Short Communications

A Note on Solubility and Excess Gibbs Energy of Graphite in Liquid Iron

The solubility of graphite (gr) in liquid iron, assessed in [93Oka], and additional data by Oden in [89Ode] are in very good agreement as shown in Fig. 1. This note presents the related thermodynamic properties of carbon dissolved in liquid iron at graphite saturation. The dissolution process and the corresponding change in the partial heat capacity, ΔC_p, are:

C(gr) = C[in Fe(L)], (dissolution)

$$\Delta C_p = C_p[\text{C in Fe(L)}] - C_p^0(\text{gr}) \quad \text{(Eq 1)}$$

The same process for hypothetical ideal dissolution of graphite is $\Delta C_p(\text{ideal}) = C_p[\text{ideal C in Fe}] - C_p^0(\text{gr})$, and the subtraction of this equation from Eq 1 yields the excess partial heat capacity of dissolution, $C_p^{ex} = C_p[\text{C in Fe}] - $

Fig. 1 Solubility of graphite in liquid iron.

$C_p[\text{ideal C in Fe}]$. C_p^{ex} can be expressed as a linear function of temperature, T, in K, with constants A and B, as follows:

$$C_p^{ex} = \Delta A + 2\Delta BT \quad \text{(Eq 2)}$$

The accuracy of high temperature data seldom justifies a cubic or higher order equation in T, and $\Delta B = 0$ does not represent the solubility data well.

Graphite is usually taken as the standard state [94Gok] so that the activity of dissolved carbon at saturation is unity; i.e., $a_C = 1 = \gamma_C X_C(\text{satn})$, where γ_C and $X_C(\text{satn})$ are the activity coefficient and the mole fraction, respectively. The excess partial Gibbs energy, G_C^{ex}, designated as g_C for simplicity in notation, is then:

$$g_C \equiv RT \ln \gamma_C = -RT \ln X_C(\text{satn}) = H_0$$
$$- \Delta AT \ln T - \Delta BT^2 + IT \quad \text{(Eq 3)}$$

where R is the gas constant; H_0 is the integration constant in the excess partial enthalpy of solution, $H_C^{ex} = H_0 + \Delta AT + \Delta BT^2$; and I is the integration constant related to the entropy term [75Gok]. Four well spaced values are used in Fig. 1 to obtain the constants in Eq 3:

$$g_C \text{ (J/mol)} = -RT \ln X_C(\text{satn}) =$$
$$-1572 - 3.652 \, T \ln T - 0.002316 \, T^2$$
$$+ 45.613 \, T \quad \text{(Eq 4)}$$

Selected values of $X_C(\text{satn})$ are as follows: 0.1773 [1500 K]; 0.1951 [1700 K]; 0.2241 [2000 K]; 0.2788 [2500 K]. The value of H_C^{ex} computed from the foregoing constants is about +15

kJ/mol, in line with the enthalpy of formation of Fe_3C, though this is not a rigorous comparison. The value of C_p^{ex} computed from Eq 2 at 2000 K is +12.92 J/mol·K. According to [85Ber], large positive values of C_p^{ex} are usually associated with large negative values of H_C^{ex}, contrary to the foregoing results,, though no such qualitative correlation exists for the interstitial solutes. Therefore, it is recommended that Eq 3 be regarded as an empirical equation representing the solubility well, and the derived thermodynamic properties should be considered as very approximate relations.

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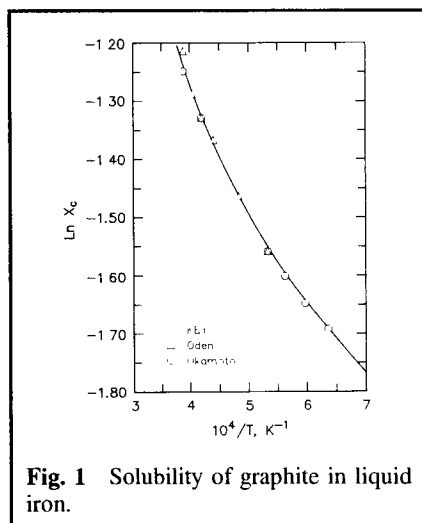
Conversion from the Wagner ε Formalism to a Margules Formalism
Discussion of a paper by Gokcen

Gokcen[1] recently discussed the relationships between the Wagner interaction coefficients[2] defined by the ε formalism for dilute solutions

$$\ln \gamma_2 = \ln \gamma_2^0 + \varepsilon_{22} X_2 + \varepsilon_{23} X_3 + \dots \quad \text{(Eq 1)}$$

and Margules coefficients, which in principle apply to the whole range of

composition. He stated that even if the ε formalism is modified to obey the Gibbs-Duhem relation, as proposed by Schuhmann[3] and Pelton and Bale,[4] "it is evident that the Margules-type equations are preferable to the equations with linear terms...." The argument is that the ε formalism is a dilute solution approximation whereas the Margules

equation applies to the whole range of composition. Gokcen further mentions that other power series could be used, but, "the use of one type of equation, preferably the Margules equation, would enhance communication among thermodynamicists of alloys." Note that the use of a single type would also simplify the software used for com-

puter calculations. The expression recommended by Gokcen is:

$$G_m^{ex} = X_1X_2(A_{21}X_1 + A_{21}X_2)$$

$$+ X_1^2X_2^2(B_{21}X_1 + B_{21}X_2)... \qquad \text{(Eq 2)}$$

Note that the expression most generally recommended is instead based upon Redlich-Kister polynomials:

$$G_m^{ex} = X_1X_2(L_{12}^0 + L_{12}^1(X_1 - X_2)$$

$$+ L_{21}^2(X_1 - X_2)^2 + ... \qquad \text{(Eq 3)}$$

For a binary system, Eq 2 and 3 are completely equivalent but not for ternary and higher-order systems.[5]

The wealth of data presented in terms of the Wagner ε formalism may be used directly by applying the modification proposed by Schuhmann[3] and Pelton and Bale.[4] However, in order to transform the information to a power series formalism covering the whole range of composition, a reassessment is necessary. It would be of great value if the information could be directly converted to a Margules type of representation. That can in fact be done by introducing a hypothetical standard state for each solute.[6] This is in essence what Darken[7] did when proposing his quadratic formalism because his basic equation can be written as:

$$G_m = X_1G_1^0 + \sum_2^n X_k(G_k^0 + M_k)$$

$$+ RT\Sigma X_i \ln X_i + 0.5 \sum_{i=1}^n \sum_{j=1}^n X_iX_jL_{ij} + ...$$

$$\text{(Eq 4)}$$

where all $L_{ii}=0$ and $L_{ij}=L_{ji}$. The quantity $G_k^0 + M_k$ defines the hypothetical standard state. Of course, this expression only applies to dilute solutions, but that is the region where the ε coefficients have been determined. They should be applied only there.

Equation 2 yields the following expression for the chemical potential of a solute, $j>1$, if all the L parameters are constants; i.e., all $L_{ij}^n=0$ for $n>0$ in Eq 3:

$$G_j = G_j^0 + M_j + L_{1j}$$

$$+ RT\ln X_j + \sum_{k=2}^n (L_{kj} - L_{1j} - L_{1k})X_k +$$

$$0.5 \sum_{k=2}^n \sum_{l=2}^n (L_{1k} + L_{1l} - L_{kl})X_kX_l \qquad \text{(Eq 5)}$$

Comparison with the ε formalism, Eq 1, yields:

$$L_{kj} - L_{1j} - L_{1k} = \varepsilon_{kj}RT \qquad \text{(Eq 6)}$$

and with $k=j$ we obtain, because $L_{jj}=0$,

$$-2L_{1j} = \varepsilon_{jj}RT \qquad \text{(Eq 7)}$$

and with $j=k$,

$$-2L_{1k} = \varepsilon_{kk}RT \qquad \text{(Eq 8)}$$

Combination yields:

$$L_{kj} = [\varepsilon_{kj} - (\varepsilon_{jj} + \varepsilon_{kk})/2]RT \qquad \text{(Eq 9)}$$

Finally,

$$M_j = [\ln\gamma_j^0 + \varepsilon_{jj}/2]RT \qquad \text{(Eq 10)}$$

The last summation in Eq 9 is identical to the modification of the Wagner ε formalism proposed by Schuman[3] and

Pelton and Bale.[4] The introduction of hypothetical standard states is thus equivalent to their method of modifying the ε formalism to obey the Gibbs-Duhem relation. With the present method, the data on solutes on Fe melts, compiled by Sigworth and Elliott[8] were recently converted to the Redlich-Kister formalism and successfully introduced into the TERMO-CALC data bank system.[9]

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N.A. Gokcen, Author's reply

I appreciate the discussion by Professor Hillert, allowing me to clarify and re-emphasize important points in my paper. (In this reply, the numbers for references and equations in Hillert's discussion are preceded by H, and those in my paper are preceded by G. My new equations use letters only.)

The modifications of the linear ε_{ij} formalism by Schuhmann (H3) and Pelton and Bale (H4) are equivalent to the

quadratic Margules equation, Eq G3, in terms of x_2 and x_3. Thus, the substitution of $1 - x_2 - x_3$ for x_1 in (G3) yields:

$$G_2^{ex} \equiv g_2 = A_{12} - 2A_{12}x_2$$

$$+ (A_{23} - A_{12} - A_{13})x_3$$

$$+ [A_{12}x_2^2 + A_{13}x_3^2$$

$$+ (A_{12} + A_{13} - A_{23})x_2x_3] \qquad \text{(Eq A)}$$

The first three terms are the linear Wagner equation, G4, and the terms in brackets [ ] are $g_1 \equiv g_1$(solvent). Pelton and Bale added g_1(solvent) to the linear Wagner equation, which is identical with the terms in brackets [ ], so that the Gibbs-Duhem relation is obeyed at finite solute concentrations. It is evident that such a procedure takes us right back to the original quadratic Margules equation. This point was not mentioned