RT}$ and

$$\delta = [1 - 2x_\gamma(1 + 2J_\gamma) + x_\gamma^2(1 + 8J_\gamma)]^{1/2}. \qquad [A3]$$

Rearranging the first term on the right hand side of Eq. [A2] and multiplying each term on this side by $x_\gamma/(1 - x_\gamma)$ gives:

$$\ln a_{Fe_\gamma} = -\int\left[\frac{-5}{(1 - x_\gamma)(1 - 2x_\gamma)} - \frac{6}{(1 - x_\gamma)(1 - 2x_\gamma)} + \frac{6x_\gamma(\delta + 2J_\gamma\delta - 1 - 2J_\gamma + x_\gamma + 8x_\gamma J_\gamma)}{(1 - x_\gamma)\delta(-1 + x_\gamma + 2x_\gamma J_\gamma + \delta)}\right.$$
$$\left. - \frac{6x_\gamma(\delta - 4\delta J_\gamma - 1 - 2J_\gamma + x_\gamma + 8J_\gamma x_\gamma)}{(1 - x_\gamma)\delta(2J_\gamma - 1 + x_\gamma - 4x_\gamma J_\gamma + \delta)}\right] dx_\gamma. \qquad [A4]$$

A common denominator is then found for the last three terms of Eq. [A4]; after much additional manipulation the equation is reduced to:

$$\ln a_{\mathrm{Fe}_\gamma} = -\int \left[-\frac{5}{(1-x_\gamma)(1-2x_\gamma)} + \frac{6}{\delta(1-2x_\gamma)}\right] dx_\gamma . \qquad [A5]$$

The first term of this integral can be integrated directly as:

$$5 \ln \frac{2(x_\gamma - 1)}{2x_\gamma - 1} .$$

The second term is in the form

$$-6 \int \frac{dX}{v\sqrt{X}}$$

where

$$v = 1 - 2x_\gamma$$

and

$$X = 1 - 2(1 + 2J_\gamma)x_\gamma + (1 + 8J_\gamma)x_\gamma^2$$

and upon integration becomes:

$$-6 \ln \left\{\frac{4 - 8J_\gamma + 4x_\gamma(4J_\gamma - 1) + 4[1 - 2(1 + 2J_\gamma)x_\gamma + (1 + 8J_\gamma)x_\gamma^2]^{1/2}}{1 - 2x_\gamma}\right\} .$$

Therefore,

$$\ln a_{\mathrm{Fe}_\gamma} = \left[5 \ln \frac{2(x_\gamma - 1)}{2x_\gamma - 1} - 6 \ln \frac{4 - 8J_\gamma + 4x_\gamma(4J_\gamma - 1) + 4[1 - 2(1 + 2J_\gamma)x_\gamma + (1 + 8J_\gamma)x_\gamma^2]^{1/2}}{1 - 2x_\gamma}\right] \Bigg|_{x_\gamma = 0}^{x_\gamma = x_\gamma} \qquad [A6]$$

Applying the limits, this relationship becomes upon rearrangement:

$$\ln a_{\mathrm{Fe}_\gamma} = 5 \ln \frac{1 - x_\gamma}{1 - 2x_\gamma} + 6 \ln \left\{\frac{1 - 2J_\gamma + (4J_\gamma - 1)x_\gamma - [1 - 2(1 + 2J_\gamma)x_\gamma + (1 + 8J_\gamma)x_\gamma^2]^{1/2}}{2J_\gamma(2x_\gamma - 1)}\right\} . \qquad [A7]$$

Equation [A7] is identical to Eq. [10] which ADP derived[1] using the a_γ expression of the LFG formalism.[6,7] Complete details of the present derivation can be obtained from the authors.

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