

## **A MATHEMATICAL DESCRIPTION OF THE THERMODYNAMIC BEHAVIOUR OF MULTI- COMPONENT SLAG SYSTEMS WITH THE USE OF SOLUTION SPECIES**

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For a better understanding and control of the chemistry of smelting processes, the importance of adequate description of the thermodynamic behaviour of slag, metal and matte solutions has been increasingly realized. In this regard, the concept of associated solution species has gained wide acceptance over the past two decades for its efficacy and flexibility in representing the properties of complex slag and matte solutions.

This paper reviews the highlights of this approach and the author's experience in applying it for describing the thermodynamic properties of iron silicate slag systems wherein the hypothetical chemical species are considered to behave in a non-ideal manner. The activity coefficients of the solution species are described with the help of three-suffix Margules equations with zero ternary interactions which correspond, in the author's opinion, to a generalized form of the regular solution behaviour. Examples from the lime containing iron silicate quaternary and the nickel containing quinary and their subsystems are examined briefly.

### **INTRODUCTION**

A large body of experimental data is available on the thermodynamic properties of iron-silicate slags. However, it is fragmentary. Many regions of temperature and composition exist where data are lacking. This deficiency and the lack of an adequate mathematical description of thermodynamic properties of these complex solutions contribute to under-utilization of this valuable information in process modelling and design.

During the last decade, the associated solution species approach has been applied with considerable success in correlating the thermodynamic properties of multi-component slags as a function of their composition and temperature. These slags systems exhibit a highly non-ideal behaviour which defies simpler treatments.

The author and his coworkers have found this approach unusually versatile and flexible[1-3]. Our effort has been to find the simplest mathematical formulation, consistent with basic thermodynamic principles, that will describe the known systems behaviour without bias, that can be extrapolated with reasonable confidence to unmeasured regions of temperature and composition, that can be readily extended from binaries to ternaries to more complex systems, and that lends itself to computer calculation. However, the method is empirical. Thus, our correlations should be judged entirely on the basis of their ability to satisfy this goal.

The germinal idea of our approach came from the application of Darken's quadratic formalism to the terminal regions of binary solutions[4]. He showed that the central region of many binaries and most M-O binaries was characterized by the presence of a maximum in the "excess stability" function, that the position of the maximum often corresponded to solution compositions where stoichiometric binary compound exists. In order to describe the whole composition range including the central region, it is usually necessary to assume the presence an associated solution species, having the composition of the maximum, in equilibrium with terminal species.

The second feature of our correlation is that the solution species behave non-ideally; their activity coefficients being described by a simple form of the Margules equation with zero ternary interactions:

$$\ln \gamma_i = \frac{1}{2} \sum_j (k_{ij} + k_{ji}) N_j - \frac{1}{2} \sum_j \sum_p k_{jp} N_j N_p + \sum_j (k_{ij} - k_{ji}) N_j (\frac{1}{2} N_j - N_i) + \sum_j \sum_p (k_{jp} - k_{pj}) N_p N_j^2 \quad (1)$$

These equations are consistent with the Gibbs-Duhem equation and with Henry's and Raoult's laws as limiting cases. This built-in consistency with basic thermodynamic principles imparts a very significant advantage as will become clear later. The above expression is capable of describing non-symmetrical activity behaviour in a binary even with only two end components considered as solution species and thus possesses considerable flexibility. In the special case where  $k_{ij} = k_{ji}$ , the equations are reduced to the conventional regular solution equations predicting a symmetrical behaviour.

#### CORRELATION FOR THE QUATERNARY SYSTEM Fe-O-SiO<sub>2</sub>-CaO

Slags in the Fe-O-SiO<sub>2</sub>-CaO and its associated subsystems were described in terms of six non-ideal species  $\text{FeO}_{1.5}$ ,  $\text{FeO}$ ,  $\text{Fe}$ ,  $\text{SiO}_2$ ,  $\text{CaO}$  and  $(\text{CaO})_2 \cdot \text{SiO}_2$ . The equilibrium constants for the formation of these species and the Margules parameters are listed in Table I. A considerable time and painstaking effort were required to find the "best values" of these parameters. The equilibrium constant for the formation of  $\text{Fe}$  was fixed at unity to ensure that  $a_{\text{Fe}}$  will always equal the activity of the real liquid iron component. For this quaternary system the relation  $k_{ij} = C_{ij}/T$  was found satisfactory for describing the temperature dependence temperature of the Margules constants. This simplified relation implies that the solution species for the Fe-O-SiO<sub>2</sub>-CaO system possess zero values of partial molal excess entropy and, therefore, exhibit a regular solution behaviour.

It is axiomatic that the values of above parameters must remain unchanged when the description is extended to slag compositions in quaternaries and higher systems. Auxiliary data for the saturation of liquid silicate slags with solid iron, magnetite, fayalite and dicalcium silicate were taken from literature[1,2].

Representation of the slag equilibrium with wustite required additional correlation capable of describing the behaviour of the wustite phase as a function of composition and temperature. Both the solution of oxygen in solid iron and the wustite phase could be described by considering the three species  $\text{FeO}_{1.5}$ ,  $\text{FeO}$  and  $\text{Fe}$  behaving in a non-ideal fashion according to Eq. (1). The parameters for the correlation have been presented earlier[1].

## COMPARISON OF THE CORRELATION WITH EXPERIMENTAL DATA

The capability of the correlation to reproduce experimental data on thermochemical properties is expressed in terms of standard deviation of the fit to data from different sources as presented earlier[1,2] for the Fe-O, Fe-O-SiO<sub>2</sub>, Fe-O-CaO, CaO-SiO<sub>2</sub> and Fe-O-SiO<sub>2</sub>-CaO melts as well as for the wustite phase.

### The Fe-O Binary

For the Fe-O binary, the calculated phase diagram in Figure 1 is in excellent agreement with that given by Darken and Gurry[5, 6]. The correlation for the solid Fe-O binary accurately describes the oxygen activity behaviour within the wustite phase and its boundaries saturated with solid iron as well as magnetite. Similarly, the ability of the model (Table I) to describe the thermochemical behaviour in the liquid oxide region, miscibility gap with liquid iron and equilibria with magnetite, wustite and solid iron is remarkable.

### The Fe-O-SiO<sub>2</sub> Ternary

Figure 2 shows a projection of the liquidus surface giving isobars and isotherms for the saturation surfaces all calculated from the parameters listed in Table I along with those for the solid Fe-O binary.

The overall behaviour of the model compares very well with the phase diagram summarized by Muan and Osborn[8] with some noteworthy differences. Unlike the construction reported by Muan and Osborn, the predicted phase boundary corresponding to liquid slag cosaturated with wustite and fayalite shows an increasing silica content as temperature is decreased and  $X_o/X_{Fe}$  ratio is increased in the liquid slag. This behaviour is in agreement with the observation made by Schuhmann and coworkers[9].

With respect to temperature, two of the predicted invariant points, (i) silica + fayalite + iron + liquid, and (ii) wustite + fayalite + iron + liquid show excellent agreement with those reported by Muan and Osborn, the deviation being within 1°C. For the lowest temperature invariant point, where liquid slag coexists with silica, fayalite and magnetite, the predicted temperature is 1146°C, slightly higher than 1140°C as obtained by Muan[10].

The other invariant point, where liquid slag is saturated with wustite, fayalite and magnetite, is predicted to be at a temperature of 1163°C which is substantially higher than 1150°C as obtained experimentally by Muan[10] and estimated earlier by Darken[11] using extrapolation of the data on the univariant equilibrium wustite-magnetite-melt. Further, this invariant point falls within the subtriangle fayalite-magnetite-silica according to the model. Muan and Osborn[8] place this invariant point within the subtriangle fayalite-magnetite-FeO. Even though the composition of the slag at the invariant point does not differ much between the model prediction and the Muan and Osborn diagram, its position in a different subtriangle changes it from a ternary eutectic (Muan and Osborn) to a ternary peritectic (the model) as required by the laws governing ternary systems[12]. More precise measurements will be needed to determine these two invariant points.

### The Quaternary Fe-O-SiO<sub>2</sub>-CaO

Figure 3 shows an isothermal section of the quaternary phase diagram at 1600°C when saturated with liquid iron including phase boundaries for co-saturation with SiO<sub>2</sub>, CaO, (CaO)<sub>2</sub>SiO<sub>2</sub> and (CaO)<sub>3</sub>SiO<sub>2</sub>, and iso-activity contours for FeO. The results have been plotted on a ternary basis by combining the small amount of Fe<sub>2</sub>O<sub>3</sub> with FeO to yield an equivalent value of FeO(tot). Figure 3 is in good agreement with the phase diagram proposed for this

temperature by Muan and Osborn[10]. The tendency for the isoactivity contours to "peak" at the interaction with the join  $\text{FeO}(\text{tot})\text{-(CaO)}_2\text{SiO}_2$  is clearly pronounced. The saturation boundaries for  $\text{SiO}_2$ ,  $(\text{CaO})_2\text{SiO}_2$ ,  $(\text{CaO})_3\text{SiO}_2$  and  $\text{CaO}$  have similar shapes and positions as predicted by others. The ability to predict the unusual shapes of the saturation boundary for  $(\text{CaO})_2\text{SiO}_2$  and the isoactivity contours is a clear illustration of the power of the mathematical correlation to describe complex thermochemical behaviour.

For slags richer than 65 mol%  $(\text{CaO}+\text{SiO}_2)$ , including data for the binary  $\text{CaO-SiO}_2$ , systematic deviations were noted between the predictions from the correlation and experimental data. This is attributed to an inadequate choice between conflicting data on the binary  $\text{CaO-SiO}_2$  at the time these correlations were made. More accurate and complete data will be required for the binary  $\text{CaO-SiO}_2$  to enable development of a correlation for the quaternary  $\text{Fe-O-SiO}_2\text{-CaO}$  that is valid all the way to 100%  $(\text{CaO}+\text{SiO}_2)$ . The parameters and equations of Table I are presently capable of reproducing the measured thermodynamic behaviour in the system  $\text{Fe-O-SiO}_2\text{-CaO}$  for the restrictions: (a)  $1150^\circ\text{C} < T < 1600^\circ\text{C}$ , (b) atom ratio  $\text{O/Fe} < 4/3$  and (c)  $\text{mol}\% (\text{CaO} + \text{SiO}_2) < 65$ .

### APPLICATION OF THE ASSOCIATED SPECIES MODEL TO OTHER SYSTEMS

The associated species approach has been applied successfully to correlate thermochemical properties of various kinds of liquid solutions including mattes such as  $\text{Cu-S}$ [13],  $\text{Co-S}$ [14],  $\text{Ni-S}$ [15], and alloys such as  $\text{Cu-Bi}$ ,  $\text{Cu-Sb}$ [16],  $\text{Cu-In}$ [17], apart from liquid oxides.

A major advantage of this approach is the ability to develop models of ternary and higher systems from the models of binary systems without alternating the parameters of the latter (binary models). This ability has been illustrated for the ternary  $\text{Cu-Bi-Sb}$ [16],  $\text{Cu-Ni-S}$ [15] and  $\text{Fe-O-SiO}_2$ , the quaternary  $\text{Fe-O-SiO}_2\text{-CaO}$ [2] and the quinary  $\text{Fe-Ni-O-SiO}_2\text{-CaO}$ [18]. However, modelling of real multicomponent solutions encountered in pyrometallurgical processes will require extensive and reliable experimental data as well as painstaking efforts to use the data for determining the relevant model parameters.

Table I. Correlation for the Quaternary system  $\text{Fe-O-SiO}_2\text{-CaO}$

(a) Formation equilibria for species

$\text{Fe(l)} + 3/4\text{O}_2(\text{g}) =$	$\text{FeO}_{1.5}$	$\ln K_1 = -12.8846 + 44760/T$
$\text{Fe(l)} + 1/2\text{O}_2(\text{g}) =$	$\text{FeO}$	$\ln K_2 = -6.3763 + 29471/T$
$\text{Fe(l)} =$	$\text{Fe}$	$\ln K_3 = 0.0$
$\text{SiO}_2(\text{s}) =$	$\text{SiO}_2$	$\ln K_4 = 0.96864 - 5970/T$
$\text{CaO(s)} =$	$\text{CaO}$	$\ln K_5 = 0.6777 - 3247/T$
$2\text{CaO(s)} + \text{SiO}_2(\text{s}) =$	$(\text{CaO})_2\text{SiO}_2$	$\ln K_6 = 4.4872 + 4.4677/T$

(b) Margules Constants,  $C_{ij}$

i/j	$\text{FeO}_{1.5}$	$\text{FeO}$	$\text{Fe}$	$\text{SiO}_2$	$\text{CaO}$	$(\text{CaO})_2\text{SiO}_2$
$\text{FeO}_{1.5}$	0	-1173	9882	-445	-7655	-5270
$\text{FeO}$	-2461	0	9199	-11115	-115	-129
$\text{Fe}$	9982	7188	0	7376	8242	7376
$\text{SiO}_2$	-147	-4165	7376	0	-8700	-13614
$\text{CaO}$	-7655	115	8242	-29000	0	-344
$(\text{CaO})_2\text{SiO}_2$	-5270	-129	7376	-13614	-344	0

## REFERENCES

1. Goel R.P., H.H.Kellogg and J.Larrain, *Metall. Trans.*, **11B** (1980) 107-117
2. Goel R.P. and H.H.Kellogg in *Proceedings of 2nd Int. Sym. on Metallurgical Slags and Fluxes.*, Eds. H.A.Fine and D.R.Gaskell, TMS-AIME, Warrendale, PA, USA, pp.347-355 (1984).
3. Kellogg H.H. and R.P.Goel, Unpublished Research, Columbia University, New York, USA.
4. Darken L.S., *Trans. Metall. Society (AIME)* **197** (1953) 1089-1096
5. Darken L.S. and R.W. Gurry, *J. Am. Chem. Society*, **68** (1946) 798-816
6. Darken L.S. and R.W.Gurry, *J. Am. Chem. Society*, **67** (1945) 1398-1412
7. Schuhmann R. Jr. and P.J.Ensio, *Trans. (AIME)*, **191** (1951) 401-411
8. Muan A., and E.F. Osborn, Addison Wesley, Reading, MA (1965)
9. Schuhmann R. Jr., R.G.Powell and E.J.Michal, *Trans. (AIME)*, (1953) 1097
10. Muan A., *Trans. (AIME)*, (1955) 965
11. Darken L.S., *J. Am. Chem. Soc.*, **70** (1948) 2046
12. Goel R.P., Doctor of Eng. Sc., Thesis, Columbia Univ., New York, (1978)
13. Larrain J.M., S.L.Lee and H.H.Kellogg, *Can. Met. Quart.*, **18** (1980) 395-400
14. Fosnacht D.R., R.P.Goel and J.Larrain, *Metall. Trans.*, **11B** (1980) 69-71
15. Lee S.L., J.M.Larrain and H.H.Kellogg, *Metall. Trans.* **11B** (1980) 251-255
16. Kellogg H.H., Y.H.Kim, T.Stapurewicz, D.Verdonik and G.Archer, in *Phys. Chem. of Extractive Met.*, Eds. V.Kurdryk and Y.K.Rao, TMS-AIME, Warrendale, PA, USA, pp.3-21, (1985)
17. Kellogg H.H., in *Proceedings of H.H.Kellogg International Symposium on Quantitative Description of Metal Extraction Processes*, Eds. N.J.Themelis and P.F.Duby, TMS-AIME, Warrendale, PA, USA, pp.3-15 (1991)
18. Kellogg H.H., *Can. Met. Quart.*, **26(4)** (1987) 285-298