Improvement in Applicability of Commercially Available Slag Models for Thermodynamic Estimations in Steel Refining Slag

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Abstract: Most engineering materials are multi-component in nature. Processing of such a material is governed by the thermodynamic properties of its constituents. However, measurement of these thermodynamic parameters is not easy, and becomes increasingly complicated as one moves from binary and ternary to multi-component systems. In the absence of direct measurement, commercially available computer-based packages are increasingly being used by scientists and engineers for estimation of thermodynamic properties in multi-component systems. Users may be tempted to accept such results as adequately reliable. It should be noted that any such package is validated over a limited range of chemical composition, usually where experimentally measured values are available. Its use outside this range brings in the risk of significant error in estimation.

Activities of individual constituents were measured experimentally in multi-component oxide systems containing CaO, SiO_2, FeO, Fe_2O_3, MgO, P_2O_5 and Al_2O_3. The results were compared with values obtained using three different commercial thermodynamic packages, each based on a separate model and set of assumptions. Significant differences were observed while computing the thermodynamic activities of FeO, Fe_2O_3 and P_2O_5. Further, the error in estimation of activity values was found to be non-random. The results indicate that different packages should be used for estimating the thermodynamic properties of different species and individual models require further adjustments for improving the reliability of predictions. The observations are important for selection of appropriate package suitable for a particular material system.

Keywords: Activity, Activity coefficient, Thermodynamic package, Computational thermodynamics

1. Introduction

Manufacture of steel requires oxidation of several impurity elements from the liquid metal. The slag phase remains in contact with liquid steel throughout the refining process and absorbs the products of oxidation of most of the elements, with the prominent exception of carbon. Thus, the extent of refining depends on the activities of the relevant oxides in the slag phase.

The activities of FeO, Fe_2O_3 and P_2O_5 in oxygen steelmaking slags had been measured by the authors and reported earlier. [1–4] The activities of these species, corresponding to the chemical compositions encountered, were also computed using commercially available thermodynamic softwares. [5] The results of the computations were observed to differ, often substantially, from the measured values. It was therefore felt necessary to explore the nature of deviation for different oxide species involved, and also to develop a correlation for improving the reliability of prediction of the thermodynamic properties.

2. Methodology

The details of the experiments for measurement of $a(\mathrm{FeO})$, $a(\mathrm{Fe_2O_3})$ and $a(\mathrm{P_2O_5})$ have been described elsewhere. [1, 3] The activity of FeO was calculated from the oxygen dissolved in liquid iron held in equilibrium with FeO-containing slag, considering appropriate standard states.

$$\mathrm{Fe}\ (l) + [\mathrm{O}] = \mathrm{FeO}\ (l) \qquad (1)$$

$$\Delta G^\circ = -121983 + 52.26\,T\ (\mathrm{J\ mol^{-1}})\ ^{[6]}$$

$$= -\mathrm{R}T \ln \{a(\mathrm{FeO})/h_{[\mathrm{O}]}\}$$

$$a(\mathrm{FeO}) = X(\mathrm{FeO}) \cdot \gamma(\mathrm{FeO}) = h_{[\mathrm{O}]} \times \exp(-\Delta G^\circ/\mathrm{R}T)$$

The activities of $\mathrm{Fe_2O_3}$ and $\mathrm{P_2O_5}$ were similarly obtained using the relations (2) and (3). However, for sake of conciseness, the detailed calculations have not been presented here since the same has already been published elsewhere. [4, 7]

$$2[\mathrm{P}] + 5[\mathrm{O}] = \mathrm{P_2O_5}\ (l) \qquad (2)$$

$$\Delta G^\circ = -705700 + 556.47\,T\ (\mathrm{J\ mol^{-1}})\ ^{[8]}$$

$$= -\mathrm{R}T \ln \{a(\mathrm{P_2O_5}).h_{[\mathrm{P}]}^{-2}.h_{[\mathrm{O}]}^{-5}\}$$

$$a(\mathrm{P_2O_5}) = X(\mathrm{P_2O_5}) \cdot \gamma(\mathrm{P_2O_5}) = h_{[\mathrm{O}]}^{5} \times h_{[\mathrm{P}]}^{2} \times \exp(-\Delta G^\circ/\mathrm{R}T)$$

$$2\ \mathrm{Fe}\ (l) + 1.5\ \mathrm{O_2}\ (g) = \mathrm{Fe_2O_3}\ (l) \qquad (3)$$

$$\Delta G^\circ = -815000 + 251.1\,T\ (\mathrm{J\ mol^{-1}})\ ^{[9]}$$

$$= -\mathrm{R}T \ln \{a(\mathrm{Fe_2O_3})/h_{[\mathrm{O}]}^{1.5}\}$$

$$a(\mathrm{Fe_2O_3}) = X(\mathrm{Fe_2O_3}) \cdot \gamma(\mathrm{Fe_2O_3}) = h_{[\mathrm{O}]}^{1.5} \times \exp(-\Delta G^\circ/\mathrm{R}T)$$

Activities of all these three oxides were estimated using the thermodynamic software ThermoCalc®, using the *SLAG2* and *TCFE3* databases. Activity of FeO was also computed through the package FACTSage®, using appropriate database(s) for constituents in slag and steel phases. $a(\mathrm{P_2O_5})$ could not be computed using FACTSage® since the slag models in-built in this software did not allow considering $\mathrm{P_2O_5}$ as a distinct equilibrium species. In addition, activities for a few compositions were also estimated using the software MTDATA®. All the computations were carried out for temperature of 1873 K (1600°C), irrespective of the software used.

3. Results and Discussion

3.1 Activity of FeO

The activity of FeO, obtained using the different packages, is compared with the measured values in Figure 1. FeO activity is under-predicted for most of the compositions considered, by all the three packages. The results obtained with MTDATA® appear to be closest to the measured values, followed by those from ThermoCalc®, while the computations using FACTSage® exhibit maximum deviation.

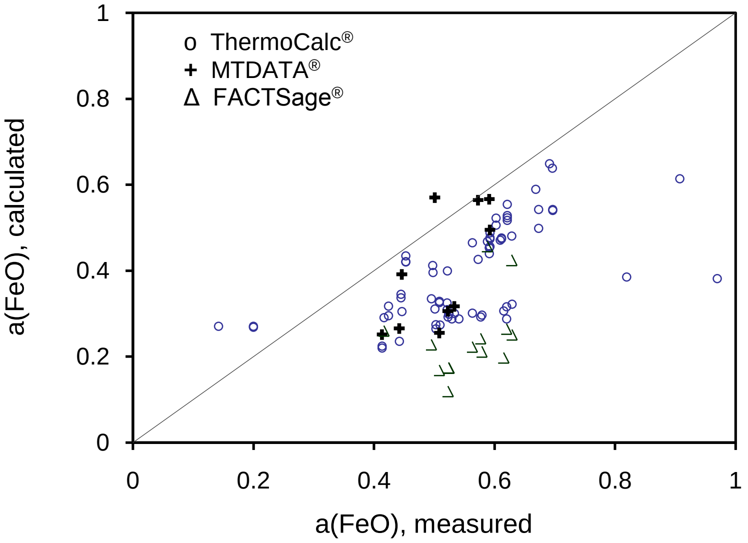

Figure 1: Activity of FeO, measured *vs.* calculated using standard packages

Similar comparison, in terms of the activity coefficient of FeO, has been illustrated in Figure 2. γ(FeO) computed using FACTSage® deviates the most from the measured values, and shows only marginal variation over the range of γ(FeO) encountered. The difference between the computed and measured values of γ(FeO), henceforth referred to as "*deviation in estimation*" of γ(FeO), has been plotted in Figure 3 as a function of the activity coefficient of FeO. This figure indicates that the error in γ(FeO) estimation is non-random and also varies with changing value of γ(FeO). The trend is similar for all the three thermodynamic packages considered. The computed value of activity coefficient is probably more sensitive to the chemical parameter(s) of the system(s) investigated, than considered in the packages.

$$\Delta\,\gamma(\text{FeO})_{\text{package}} = \gamma(\text{FeO})_{\text{computed}}\,(\textit{using package}) - \gamma(\text{FeO})_{\text{measured}}$$

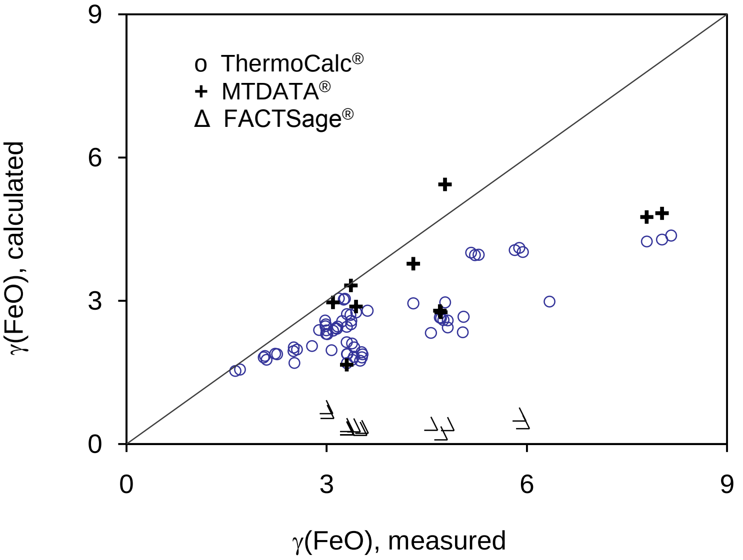

Figure 2: Activity coefficient of FeO, measured *vs.* calculated using standard packages

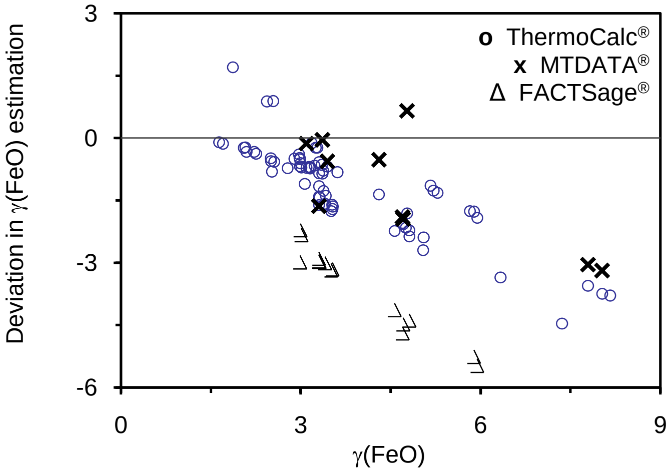

Figure 3: Variation of deviation in estimation of γ(FeO) with activity coefficient of FeO

It was seen in an earlier work of the authors that, among the chemical constituents of the slag, FeO concentration exerted the maximum influence on the activity coefficient of FeO, probably due to a relatively large self-interaction parameter. [3] Figure 4 shows the plot of Δ γ(FeO) *vs.* *X*(FeO). In spite of the significant level of scatter, it is clear that FeO molar fraction exerts a strong influence.

Attempts were made to check whether bascity of the slag exerted any major influence on Δ γ(FeO). However, no significant correlation could be observed.

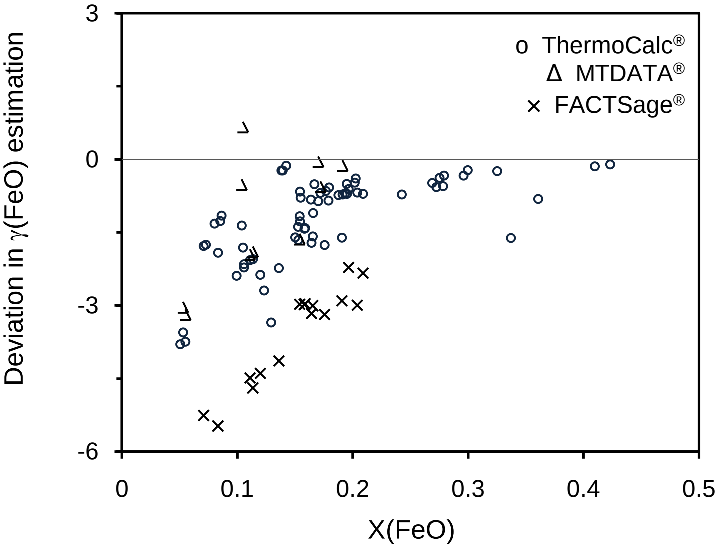

Figure 4: Influence of FeO concentration on the deviation in estimation of γ(FeO), using standard packages

3.2 Activity of P_2O_5

The activity coefficient of P_2O_5 computed by MTDATA® agrees reasonably well with the experimental measurements, as can be seen in Figure 6. However, ThermoCalc® under-predicts γ(P_2O_5) by as much as 5 – 7 orders of magnitude. As mentioned already, computation of γ(P_2O_5) using FACTSage™ was not possible. Unlike in the case of $\gamma(FeO)$, variation of $\gamma(P_2O_5)$, as well as $X(P_2O_5)$ and basicity, has practically no influence on the error in its estimation, as illustrated in Figures 7 and 8.

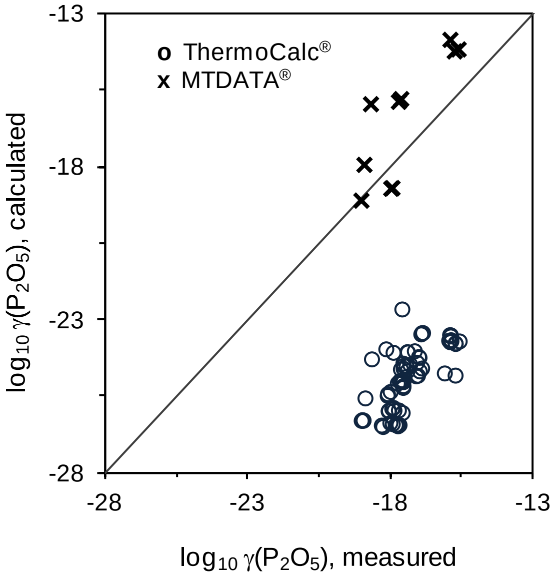

Figure 6: Activity coefficient of P_2O_5, measured *vs*. calculated using standard packages

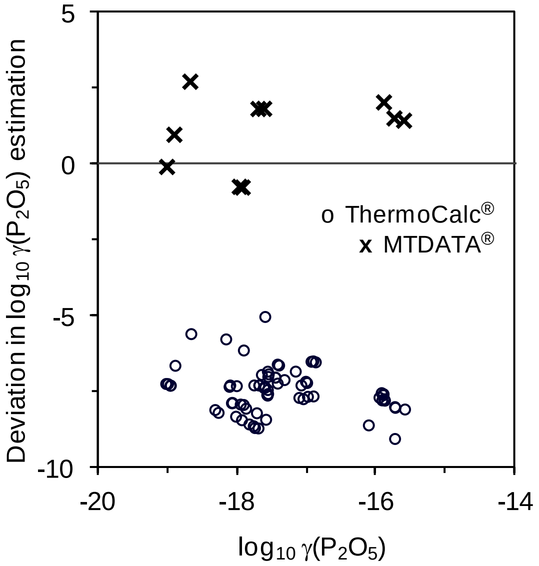

Figure 7: Variation of deviation in estimation of $\gamma(P_2O_5)$, using standard packages, with its activity coefficient

Figure 9 shows the influence of basicity on the error in estimation of P_2O_5. The error may appear to move in the negative direction with increasing basicity, but the magnitude of scatter is also significant. The error in estimation of $\gamma(P_2O_5)$ was compared with variation in concentrations of CaO, SiO_2 and FeO as well, but no correlation could be observed. Therefore, it may be inferred that $\gamma(P_2O_5)$ computed by ThermoCalc® contains a proportionate error of 5 – 7 orders of magnitude. MTDATA®, on the other hand, tends to over-predict $\gamma(P_2O_5)$, but within 1 – 2 orders of magnitude.

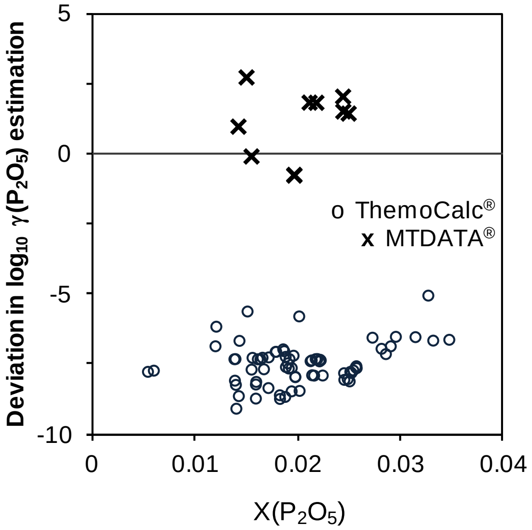

Figure 8: Variation of deviation in estimation of $\gamma(P_2O_5)$, using standard packages, with its concentration

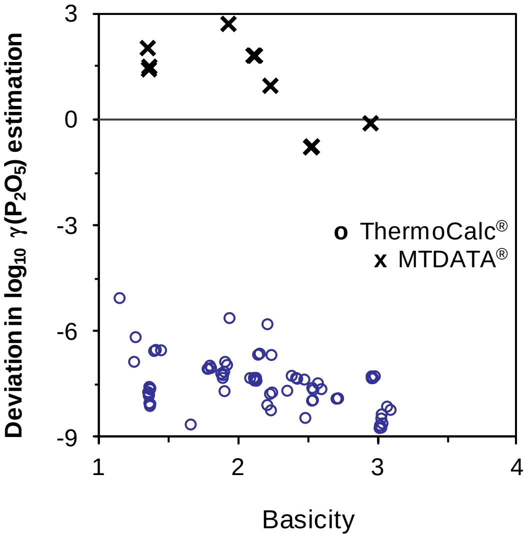

Figure 9: Variation of deviation in estimation of $\gamma(P_2O_5)$, using standard packages, with basicity

3.3 Activity of Fe_2O_3

The comparison between the measured and computed values of $\gamma(Fe_2O_3)$ has been shown in Figure 10, on log-log scale. It can be seen that the computations from ThermoCalc® are almost uniformly scattered within an error band of ± 1. The results from MTDATA, though much less in number, tend to over-predict the activity coefficient of Fe_2O_3. However, the error is seen to remain within one order of magnitude.

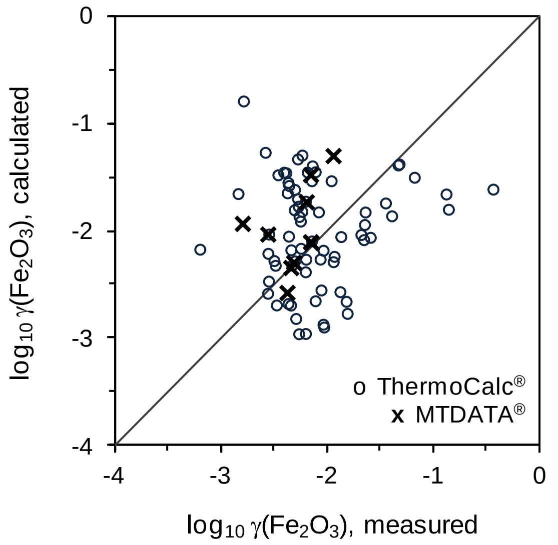

Figure 10: Activity coefficient of Fe_2O_3, measured *vs.* calculated using standard packages

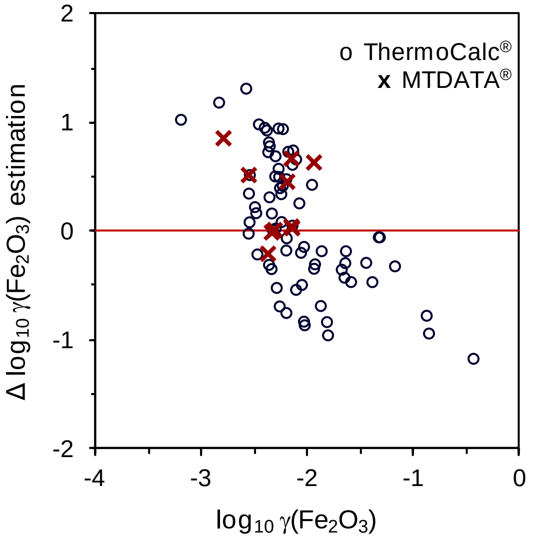

Figure 11: Variation of deviation in estimation of $\log_{10} \gamma(Fe_2O_3)$, using standard packages, with $\log_{10} \gamma(Fe_2O_3)$

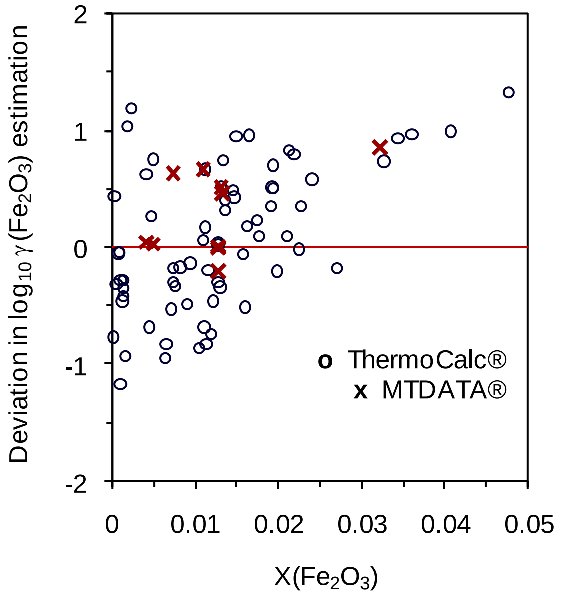

Figure 12: Variation of deviation in estimation of $\gamma(Fe_2O_3)$, using standard packages, with its concentration

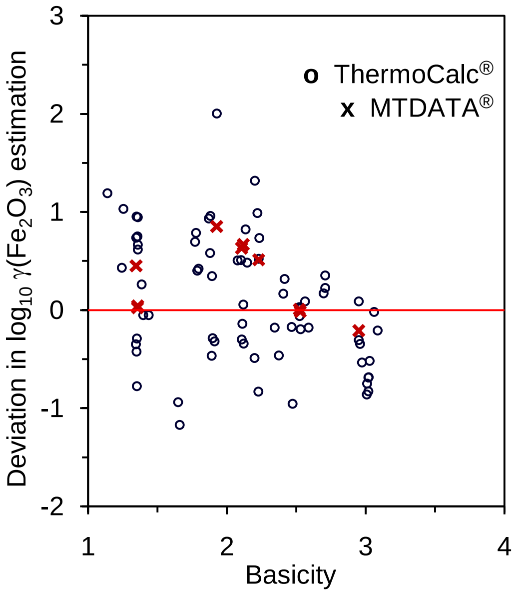

Figure 13: Variation of deviation in estimation of $\log_{10} \gamma(Fe_2O_3)$, using standard packages, with basicity

It is further seen in Figure 11 that the error in estimation of the activity coefficient of Fe_2O_3 moves in negative direction at higher values of $\gamma(Fe_2O_3)$. An opposite trend is seen in Figure 12 where the error in $\gamma(Fe_2O_3)$ estimation, particularly the results obtained from ThermoCalc®, shows an increasing trend with concentration. This behavior may be explained by the fact that the concentration of Fe_2O_3 has a strong negative influence on its activity coefficient, as was observed by the authors earlier. [4]

The variation of error in $\gamma(Fe_2O_3)$ estimation with respect to basicity has been illustrated in Figure 13. The figure tends to indicate a decreasing trend but the magnitude of scatter exceeds any systematic decrease. Hence, no definite correlation can be drawn from Figure 13. Figure 14, in contrast, clearly shows that variation in FeO concentration has no influence on the estimation of the activity coefficient of Fe_2O_3.

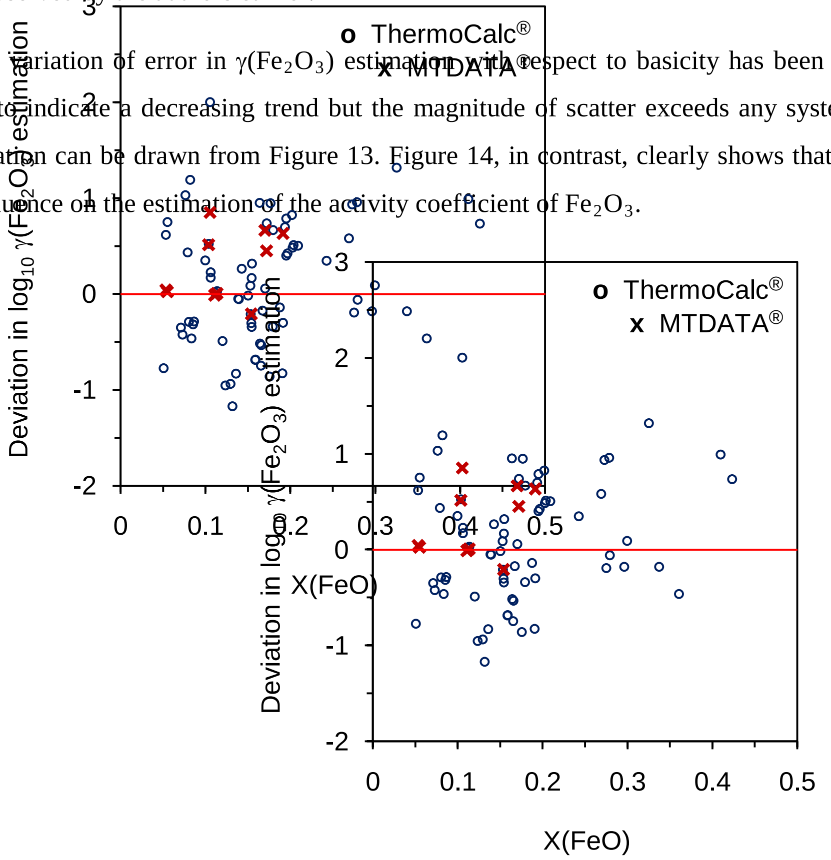

Figure 14: Variation of deviation in estimation of $\log_{10} \gamma(Fe_2O_3)$, using standard packages, with FeO concentration

3.4 Correction to the estimation of γ(FeO)

Figure 4 clearly shows that the deviation in estimation of γ(FeO) is strongly a function of the FeO concentration, for all the three thermodynamic packages considered. A regression analysis between the FeO concentration (in molar fraction) and the error in estimation while using the ThermoCalc® package yields the following relation.

$$\Delta\,\gamma(\mathrm{FeO})^{\mathrm{TC}} = \gamma(\mathrm{FeO})^{\mathrm{TC}} - \gamma(\mathrm{FeO})^{\mathrm{measured}} = 1.401 \ln X(\mathrm{FeO}) + 1.3508 \qquad (4)$$

where $\gamma(\mathrm{FeO})^{\mathrm{TC}}$ = activity coefficient computed using the ThermoCalc® package.

The activity coefficient of FeO, estimated using ThermoCalc®, could be modified using this correlation.

$$\gamma(\mathrm{FeO})^{\mathrm{TC,\ revised}} = \gamma(\mathrm{FeO})^{\mathrm{TC}}{}_{i} - \Delta\,\gamma(\mathrm{FeO})^{\mathrm{TC}}{}_{i}$$

$$= \gamma(\mathrm{FeO})^{\mathrm{TC}} - 1.401 \ln X(\mathrm{FeO}) - 1.3508 \qquad (5)$$

Figure 15 shows the agreement between the γ(FeO) values obtained using equation (5) and the measured activity coefficient. The improvement in predictions, compared to Figure 2, is quite obvious.

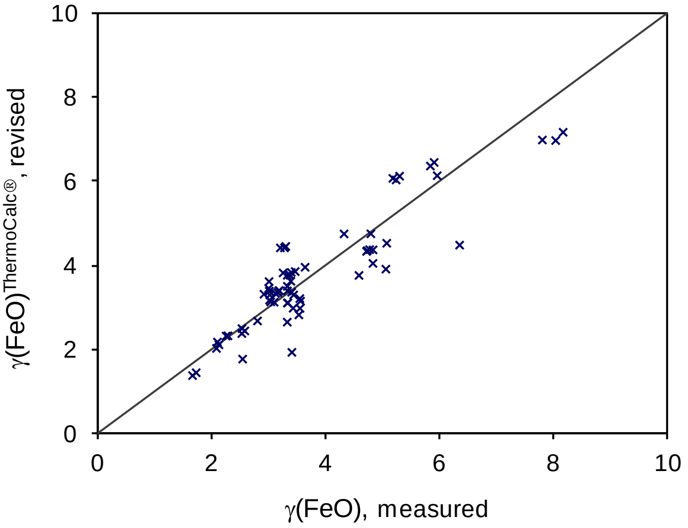

Figure 15: Activity coefficient of FeO, measured *vs*. revised calculation using ThermoCalc®

Similar exercise was repeated for calculations done using the MTDATA® and FACTSage® thermodynamic packages as well. The corresponding relations for obtaining better prediction of FeO activity coefficient are given below.

$$\gamma(\mathrm{FeO})^{\mathrm{MTDATA,\ revised}} = \gamma(\mathrm{FeO})^{\mathrm{MTDATA}}{}_{\mathrm{i}} - 2.15 \ln X(\mathrm{FeO}) - 3.32 \qquad (6)$$

$$\gamma(\mathrm{FeO})^{\mathrm{FACTSage,\ revised}} = \gamma(\mathrm{FeO})^{\mathrm{FACTSage}}{}_{\mathrm{i}} - 3.0497 \ln X(\mathrm{FeO}) - 2.3305 \qquad (7)$$

It can be seen in Figure 16 that the reliability of prediction with both MTDATA® and FACTSage® has improved significantly by incorporating the correction correlations, given in equations (6) and (7). The magnitude of improvement becomes even more pronounced when the results obtain with FACTSage® in Figure 16(b) is compared with the trend seen in Figure 2.

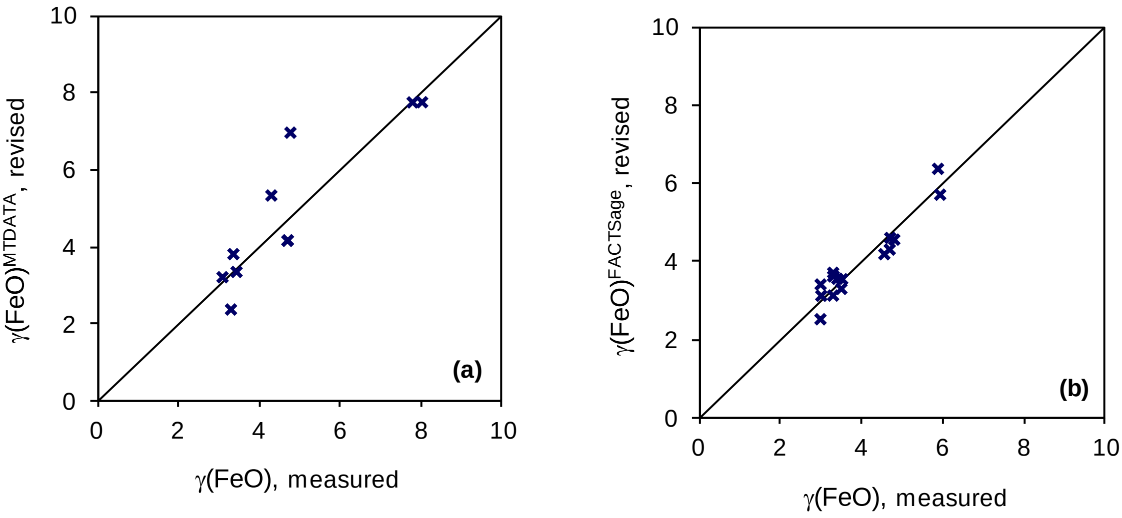

Figure 16: Activity coefficient of FeO, measured *vs*. revised calculation using
(a) MTDATA® and (b) FACTSage®

It should be mentioned here that the correlations (5), (6) and (7) obtained by the authors is applicable to the composition range covered in this work, primarily covering steel refining slag systems at 1873 K. These are yet to be validated at other compositions and temperatures. While the underlying principle holds good, use of the numerical coefficients for other slag systems should be done with caution.

4. Conclusions

The estimations of the activity coefficients of FeO, P_2O_5 and Fe_2O_3, obtained from MTDATA® agree most closely with the experimental measurements. Computations using ThermoCalc® show higher extent of scatter while the results obtained from FACTSage® (for FeO) exhibit maximum deviation.

The magnitude of difference between measured and computed values of γ(FeO) decreases with increasing FeO concentration. The error for estimation of $\gamma(P_2O_5)$, however, shows no definite correlation with any compositional parameter. The amplitude of scatter in the computed values of $\gamma(Fe_2O_3)$ tends to decrease with increasing concentration, and basicity, but no definite correlation can be drawn.

It is possible to improve the goodness of prediction of the thermodynamic parameters computed by the packages, using simple correction factors or correlations. A sample case of FeO activity coefficient has been presented in the paper.

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Nomenclature

ThermoCalc is a trademark of ThermoCalc Software AB, Stockholm, Sweden.

MTDATA is a trademark of National Physical Laboratory, Teddington, UK.

FACTSage is a trademark of GTT Technologies, Herzogenrath, Germany.

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