

Communications

Discussion of "Quadratic Formalism for Mg in Liquid Fe"*

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Zhang *et al.* have recently reported on the Mg vapor pressure of liquid Fe-Mg solutions.^[1] Their Figure 1 demonstrates that their data represent a very strong deviation from Henry's law already at Mg contents below 0.06 wt pct. It can hardly be due to such a strong deviation of the Mg gas from the ideal gas law. For the present discussion, we shall thus approximate the Mg gas as ideal.

Zhang *et al.*^[1] represented their results with the following expression:

$$\log [\text{pct Mg}] = 0.059(P_{\text{Mg}})^{2.1} \quad [1]$$

but it is evident that there was a misprint. The left-hand side should simply be [pct Mg]. Here, "pct" stands for weight percent. It seems very difficult to explain the exponent 2.1. In order to examine the data in more familiar terms, an attempt will now be made to represent them with the regular solution model

$$G_m = \sum x_i({}^\circ G_i + RT \ln x_i) + Lx_{\text{Fe}}x_{\text{Mg}} \quad [2]$$

which yields

$$G_{\text{Mg}} = {}^\circ G_{\text{Mg}} + RT \ln x_{\text{Mg}} + (1 - x_{\text{Mg}})^2 \cdot L \quad [3]$$

$$\begin{aligned} RT \ln a_{\text{Mg}} &= G_{\text{Mg}} - {}^\circ G_{\text{Mg}} \\ &= RT \ln x_{\text{Mg}} + (1 - 2x_{\text{Mg}} + x_{\text{Mg}}^2) \cdot L \end{aligned} \quad [4]$$

The x_{Mg}^2 term can be omitted because all the data fall below $x_{\text{Mg}} = 0.0015$. Assuming that the Mg gas is ideal and using an equation for the vapor pressure of pure liquid Mg given by Guichelaar *et al.*,^[2] we find at 1873 K a value of $P^0 = 20$ bar. We may thus transform Eq. [4] into

$$\begin{aligned} \ln P &= \ln 20 + \ln [\text{pct Mg}] - 3.77 \\ &\quad + (1 - 2[\text{pct Mg}]/43.54) \cdot (L/RT) \\ &= -0.77 + \ln [\text{pct Mg}] \\ &\quad + (1 - 0.04593[\text{pct Mg}]) \cdot (L/RT) \end{aligned} \quad [5]$$

where P is expressed in bar. The data can be well fitted to this expression, as shown in Figure 1, and a least-square fit yields

$$\ln P = 3.52 + \ln [\text{pct Mg}] - 11.9[\text{pct Mg}] \quad [6]$$

We thus get two conditions which cannot be satisfied at the same time,

$$3.52 = -0.77 + L/RT \quad [7]$$

$$-11.9 = -0.04593 \cdot (L/RT) \quad [8]$$

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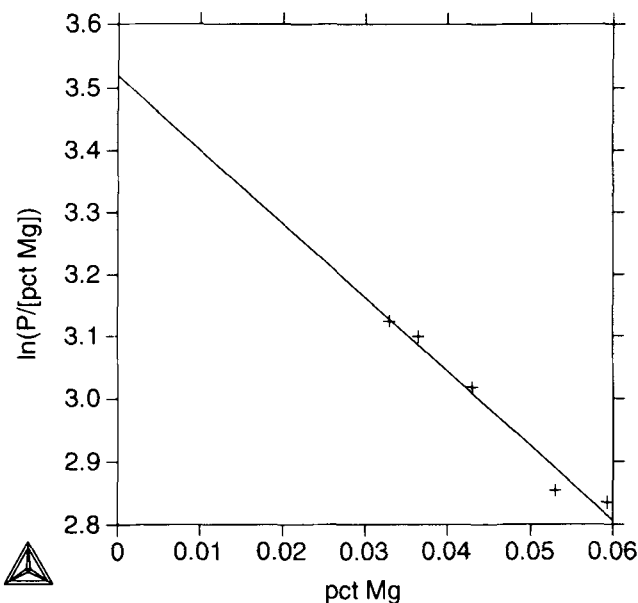


Fig. 1—Vapor pressure data for Mg in liquid Fe, plotted according to Darken's quadratic formalism at very low contents. The straight line was obtained from a least-squares fit.

Evidently, we need another parameter in spite of the fact that we are concerned with only very dilute solutions. This problem can be solved by introducing a sub-regular coefficient, but a different alternative is offered by Darken's quadratic formalism.^[3] As emphasized by Hillert,^[4] this formalism is obtained from the regular solution model by introducing a new state of reference for the solute, (${}^\circ G_i + M_i$), instead of ${}^\circ G_i$. This would change Eq. [5] into

$$\begin{aligned} \ln P &= M/RT - 0.77 + \ln [\text{pct Mg}] \\ &\quad + (1 - 0.04593[\text{pct Mg}]) \cdot (L/RT) \end{aligned} \quad [9]$$

Comparison with Eq. [6] yields

$$L = 259.09RT \quad [10]$$

$$M = (3.52 + 0.77 - 259.09)RT = -254.8RT \quad [11]$$

where T is 1873 K for all the data and L is thus equal to 4,000,000 J/mol, which is a very high value. The highest negative ϵ_i^j value reported for any solute in liquid Fe is -13 for Si,^[5] and at 1873 K, it corresponds to an L value of only 100,000 J/mol. We may thus conclude that although the data reported by Zhang *et al.*^[1] can be well described with Darken's quadratic formalism, they require an exceptionally high interaction energy. It may also be regarded as a strange coincidence that the values of L and $-M$ are so similar.

REFERENCES

- Xiaodong Zhang, Qiyong Han, and Dong Chen: *Metall. Trans. B*, 1991, vol. 22B, pp. 918-21.
- P.J. Guichelaar, P.K. Trojan, and R.A. Flinn: *Metall. Trans.*, 1971, vol. 2, pp. 3305-13.
- L.S. Darken: *Trans. TMS-AIME*, 1967, vol. 239, pp. 80-89.
- M. Hillert: *Metall. Trans. A*, 1986, vol. 17A, pp. 1878-79.
- J.F. Elliott, M. Gleiser, and V. Ramakrishna: *Thermodynamics for Steel Making*, Addison-Wesley, London, 1963.