

Estimation of Self and Ternary Interaction Coefficients in Solid Fe-C, Fe-Mn and Fe-Mn-C Systems at 1623 K

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Introduction

- Metallurgical processes need reliable thermodynamic data for the purpose of assessing reaction feasibility. Interaction coefficient and activity coefficient data are crucial for studying the reactions involving components in non-ideal solution.
- In the Fe-based systems, most of the reported interaction coefficients (ϵ_i^j) and activity coefficients of solutes at zero concentration (γ_i^0) have been measured in liquid solutions, the data with the solid iron-base alloys are meager.
- Thermo-Calc generated equilibrium compositions of the coexisting liquid iron and austenite phases along with the first-principle activity relationship of components (solutes) at equilibrium are utilised to find out the ϵ_i^j and γ_i^0 in Fe-C and Fe-Mn binary, and Fe-C-Mn pseudobinary systems, in the current work.

Model

- The activity coefficient vs. composition relationship in a A-B-C-D multicomponent system is given by Wagner's ϵ formalism as: $\ln\gamma_B = \ln\gamma_B^0 + \epsilon_B^B x_B + \epsilon_B^C x_C + \epsilon_B^D x_D$.
- Here, the activity coefficient of solute (B) at a given composition (x) of a liquid iron/steel can be found out when the interaction coefficients (ϵ) and the activity coefficient (γ_B^0) are all known. Now, how about the reverse? The reverse may find out all the interaction coefficients simultaneously from a sufficient number of known activity coefficients at different compositions of the system.
- For concentrated solutes, the above equation should be replaced by the quadratic formalism, as derived in details by Ghosh [1] and given here:

$$\ln\gamma_B = \ln\gamma_B^0 + \epsilon_B^B(x_B - 0.5x_B^2) + \epsilon_C^C(-0.5x_C^2) + \epsilon_D^D(-0.5x_D^2) + \epsilon_B^C(x_C - x_Bx_C) + \epsilon_B^D(x_D - x_Bx_D) + \epsilon_C^D(-x_Cx_D) \quad (1)$$

- As we are interested in getting the activity coefficients and interaction coefficients at a specific temperature (in this case 1623 K), temperature dependence terms for both are also derived. This has been done by starting as follows: $[\delta/\delta T(\epsilon_i^j)]_{P, composition} = [\delta/\delta T(\delta \ln\gamma_i/\delta x_j)_{x_i=0, x_j=0}]_{P, composition}$; this is followed by the use of i) the properties of exact differential, ii) the Gibbs-Helmholtz relation written in terms of excess properties, and iii) the simplifying condition of ideal entropy of mixing (i.e., zero partial molar excess entropy), to arrive at the following two desired relations: $T(\epsilon_i^j) = \text{constant}$, $T(\ln\gamma_i^0) = \text{constant}$

Procedure & Results

- First, the carbon (C) equilibrium between liquid and solid iron in the Fe-C binary system is considered. At 1623 K, the coexisting liquid and austenite in the Fe-C binary phase diagram have the following compositions, according to the Thermo-Calc [2]-generated Figure 1 (b): Liquid: $x_{Fe}=0.89701$ and $x_C=0.10299$ (Point B in Fig. 1(b)), Austenite: $x_{Fe}=0.95549$ and $x_C=0.04451$ (Point A in Fig. 1(b))

Fig. 1. (a) Fe-C binary phase diagram generated by using the TCFe7 database of the Thermo-Calc (b) Portion of the diagram giving the compositions of the coexisting austenite (Point A) and liquid (Point B).

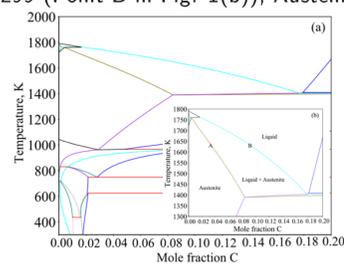
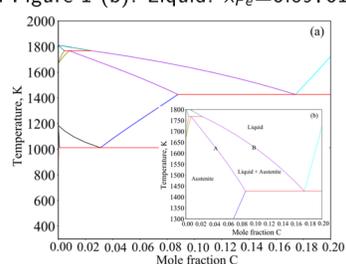


Fig. 2. (a) Fe-C-4 wt% Mn pseudobinary phase diagram generated by using the TCFe7 database of the Thermo-Calc (b) Portion of the diagram giving the compositions of the coexisting austenite (Point A) and liquid (Point B).

- The criterion of carbon equilibrium in terms of partial molar free energy (\bar{G}_i) is: $\bar{G}_C(\text{solid}) = \bar{G}_C(\text{liquid})$
- Subtracting the standard molar free energy $G_{C(s)}^0$ of solid carbon (graphite) from either side of the above equation, substituting $\bar{G}_i - G_i^0 = RT \ln a_i$ and writing a_C as the product $\gamma_C \cdot x_C$, one gets: $\ln\gamma_C(\gamma) = \ln(x_C(l)/x_C(\gamma)) + \ln\gamma_C(l)$
- Now applying the quadratic activity coefficient vs. composition relation (Eq.(1)) for solutes (carbon, here) in both solid and liquid solutions:

$$\ln\gamma_C^0(\gamma) + \epsilon_C^C(\gamma)[x_C(\gamma) - 0.5x_C^2(\gamma)] = \ln(x_C(l)/x_C(\gamma)) + \ln\gamma_C^0(l) + \epsilon_C^C(l)[x_C(l) - 0.5x_C^2(l)] \quad (2)$$

- The reported values of $\gamma_C^0(\gamma)$ at 1273 K is 8.75 [3], $\gamma_C^0(l)$ at 1873 K is 0.57 [4], and $\epsilon_C^C(l)$ at 1873 K is 11 [5]. Applying the temperature corrections formulae, the following values are obtained at 1623 K $\gamma_C^0(\gamma) = 5.39$, $\gamma_C^0(l) = 0.52$ and $\epsilon_C^C(l) = 12.69$.
- Substituting these values and the Thermo-Calc generated equilibrium composition in equation (2) we will get $\epsilon_C^C(\gamma) = -5.85$, which is the first of the four new data generated in the current study.
- Let us now consider the Fe-Mn binary system and the Thermo-Calc [2]-generated compositions at 1623 K are: Liquid: $x_{Fe}=0.56265$ and $x_{Mn}=0.43735$, Austenite: $x_{Fe}=0.62210$ and $x_{Mn}=0.37790$
- Applying the criterion of manganese equilibrium in terms of partial molar free energy and following the same procedure as Fe-C binary system by considering $G_{Mn}^0(\text{liquid}) - G_{Mn}^0(\text{solid}) = \Delta G_{\text{melting}, Mn}^0$, $a_i = \gamma_i x_i$, we have: $\ln x_{Mn}(\gamma) + \ln\gamma_{Mn}(\gamma) = (\Delta G_{\text{melting}, Mn}^0/RT) + \ln x_{Mn}(l) + \ln\gamma_{Mn}(l)$. Now, substituting $\Delta G_{\text{melting}, Mn}^0 = 12134 - 7.95TJ$ and then expanding the equation using the quadratic activity coefficient vs. composition relation (Eq.(1)):

$$\ln\gamma_{Mn}^0(\gamma) + \epsilon_{Mn}^{Mn}(\gamma)[x_{Mn}(\gamma) - 0.5x_{Mn}^2(\gamma)] = 0.08913 + \ln\gamma_{Mn}^0(l) + \epsilon_{Mn}^{Mn}(l)[x_{Mn}(l) - 0.5x_{Mn}^2(l)] \quad (3)$$

- The reported value of $\gamma_{Mn}^0(l)$ at 1873 K is 1.3 [4] and the interaction coefficient, $\epsilon_{Mn}^{Mn}(l)$, at 1823 K is -0.0026. Using the interconversion formula ($\epsilon_i^j = \text{Atomicweight}_{Fe}/230.3 \cdot \text{Atomicweight}_{Mn} \cdot \epsilon_i^j$), ϵ_i^j at 1823 K is -0.0026. Next, applying the temperature correction, $\gamma_{Mn}^0(l)$ and $\epsilon_{Mn}^{Mn}(l)$ are 1.354 and -0.66056 at 1623 K.
- Substituting in Eq. (3), these values, along with the x_{Mn} -s of liquid and austenite at 1623 K, the following relation is obtained:

$$\ln\gamma_{Mn}^0(\gamma) + \epsilon_{Mn}^{Mn}(\gamma)(0.30649) = 0.16619 \quad (4)$$

- To determine these two unknowns in equation (4), $\gamma_{Mn}^0(\gamma)$ and $\epsilon_{Mn}^{Mn}(\gamma)$, we consider manganese equilibrium between liquid and austenite in a Fe-C-Mn pseudobinary system. However, this will inevitably bring in a third unknown $\epsilon_C^{Mn}(\gamma)$. To resolve this, carbon equilibrium between liquid and austenite in the pseudobinary is considered as well.
- According to the Thermo-Calc-generated Figure 2 (b), the coexisting liquid and austenite in the Fe-C-4 wt% Mn pseudobinary phase diagram have the following compositions at 1623 K: Liquid (Point B): $x_{Fe}=0.85097$, $x_{Mn}=0.05611$, $x_C=0.09292$, Austenite (Point A): $x_{Fe}=0.92511$, $x_{Mn}=0.03874$, $x_C=0.03615$
- Starting with the criterion of manganese equilibrium and following the same procedure as before, the following relation is obtained:

$$\ln\gamma_{Mn}^0(\gamma) = 0.31346 + \ln\gamma_{Mn}^0(l) \quad (5)$$

- The use of the quadratic activity coefficient vs. composition relation (Eq.(1)) for manganese, in both solid and liquid solutions gives:

$$\ln\gamma_{Mn}^0(\gamma) + \epsilon_{Mn}^{Mn}(\gamma)[x_{Mn}(\gamma) - 0.5x_{Mn}^2(\gamma)] + \epsilon_C^C(\gamma)[-0.5x_C^2(\gamma)] + \epsilon_{Mn}^C(\gamma)[x_C(\gamma) - x_C(\gamma)x_{Mn}(\gamma)] = 0.31346 + \ln\gamma_{Mn}^0(l) + \epsilon_{Mn}^{Mn}(l)[x_{Mn}(l) - 0.5x_{Mn}^2(l)] + \epsilon_C^C(l)[-0.5x_C^2(l)] + \epsilon_{Mn}^C(l)[x_C(l) - x_C(l)x_{Mn}(l)] \quad (6)$$

- Putting all the available values in equation (6) and noting $\epsilon_{Mn}^C(l) = -3.13234$ at 1623 K, we obtain:

$$\ln\gamma_{Mn}^0(\gamma) + \epsilon_{Mn}^{Mn}(\gamma)(0.03799) + \epsilon_C^C(\gamma)(0.03474) = 0.24687 \quad (7)$$

- Next, starting with the criteria for carbon equilibrium, continuing upto the quadratic coefficient vs. composition relation (Eq.(1)) for Fe-C-Mn pseudobinary system and substituting all the available interaction coefficients and activity coefficient, along with the x_{Mn} -s and x_C -s of liquid and austenite at 1623 K, we get:

$$\epsilon_{Mn}^C(\gamma)(0.03734) - \epsilon_{Mn}^{Mn}(\gamma)(0.00075) = -0.21551 \quad (8)$$

- Solving equations (4),(7) and(8), three more new data, which pertain to manganese, are generated: $\gamma_{Mn}^0(\gamma) = 1.63$, $\epsilon_{Mn}^{Mn}(\gamma) = -1.05$, $\epsilon_{Mn}^C(\gamma) = -5.79$

Validity check

- A negative value (-5.85) of $\epsilon_C^C(\gamma)$ can be justified by the fact that the value of $\gamma_C^0(\gamma)$ is greater than 1 (5.39). The value of γ_C should decrease, in accordance with the property of binary solution, from 5.39 (toward 1) with increasing x_C . Similarly, the negative value (-1.05) of $\epsilon_{Mn}^{Mn}(\gamma)$ can be justified by the value of $\gamma_{Mn}^0(\gamma)$ being greater than 1 (1.63).
- The reliability of the current method is examined by cross-checking the value of $\gamma_C^0(\gamma)$, which is the only measured data [3] available with solid iron-base alloys. The value of $\gamma_C^0(\gamma)$ turned out to be 4.46 compared to the measured value of 5.39, showing a deviation of 17%, which may be considered reasonable.

References

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