INTERACTION PARAMETERS OF OXYGEN AND DEOXIDANTS IN LIQUID IRON

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Abstract

During decades before the evolution of more powerful computational tools, simplified formalisms such as the Wagner dilute solution formalism, have been successfully used in the study of deoxidation reactions of steel. This formalism relies on the introduction of interaction coefficients to account for deviations from Henry's Law. With the evolution of thermodynamic modeling and of the CALPHAD method, the fact that thermodynamic descriptions using these parameters were derived to be used at relatively dilute solution has been sometimes overlooked and the formalism has been criticized for deviating from reality in non-dilute solutions. In this work, it is shown that the interaction parameters used in this formalism correlate with properties of the solutes and of the solvent. The work focuses on the interactions in systems Fe-M-O, where M is a deoxidant. Correlations between interaction coefficients and heats of formation of the corresponding oxides and with the atomic number of the deoxidants are demonstrated. This not only helps supporting the physicochemical soundness of the formalism but also provides a way of checking the consistency of data presented in this formalism.

Keywords: Steel; Deoxidation; Thermodynamics; Aluminum; Magnesium; Steelmaking.

1. Introduction

Deoxidation is one of the operations that influence the quality of steel products [1,2]. Furthermore, deoxidants can represent a significant cost in steelmaking [3]. For these reasons the prediction of the deoxidation equilibria is of paramount importance in steelmaking. These predictions make it possible to properly control steel cleanness, the type of non-metallic inclusions formed, as well as to manage the cost of deoxidant additions. Since the decades of 1940-50 the strategy for performing these calculations involved the use of dilute solution concepts and, when needed, the introduction of interaction coefficients. The concept of interaction coefficients was first proposed by Wagner [4], considering the remarks of Chipman [5] and further developed by many important contributions [6-9]. The efforts to describe thermodynamic binary and ternary solutions with consistent sets of polynomials before the introduction of Wagner's formalism have been well reviewed by Darken [10] and will not be discussed here.

With the advance of solution modeling, different physicochemical models have been proposed to describe the behavior of solutes in liquid iron. Besides, solution modeling and its relation to thermodynamic properties has made a significant advance since the advent of the CALPHAD methodology, in the 1970s [11].

Wagner's proposed methodology for dilute solutions was the application of a Taylor's series expansion of the activity coefficient, disregarding the second and higher derivatives. Using Wagner's [4] original notation:

$$ln f_2(x_2, x_3, \dots) = ln f_2^0 + \left[x_2 \frac{\partial ln f_2}{\partial x_2} + x_3 \frac{\partial ln f_2}{\partial x_3} + \cdots \right]$$
$$+ \left[\frac{1}{2} x_2^2 \frac{\partial^2 ln f_2}{\partial x_2^2} + x_2 x_3 \frac{\partial^2 ln f_2}{\partial x_2 \ \partial x_3} + \cdots \right] \ (1)$$
$$+ \cdots$$

$$ln f_2(x_2, x_3, \dots) = ln f_2^0 + x_2 \epsilon_2^{(2)} + x_3 \epsilon_2^{(3)} + \cdots \qquad (2)$$

Later, Lupis and Elliott [6] noticed that the use of first order coefficient alone was not adequate to describe the behavior of solutions that are "not very diluted". They proposed that the "introduction of higher order interaction coefficients is a necessary and convenient addition to our mathematical apparatus". It is clear that these authors were in search of a mathematical way of handling the behavior of solutes in dilute solutions and were aware of the limitations this approach would have for less diluted solutions.

This lead to the formalism of interaction coefficients for dilute solutions [3,12-14], widely used today. This formalism is expressed in Eq. 3. In this

formalism, there is seldom sufficient accurate data to introduce higher order terms.

$$ln\gamma_i = ln\gamma_i^0 + \sum_{j=2}^{m} \varepsilon_i^{(j)} X_j + \sum_{j=2}^{m} \rho_i^{(j)} X_j^2 +$$

$$+ \sum_{j=2}^{m} \sum_{\substack{k=2 \\ k \neq j}}^{m} \rho_i^{(j,k)} X_i X_j + \cdots \qquad (3)$$

With the evolution of solution modeling techniques and the availability of greater computational power, criticism of this approach has emerged, mostly on two fronts. First, from the point of view of the thermodynamic consistency of the mathematical technique proposed, several relevant improvements were proposed [6-9], as mentioned above. Second, somewhat unfairly, the inadequacy of the model to describe non-diluted solutions has been considered as a shortcoming. Wagner [4] as well as Lupis and Elliott [6,7] were extremely clear in limiting their approach to dilute solutions. Furthermore, Darken [10] also observed that the Wagner formalism could describe the terminal solutions but not the intermediate range; this lead to the introduction of his "quadratic formalism". In a less frequently cited paper, St.Pierre [15] also discussed the artifacts expected when the formalism is extended to high concentrations and when the second order interaction coefficient is either taken in consideration or disregarded. Gustafsson and Melberg [16], in the context of steel deoxidation, also discussed these aspects, considering two points: (a) how dilute a solution must be to be properly described with first order interaction coefficients only, and (b) the meaningless shape of the solubility curves when the solutions are not dilute. When evaluating these aspects, Gustafsson and Melberg emphasized that strong solute interactions must be present in systems such as Fe-Al-O and Fe-Ca-O where relative large first order interaction coefficients are measured.

Thus, one must keep in mind that this formalism was developed with focus on the treatment of dilute solutions. It must be recognized, however, that the question of "how dilute is dilute" in order for the formalism to be properly used, discussed qualitatively by some [16] and theoretically by others [17], cannot be answered by the formalism. It is clear, however, that the model is not to be applied across the complete range of composition of one solute. The fact that this method has long been applied with success in the solution of practical steelmaking problems [3,18,19] and that conversion methods have been adopted to make possible its use in modern computational thermodynamics [20] are good indications that the method is useful and the data reliable.

It is the objective of the present work - while focusing on liquid iron deoxidation to limit the extension of the discussion- to highlight important regularities in the interaction coefficients of oxygen with metallic deoxidants. Besides, it is proposed that the observed regularities in the interaction coefficients support the existence of physicochemical basis for these coefficients. Should these regularities exist, they can be a powerful tool as a first check for the consistency of experimental data and of model coefficients.

Furthermore, this work will briefly discuss the conversion of data from the Wagner formalism to other solution models and vice versa. The fact that the all conversion techniques require the *a priori* selection of a solution model for the ternary solution, a fact not always made clear in the literature, will also be highlighted.

## 2. Regularities in the interaction behavior of deoxidants and oxygen in liquid steel

All deoxidants react to form compounds (oxides) when they are not in solution in iron. Some observations concerning the interaction coefficients of these elements that react to form compounds also when they are in solution in a third element (the solvent, iron in this case) appear to be pervasive. Thus, it is frequent that the "solubility product", normally a simple hyperbole when expressed as a function of solute activities, deviate from this type of equation when expressed as function of the concentrations of the solutes. This is clearly noticed in many cases. A few examples are NbC [21], TiC [22] and $M_{23}C_6$ [23,24] in austenite and Cr_2O_3 in liquid iron [24,25].

Hildebrand, through the regular solution model [26], was probably the first to propose a physicochemical model to treat the fact that different atom pairs in a solution can have different energetic interactions. The model received its name from the "regularities" observed in certain solutions. While the regular solution model considered the differences in interaction energies and their effect on the enthalpy change on mixing, it did not consider that these different pair-energies could have an effect in the configurational entropy of the solution. Thus, the regular solution model is somewhat limited to solutions where interactions are not too strong. Guggenheim improved on the regular solution model with the quasi-chemical treatment [27]. He introduced a more accurate way of calculating the configurational entropy, taking in consideration the different energy of the pairs and thus the different probabilities of pair formation. Chipman, when analyzing the behavior of deoxidizers in steel, imagined a simple physicochemical model in which the deoxidizer would have more ability than iron to "*share electrons*

with the oxygen atoms, thus…tying up oxygen and reducing its activity" [19]. Some years later Wagner proposed a mathematical treatment through a series expansion of the effect of solutes on the activity coefficients of other solutes [4], as mentioned in the introduction to this work. The mathematical shortcomings of this treatment in solutions that are not "at infinite dilution" are known and were discussed elsewhere [6-9], and will not be discussed here. Rather, this work focuses on presenting regularities observed on the Wagner first order interaction coefficients in the case of iron as solvent and oxygen and a metallic deoxidant as solutes.

2.1 Relation between Interaction coefficient and Enthalpy of Formation of compound

When evaluating the aluminum deoxidation of steel, Costa e Silva, Beneduce and Avillez [29] noticed that the first order interaction coefficients were related to the enthalpy of formation of the corresponding oxide, when the interaction coefficients were plotted in a logarithmic scale, as shown in Fig. 1.
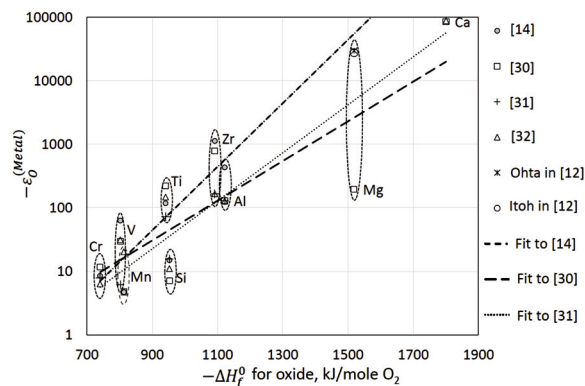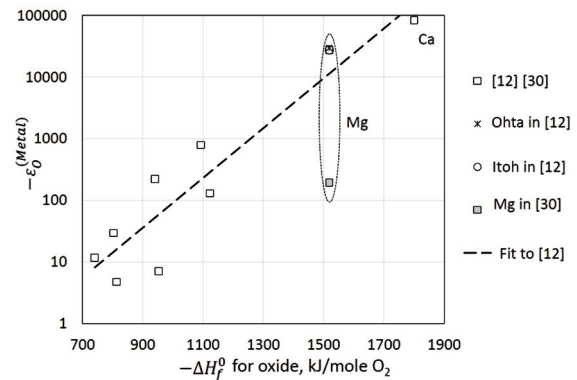

Figure 1. Relation between first order interaction coefficients in Fe-M-O systems from various compilations and the standard enthalpy of formation of the respective MxOy oxide per mole of O_2 [3]. Lines indicate least square fit between the logarithm of the interaction coefficient and the standard enthalpy of formation of the oxide for the indicated groups of data. Sources indicated in the Figure

The dependence on the enthalpy of formation of the oxides can be explored to check the consistency of first order interaction parameters. As examples, two sets of data are presented. In Fig. 2 the first order interaction coefficients proposed in [30] and the newly proposed values for $\varepsilon_O^{(Mg)}$ in the JSPS publication revised in 2010 [12] are presented. In Fig. 3 the data for $\varepsilon_O^{(Ca)}$ from JSPS [30] and from Buzek [32] and the data for $\varepsilon_O^{(Mg)}$ from Itoh and from

Otha [12] are presented together with the interaction coefficients compiled by Sigworth and Elliott [13] and converted by Lupis [14]. Both Figures indicate that the new values for $\varepsilon_O^{(Mg)}$ are more consistent with the previously evaluated data for the other elements than the previously proposed $\varepsilon_O^{(Mg)}$, and that the data for $\varepsilon_O^{(Ca)}$ from the two sources is relatively consistent with the values assessed by Sigworth and Elliott [13] for the other elements.

Sommer [33] proposed a model similar to the quasi-chemical model mentioned above, but with significant differences [34]. The association model

Figure 2. Relation between first order interaction coefficients in Fe-M-O systems from JSPS [30][12] (highlighting values for $\varepsilon_O^{(Mg)}$ newly proposed by Itoh for $\varepsilon_O^{(Mg)}$ [12] and previous one[30]), and the standard enthalpy of formation of the respective MxOy oxide per mole of O_2 from [3]. Line indicates least square fit between the logarithm of the interaction coefficient and the standard enthalpy of formation of the oxide
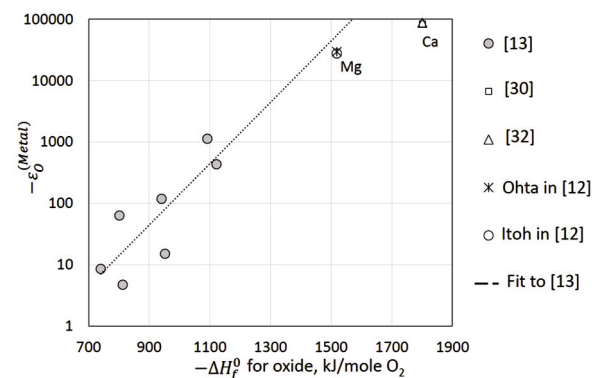
Figure 3. Relation between first order interaction coefficients in Fe-M-O systems from Sigworth and Elliott [13], values for $\varepsilon_O^{(Mg)}$ newly proposed in [12] and for $\varepsilon_O^{(Ca)}$ from JSPS [30] and Buzek [32] and the standard enthalpy of formation of the respective MxOy oxide [3]. Line indicates least square fit between the logarithm of the interaction coefficient and the standard enthalpy of formation of the oxide per mole of O_2 from [3]. The points from JSPS [30] and Buzek [32] are marked in the Figure

proposed by Sommer, considers that, besides the atomic species, the liquid contains associates of these species, when their interaction is strong. Thus, it is postulated that in a system A-B, associates can be formed through the reaction:

$$iA + jB = AiBj \qquad (4)$$

The associate formation reaction, Equation 4, has a free energy change given by:

$$\Delta G^0_{A_i B_i} = \Delta H^0_{A_i B_i} - T\Delta S^0_{A_i B_i}$$

Expanding on this model based on the contributions of [35,36], Jung, Decterov and Pelton [37] have modeled the behavior of deoxidants (M) in liquid iron. They assumed that besides M and O in solution, there should exist $\underline{M}*\underline{O}$ and $\underline{M}_2*\underline{O}$ associates in the liquid. For the reaction leading to the formation of the $\underline{M}*\underline{O}$ associates they followed Equation 4, obtaining Equation 5.

$$\underline{M}+\underline{O}= \underline{M}*\underline{O} \qquad (5)$$
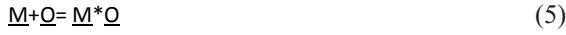
The free energy change for the hypothetical reaction given by Equation 5 is given (using Jung's symbols) by:

$$\Delta g^0_{M*O} = g^0_{M*O} - g^0_M - g^0_O \qquad (6)$$

For each composition, the concentration of "pairs" or "complexes" can then be calculated by minimizing the total free energy of the liquid phase subjected to the mass balance restrictions, i.e., the number of atoms of M and O is constant. For M and O in solution, the free energies were derived using data from Wagner's formalism. The free energy of the complexes were obtained by optimization, utilizing experimental data.

Fig. 4 shows the relationship between the g^0_{M*O} optimized by Jung and co-workers for each oxide formed during iron deoxidation and the first order interaction coefficient between oxygen and each metallic deoxidant, $\varepsilon_O^{(M)}$, at 1873K.

It seems evident that the tendency to form associates, measured by Jung, Decterov and Pelton with the parameter g^0_{M*O} is also closely related to the first order interaction parameters, which are normally interpreted as expressing the tendency for solutes to "attract each other" in a solution, when they are negative.

If the standard enthalpy of formation of the oxide is a good measure of the interaction or "attraction" between a given deoxidant and oxygen, it seems evident from its relation with the parameters shown in Figs. 1 and 2 that these are related to the interaction or "attraction", as expected. In the case of the free energy

of formation of the associates, the relation is linear. In the case of the first order interaction parameter, the relationship is logarithmic, as expect from Eq. 3 and from the relation between the activity coefficient (γ_i^0) and the Gibbs free energy of solution for the "hypothetic 1% solution of i in iron", given by Eq. 7 [3]:

$$\mu_i^{0\prime} - \mu_i^0 = \Delta G_i^{1\%} = RTln\left(\frac{\gamma_i^0 M_{Fe}}{100 M_i}\right) \qquad (7)$$

One must keep in mind that the values of the first order interaction coefficients $\varepsilon_O^{(Metal)}$ are not independent of second order coefficients $\rho_o^{(Metal)}$ [17]. Since some of the first order coefficients presented in Fig. 1 were derived together with second order coefficients, part of the dispersion observed in that figure might be ascribed to that. Furthermore, the extrapolation technique used to determine these coefficients (see [38] for instance) might also introduce dispersion.
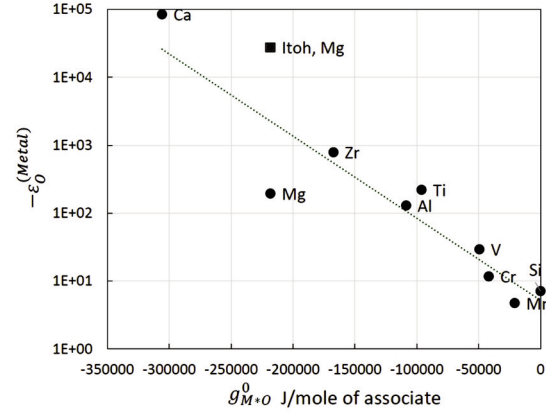

Figure 4. *Relation between g^0_{M*O} optimized by Jung, Decterov and Pelton [37] in Fe-M-O system and the first order interaction coefficients $\varepsilon_O^{(M)}$ given by JSPS [30] and $\varepsilon_O^{(Mg)}$ by Itoh, cited in [12]. Line indicates least square fit to the data of [30]*

## 2.2 Relation between Interaction coefficient and atomic number

Neumann and Schenk [39] studied the interaction between carbon and alloying elements in steel in the liquid phase. They defined the interaction by relating the effect of the second solute on the solubility of carbon in liquid iron. Thus, they defined an "interaction coefficient" $\varepsilon NS_C^{(element)}$ expressing the effect of a second solute on the solubility limit X_C^{max} of carbon in liquid steel at a given temperature, as presented in Eq. 8. They were able to demonstrate a linear relationship between $\varepsilon NS_C^{(element)}$ and the atomic number of the elements, within the same period of the periodic table. The slope of the linear relationship was

approximately constant for all periods.

$$\varepsilon NS_C^{(i)} = \frac{\partial \ln(X_C^{max})}{\partial \ln(X_i)} \qquad (8)$$

Later, Wada and Saito [40] confirmed the periodicity of the first order interaction coefficients and proposed a method to calculate these coefficients based on "interchange energies". Ohtani and Gokcen [41] evaluated the periodicity of first order interaction coefficients in several iron based ternary systems, including many Fe-O-X systems. They also confirmed the periodicity of the first order interaction coefficients in these systems and proposed that using these *"correlations it is possible to discard certain sets of data for an element if they are completely discordant and thus select the better fitting data"*.

In Fig. 5 the data of [30], including the values for $\varepsilon_O^{(Mg)}$ newly proposed in [12], are presented ordered by atomic number. It is evident that that the newly proposed values for $\varepsilon_O^{(Mg)}$ show a better agreement with the observed periodic trend in this graph than the previously proposed value.
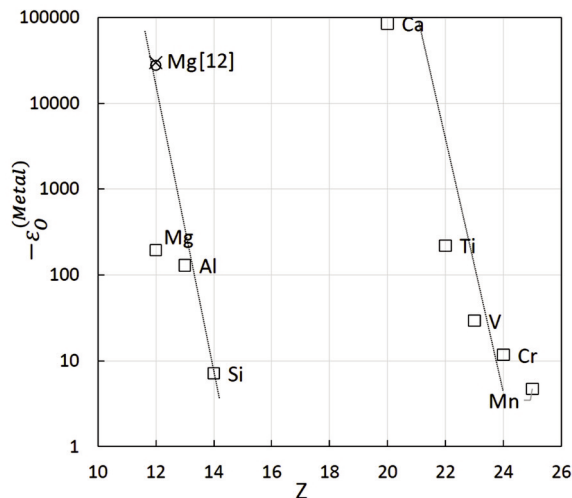
Figure 5. First order interaction coefficients compiled in [30] presented in the order of atomic numbers. The newly proposed values for $\varepsilon_O^{(Mg)}$ [12] show better agreement with the periodic trend than the previously proposed value of these parameters. Slope of lines adjusted manually to highlight periodic trend

3. Conversion of Wagner's formalism to other solution models

As discussed above, Hillert [20] proposed an efficient way to convert data from Wagner's formalism for use in computational thermodynamics. He adopted Darken's quadratic formalism to define a new hypothetical standard state for the elements in a regular solution. The conversion factor for the "new standard state" as well as the interaction coefficient for the regular solution L_{ij} were obtained from the activity coefficient and the Wagnerian interaction parameters. This has been implemented in Thermo-Calc SLAG3 database [42].

In any case, the conversion is only possible if a solution model is defined for the liquid phase. Thus, Hillert and Selleby [43] converted from their Fe-Ca-O liquid assessed with two sublattices to the Wagner formalism, and proposed a $\varepsilon_O^{(Ca)} = -31$. This value was proposed since they found there should be a "*serious systematic error*" on the experimentally determined solubility values of CaO in iron. For the case of the Fe-Al-O system, likewise, they suggest a value of $\varepsilon_O^{(Al)} = -11$, for the same reason. Apparently, the proposal for $\varepsilon_O^{(Al)}$ was based on experimental data in the range of 200-1000 ppm Al, in which case the effect of the interaction should indeed be very small. The interaction coefficient becomes important in the region where there is significant deviation from a constant solubility product. This happens at high oxygen content or, in the more usual case, at high aluminum contents. The values proposed by Hillert and Selleby deviate significantly from the trends presented in Figs. 1-5. Recently Kang and co-workers [44] have performed very careful measurements of the Fe-Al-O equilibrium and reached a value of $\varepsilon_O^{(Al)} = -25.17$. They did, however, remark that "*the oxygen content for Al content less than 1 mass% was found to be slightly higher* [than previously accepted results], *resulting in a smaller equilibrium constant*". They found an equilibrium constant at 1873K, expressed with Henrian activities, related to the hypothetic 1% solution of i in iron, of $\log(h_{Al}^2\ h_O^3) = -11.52$. The value of this constant, however, can be calculated independently of the Al-O interaction in solution in iron. Sigworth and Elliott [13] and Lindahl and Selleby [45] described the behavior of Al in the Al-Fe liquid. Their descriptions in the dilute range agree rather well. The same happens with the behavior of O in the O-Fe system, which is described by [13] and [46] with good agreement in the dilute range. Using the accepted free energy of formation of alumina either from [3] or [47] together with these descriptions of the solutes behavior in the binaries, it is quite unexpected that the equilibrium constant could deviate from the range of magnitudes of -13 to -14, as proposed by Kang and co-workers. Also relevant in the present case, the discrepancy between these values and the values measured by Kang and co-workers cannot be reconciled via interaction parameters.

Ansara [48] has reviewed the conversion equations for different solution models to the Wagner formalism. He also remarked that the conversions can only be performed after one has chosen a given solution model. Unfortunately, the examples in which he performed the conversions do not include any oxygen-deoxidant system.

4. Conclusions

Interaction parameters according to Wagner and Lupis and Elliott have been very successfully used in the study of deoxidation reactions of steel for many years. The fact that thermodynamic descriptions based on these parameters were envisaged to be used only in relatively dilute solution should not be forgotten. Attempts to extend the formalism beyond its conceived limits will lead to inadequate results. The fact that the formalism is unable to supply these limits of validity may have contributed to its improper usage and subsequent unfair criticism.

The interaction parameters bear significant correlation with properties that have physical meaning such as heat of formation of the corresponding oxides and atomic number of the deoxidants. These correlations not only help support the soundness of the formalism but also provide an interesting and useful way of checking the consistency of data presented in this formalism, as shown in the present work.

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