

Thermodynamics of steels: carbon-carbon interaction energy

H. K. D. H. Bhadeshia

Analysis of some recent and relatively accurate data on the activity of carbon in ferrite indicates that the true carbon-carbon pairwise interaction energy ω is finite and positive (corresponding to a repulsive interaction). The significance of ω terms in various thermodynamic models of interstitial solutions is also considered.

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A knowledge of the behaviour of carbon atoms in the austenite and ferrite lattices is not only useful in the interpretation of bulk thermodynamic data, but is crucial for the accurate extrapolation of the free energy surfaces of austenite and ferrite into regions where either phase may not be in thermodynamic equilibrium. Indeed, for the martensite and bainite transformations it is often the case that such extrapolation is the only means of obtaining reasonable estimates of the driving forces involved.

The interaction between carbon atoms in solid solution is usually described in terms of the pairwise interaction energy ω . For carbon in austenite it is generally agreed that this energy is finite and positive,¹⁻⁵ so that the interaction is repulsive. Hence the occupancy of a given interstitial site reduces the probability of another carbon atom residing in the neighbouring site by a factor of $\exp(-\omega/RT)$.⁶ Such repulsive interactions are thought to occur as a result of a number of factors, including steric interference, coulombic repulsion, and effects involving the Fermi surface of the conduction electrons.⁶

However, the situation is less satisfactory for the case of carbon in ferrite. In their classic thermodynamic treatment, Kaufmann *et al.*¹ took ω_a to be positive. In a more recent analysis of experimental data, Shiflet *et al.*⁵ found that ω_a is finite and negative, in agreement with the earlier work of Aaronson *et al.*² In reaching this conclusion, Shiflet *et al.* used various expressions relating the activity of carbon and ω_a . One of these expressions was as given by Darken and Smith's modification⁷ of the model of Kaufmann *et al.*, i.e.

$$\ln a_x = \ln \left[\frac{x}{3 - (12 - 8e^{-\omega_a/RT})x} \right] + C(T) \quad (1)$$

i.e. $C(T)$ is a function independent of x, ω_a . Within the context of equation (1), it is clear that it is mathematically unreasonable for ω_a to be negative; whatever the magnitude of a negative ω_a , there will exist a temperature $T' = \omega_a/[R \ln((12x-3)/8x)]$ when equation (1) requires the logarithm of a negative quantity. Furthermore, a negative value of ω_a implies the clustering of carbon atoms in the ferrite lattice. Intuitively, this does not seem likely since the distortion caused by a carbon atom in the ferrite lattice is

even larger than that in the austenite lattice. In an attempt to justify a negative ω_a , Aaronson *et al.* cite the work of Keefer and Wert⁸ which seems to provide evidence for the clustering of carbon in ferrite. However, the significance of their data⁸ is not clear – not only do they present a number of uninterpreted effects but also seem to imply a degree of clustering in austenite by consideration of some data on carbon in nickel. Any clustering in austenite would be inconsistent with the extensive work¹⁻⁵ showing that ω_γ is positive. Additionally, the experiments of Keefer and Wert⁸ need not relate to nearest neighbouring interstitial sites, in which case the repulsive component of the pairwise interaction would be the most powerful. In view of these difficulties, it was decided to re-examine the interaction of carbon in ferrite, using some recent (and relatively accurate) data⁹ on the activity of carbon in ferrite. It should be noted that although Shiflet *et al.*⁵ seem to have made a restricted examination of the data of Ref. 9, the conclusions they reached are different from those of the present work.

METHOD AND RESULTS

In addition to equation (1), the following alternative expressions are relevant towards the determination of ω_a :

$$\ln a_x = \ln \left[\left(\frac{3-4x}{x} \right)^3 (e^{4\omega_a/RT}) \left(\frac{\delta-3+5x}{\delta+3-5x} \right)^4 \right] + C(T) \quad (2)$$

$$\ln a_x = \ln \left[\left(\frac{3-4x}{x} \right)^7 (e^{4\omega_a/RT}) \left(\frac{\delta-3+x(3+2J)}{\delta-3+6J+x(3-8J)} \right)^4 \right] + C(T) \quad (3)$$

where

$$\delta = [9 - 6x(2J + 3) + (9 + 16J)x^2]^{1/2}$$

and

$$J = 1 - e^{-\omega_a/RT}$$

$C(T)$ is a function independent of x, ω_a . Both these equations are considered in Ref. 5. Equation (2) is based on the Lacher¹⁰ and Fowler and Guggenheim¹¹ formalisms while equation (3) is due to McLellan and Dunn.¹²

Using the experimental data of Lobo and Geiger,⁹ ω_a was systematically varied until the slope of $\ln a_x$ versus $f(x, \omega_a)$, (i.e. m), achieved the theoretical slope m_i of unity. Here $f(x, \omega_a)$ refers to the logarithm of the terms in square brackets in equations (1)–(3).

The McLellan and Dunn equation was found to cause abrupt changes in m with extremely small changes in ω_a , and in addition, the relation between m and ω_a did not appear to be single valued. In regions where the relationship was relatively well behaved, the value of m showed significant oscillations about m_i with very small variations in ω_a . This was found to occur over a wide range of ω_a so that it proved

NOMENCLATURE

m_i	theoretical slope of $\ln a_x$ versus $f(\omega_x, x)$
m	regression slope of $\ln a_x$ versus $f(\omega_x, x)$
$\omega_\gamma, \omega_\alpha$	pairwise interaction energy of carbon atoms in austenite or ferrite
$\omega_{\gamma_1}, \omega_{\alpha_1}$	$\omega_{\gamma, \alpha}$ determined using the theory of Kaufmann <i>et al.</i> ¹
$\omega_{\gamma_2}, \omega_{\alpha_2}$	$\omega_{\gamma, \alpha}$ determined using the theory of Lacher, Fowler, and Guggenheim ^{10,11}
a_x	activity of carbon in ferrite
x	mole fraction of carbon in ferrite
T	absolute temperature
R	gas constant

impossible to decide on the true value of the latter quantity. Consequently, the analysis of ω_x using equation (3) was abandoned.

On the other hand, the models based on equations (1) and (2) were found to exhibit well behaved relationships between m and ω_x , and the results are presented in Tables 1 and 2. In these tables, the quantities $(\omega + \sigma)$ and $(\omega - \sigma)$ represent the interaction energies when the calculated m value nearest m_i is varied by $\pm S$, where S is one standard error in m . Since m_i could not be achieved *exactly* in most cases, the ω_x values in Tables 1 and 2 correspond to the m that was found to be nearest m_i (these values of m are also given in the tables). The impossibility of achieving the exact value of $m = m_i$ may be due to the inevitable (though relatively small) experimental errors in the data of Ref. 9 and/or any shortcomings in the thermodynamic models from which equations (1)–(3) are derived.

Considering the cases in Table 1 where the ω_x is indicated to be $> 83\,740$, it was found that beyond this latter value, m could not be discerned to vary with any further increase in ω_x . In addition, the correlation coefficient between $\ln a_x$ and $f(x, \omega_x)$ did not change beyond $\omega_x = 83\,740$. This effect is simply a reflection of the fact that at this stage of the calculation procedure the term $e^{-\omega_x/RT}$ in equation (1) essentially amounts to zero.

It should also be noted that equations (1) and (2) were found to accurately represent the data of Ref. 9 since the correlation coefficients between $\ln a_x$ and $f(x, \omega_x)$ always exceeded 0.991 (and usually exceeded 0.999) at the values of m given in Tables 1 and 2. However, the 848°C data is not necessarily significant since it derives from only two activity values.

Referring to the data based on equation (1) first, it is evident that ω_x is effectively infinite in all but two cases. Thus the majority of data are strongly indicative of a large, positive ω_x . The results at 727 and 797°C are not understood, but it is possible that further experimental evaluations will resolve this problem. The analysis of the 727°C data is based on only three experimental points, and although the 797°C data are derived from five experimental points, three of these tend to cluster (*see* Ref. 9).

The same form of results was obtained using equation (2), the notable difference being that the values of ω_x were always finite. This fact is significant, and examination of equations (1) and (2) suggests that ω_x does not have the same meaning in both the formalisms. Equation (1) is compatible with $\omega_x \rightarrow \infty$ (i.e. all nearest neighbour sites blocked); in equation (2), ω_x cannot be conceived to reach infinity due to the $e^{\omega_x/RT}$ term. Hence the following

Table 1 Analysis using equation (1)

Temperature, °C	ω_x , J mol ⁻¹	m	$\omega_x + \sigma$	$\omega_x - \sigma$
682	$> 83\,740$	1.055853	∞	-31 400
702	$> 83\,740$	1.041138	∞	(83 740)*
727	-27 195	1.000019	∞	-37 680
753	$> 87\,930$	1.009917	∞	-33 500
783	$> 83\,740$	1.009939	∞	-29 300
797	-36 280	1.000001	∞	-42 290
813	$> 83\,740$	1.007599	∞	-36 430
848	$> 83\,740$			

* A lower bound ($\omega_x - \sigma$) value could not be determined in this case since the stated m also happens to be the minimum attainable m with respect to m_i .

Table 2 Analysis using equation (2)

Temperature, °C	ω_x , J mol ⁻¹	m	$\omega_x + \sigma$	$\omega_x - \sigma$
682	58 620	1.055226	109 280	-30 150
702	92 530	1.000064	100 490	77 670
727	-27 220	1.000411	92 110	-37 680
753	88 350	1.001758	104 680	-31 820
783	86 250	1.000009	94 250	-18 840
797	-36 030	1.000004	0	-41 870
813	84 160	1.005243	119 330	-36 430
848	41 870	1.073151		

boundary conditions consistent with the mathematical forms of equations (1) and (2) can be defined

$$\text{Equation (1)} \quad \infty > \omega_x \geq 0$$

$$\text{Equation (2)} \quad \psi > \omega_x \geq 0$$

(It should be noted that even in equation (2), ω_x cannot be allowed to be negative, since at some temperature T' , δ would become a complex number.) The term ψ arises from the requirement that a_x should not exceed unity.

It is therefore clear that the models are based on repulsive or nil interactions and cannot cope with clustering. The models would be consistent with a negative ω_x only if the latter varied with temperature such that the T' temperature (now itself a function of T) would never be reached. However, there appears to be no fundamental reason to indicate that this should be the case,⁷ and indeed, it seems to be generally accepted that ω (when it is considered to be a true binding energy) is independent of temperature.^{2,3,5,7}

The fact that the boundary conditions given above are different for equations (1) and (2) can be rationalized if it is considered that in the Lacher, Fowler, and Guggenheim model ω represents a true interaction energy but that in the Kaufmann *et al.* model the term

$$Z_x = (12 - 8e^{-\omega_x/RT}) \quad \text{or} \quad Z_y = (14 - 12e^{-\omega_y/RT})$$

must have discrete positive values with the physical meaning related to the number of excluded sites. ω would then be interpreted in a strictly phenomenological sense such that (ω/T) would be required to be a constant whose values are restricted to those compatible with Z_x and Z_y being natural numbers, with maximum limits determined by the form of the parent lattice.

The experimental evidence seems to be consistent with the above interpretations. In the ferrite lattice, Table 1 shows that ω_x is so high (effectively ∞) that all nearest neighbouring sites are excluded from occupation. For the austenite, the data⁵ indicate that the (ω_γ/T) values obtained

$$Z_x \leq Z_y \leq 14$$

using the Kaufmann *et al.* theory (i.e. ω_{γ_1}/T) are practically constant, while those obtained using the Lacher *et al.* theory (i.e. ω_{γ_2}/T) show systematic variation with temperature.* In fact, the correlation coefficient r relating ω_{γ}/T and T can be shown to be $r_1 = -0.413$ (when $\omega_{\gamma} = \omega_{\gamma_1}$) and $r_2 = -0.815$ (when $\omega_{\gamma} = \omega_{\gamma_2}$). However, r_1 is statistically not significant at a 90 or 95% confidence level. It should be noted that the ω_{γ} values used in the present analysis cover an extensive temperature range, i.e. 800–1300°C. The data are consistent with (ω_{γ_1}/T) being a constant corresponding to $Z_{\gamma} = 7$.

Finally, it should be noted that since the McLellan and Dunn and the Lacher, Fowler, and Guggenheim formations are mathematically similar,⁵ the general conclusions reached in the present work with respect to the latter should also apply to the former.

CONCLUSIONS

The present work indicates that the ω terms of the Kaufmann *et al.* model should be regarded as phenomenological and not directly representative of the true interaction energy between carbon atoms. On the other hand, the ω terms in the Lacher, Fowler, and Guggenheim (and the

McLellan and Dunn) theories seem to represent the true pairwise (C–C) interaction energies.

It seems that the (ω/T) terms of Refs. 1 and 7 are not a function of temperature and have values corresponding to the exclusion of discrete numbers of interstitial sites.

Contrary to previous investigations, the interaction between carbon atoms in ferrite has been found to be strongly repulsive.

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* The ω_{γ} terms referred to here are only those based on the analysis of data from experiments involving the equilibrium between austenite and CO/CO₂. These are generally considered to be the most reliable.^{1,2,5} These ω_{γ} values are based on the activity determinations of Refs. 3, 13, 14. However, the ω_{γ_2} results (quoted in Ref. 5) of Ref. 2 corresponding to the data of Ref. 14 are incorrect and were recalculated to be:

1073 K	$\omega_{\gamma_2}/T = 6.3215 \text{ J mol}^{-1} \text{ K}^{-1}$
1273 K	$\omega_{\gamma_2}/T = 5.8053 \text{ J mol}^{-1} \text{ K}^{-1}$
1473 K	$\omega_{\gamma_2}/T = 5.9979 \text{ J mol}^{-1} \text{ K}^{-1}$