

IMPACT OF EXPERIMENTATION IN THERMODYNAMIC STUDIES OF SOME METALLIC AND OXIDIC SYSTEMS

R. E. Aune, P. Fredriksson and S. Seetharaman

Division of Metallurgy, Royal Institute of Technology
SE-100 44 Stockholm, Sweden

(Received 28 September 2002, accepted 15 December 2002)

Abstract

The importance of experimentation as an ingredient to CALPHAD assessments is brought out in the present paper and is illustrated in the case of a number of metallic and oxidic systems. Two types of experimental techniques have been used in the present laboratory for thermodynamic studies, and the details are presented. The results obtained together with the assessed phase diagram in the case of a few selected systems are presented. It was shown that careful experimentation has brought new features in the case of carbide systems involving Mn, and a new 4-phase equilibrium in the case of Ni-W-O system. New data with regard to the thermodynamic activities of FeO-containing slag systems and sulphide capacities of multi-component slags, obtained by gas equilibration method, are also presented. A thermodynamic software, THERMOSLAG[®] based on the experimental data has been found to be extremely useful by the steel industries is also discussed.

Keywords: Measurements, activities, thermodynamics, modelling, oxides, alloys

1. Introduction

Knowledge of the thermodynamic properties of metallic and oxidic systems is of great importance in the modelling of high temperature materials processes. The systems considered in this context are usually multicomponent in nature, and the

thermodynamic data need often to be extrapolated from the available data to different temperature and composition ranges. Such extrapolations often require a suitable thermodynamic model. Based on these models, various thermodynamic databases have been developed around the world, as for example, Thermo Calc [1] or FACT [2]. While the predictions from these data bases often are verified with available literature data, the amount of research resources that are dedicated towards newer experimentation are diminishing every day. This seriously impairs the validation of the model predictions in the case of unknown systems, or unknown composition and temperature regions of known systems, since model predictions are strongly dependent on the accuracy and reliability of the input data. The present paper highlights the importance of experimentation in the case of thermodynamic studies of some metallic and oxidic systems. Experimental techniques involved in the measurement of thermodynamic properties of high temperature systems are often based on equilibration of the condensed system with a suitable gas phase, and monitor the changes in the partial molar Gibbs energy of a component. The usual experimental methods adopted in our laboratory are:

1. EMF method wherein the change in the partial molar Gibbs energy is harnessed in a suitable cell reaction, and
2. equilibration with a gas-mixture and following the compositional changes.

The present paper will focus on some of the measurements in a variety of metallic and slag systems, and how the results were employed in a thermodynamic mapping of the systems using the CALPHAD [3] approach. The paper also briefly present a user-friendly software suitable for use by steel-plant engineers without elaborate training for retrieval of the data and extrapolation with respect to the process conditions.

2. Experimental

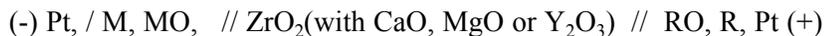
2.1. EMF Method

This method has been found to be extremely suitable for the measurements of partial molar Gibbs energies in metallic and oxidic systems. The design of the galvanic cell should be such that the reaction of interest harnesses the cell reaction and the Gibbs energy for the reaction could be calculated from the EMF of the galvanic cell. The criteria for the application of this method in galvanic cell meas-

measurements are that the electrolyte is a pure ionic conductor under the experimental conditions, and that reaction between the electrodes and the electrolyte should be negligible. The potential obtained at a constant temperature, independent of time, should be reproducible from both higher and lower temperatures level respectively. The cell should also return to its original level if a small current have been added in either direction. Thermal EMF and temperature gradients can be minimised by placing the cell within the constant heating zone of the experimental assembly and, by using similar lead material at both electrodes respectively. Concentration changes due to differences of partial pressures of the electrodes and electrolyte respectively can be minimised by using a suitable cement, which does not affect the cell behaviour.

The electronic conduction regions of a number of solid electrolytes have been defined by experimentation by Patterson [4], which is illustrated in Figure 1.

In the case of metallic and oxidic systems, zirconia-based, oxygen conducting solid electrolytes are used at relatively high oxygen partial pressures. A typical galvanic cell used for the measurements of partial molar Gibbs energies, in the case of oxide systems, is presented below:



The above cells can be used in the case of the measurements of the activities of components in oxide or alloy systems.

For highly reactive systems involving, for example metals like Mn or systems with interstitially dissolved carbon or nitrogen, it is advantageous to use calcium fluoride as the solid electrolyte. These electrolytes have anti-Frenkel defects with F^- interstitials in the ionic sublattice and are fluoride ion conductors.

A typical galvanic cell arrangement for thermodynamic measurements is shown in Figure 2 [5].

A number of metallic, oxidic as well as carbide systems have been investigated in the present laboratory. The results obtained are discussed in the later part of the paper.

2.2. Gas Equilibration Method

This has been a versatile method for the measurement of the thermodynamic activities of components in a complex oxide system in solid or liquid state. It can also be used to investigate sulphide capacities of various slag systems.

The experimental technique is based on that the system is brought to equilibrium

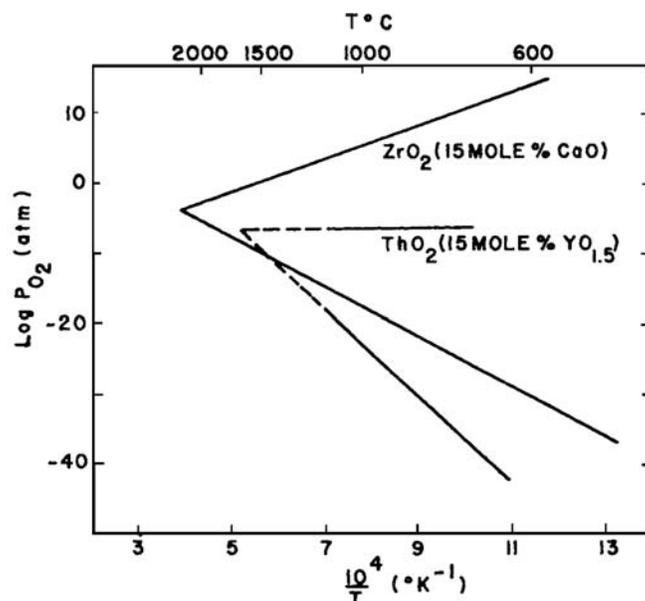


Fig.1. Electrolytic domains for ZrO_2 (CaO) and ThO_2 (Y_2O_3) electrolytes as estimated by Patterson [4]

with a gas mixture of well-defined oxygen partial pressure using suitable redox gas mixtures like $CO-CO_2$, H_2-H_2O or $CO-CO_2-SO_2$, if sulphide capacities are to be studied, at the experimental temperature.

In order to obtain accurate partial pressures of the various gases, impurity levels have to be minimised, careful calculations of the partial pressures have to be performed and, the oxygen partial pressure of the outgoing gas mixture has to be continuously monitored. An example of a gas cleaning system used by the present laboratory is presented in Figure 3. The moisture impurity in the argon gas is removed by passing the gas successively through silica gel as well as $Mg(ClO_4)_2$. To remove traces of CO_2 in the gas, a column of ascarite was introduced in the system. The gas was passed through columns of copper and magnesium turnings kept at 773 K in order to bring down the oxygen impurity level. The final oxygen level in argon cleaned in this way was found to be less than 10^{-18} atm. The CO gas was purified in a similar way. The oxygen impurity in the gas was allowed to react with CO over heated copper turnings and the resulting CO_2 was absorbed by ascarite. The moisture level in the CO_2 gas was brought down by passing the gas through silica gel as well as $Mg(ClO_4)_2$. The flow rates of the different gases was controlled by magnetic flow

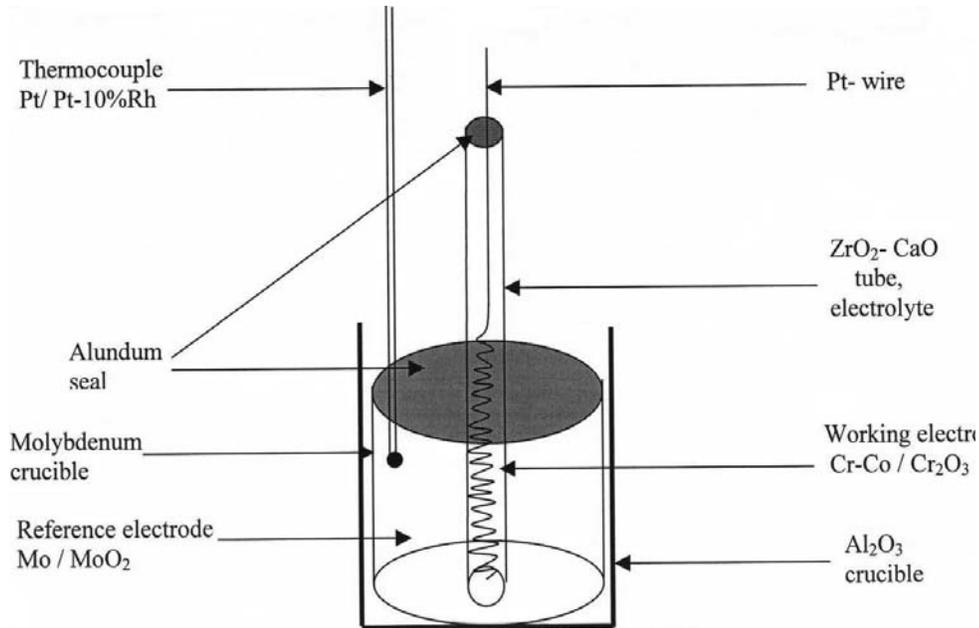


Fig.2. The galvanic cell arrangement [5]

meters and the partial pressures of the different components in the gas mixture at the experimental temperatures were calculated by using the THERMO-CALC[®] software. The oxygen partial pressure of the outgoing gas mixture was monitored continuously by a ZrO₂-CaO galvanic cell kept at 973K.

In order to minimise thermal segregation of the different gases, the total flow and the diameter of the gas injection tube above the samples, have to be selected carefully. It is also convenient to choose a sample carrier with provision for 4-5 samples simultaneously. The carrier should be designed to fit the constant heating zone and have chemically resistance to the crucible material. Cracking of the furnace tube during quenching of the samples was prevented by placing alumina powder and runners below the sample carrier. Experimental sequences between 6-24 hours have been used. After the equilibration, the sample was quenched and the contents was analysed. A typical experimental arrangement used for the measurement of the activities of FeO in oxidic melts is shown in Figure 4 [6].

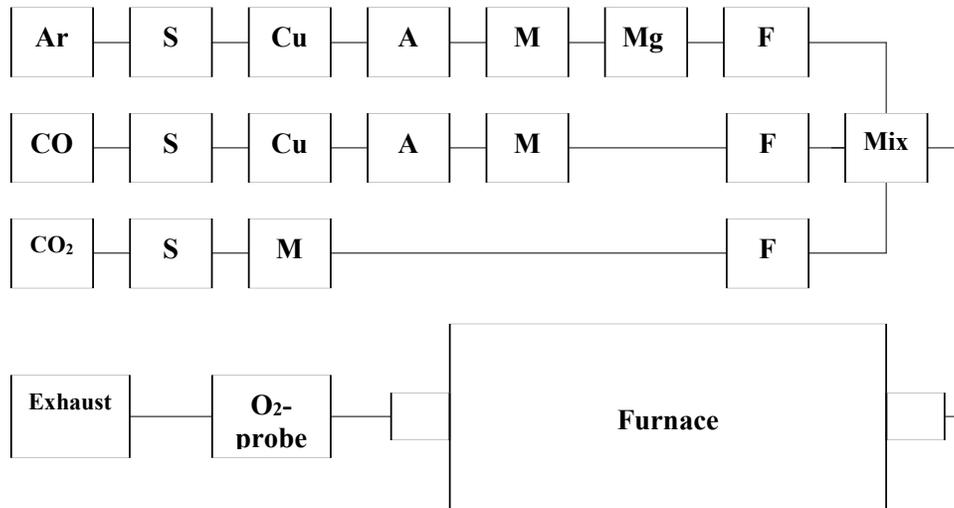


Fig.3. The gas cleaning system: S = Silica Gel, Cu = Copper turnings, A = Ascarite, M = Magnesium perchlorate, Mg = Magnesium turnings, F = Magnetic flow meters, Mix = Gas mixing chamber

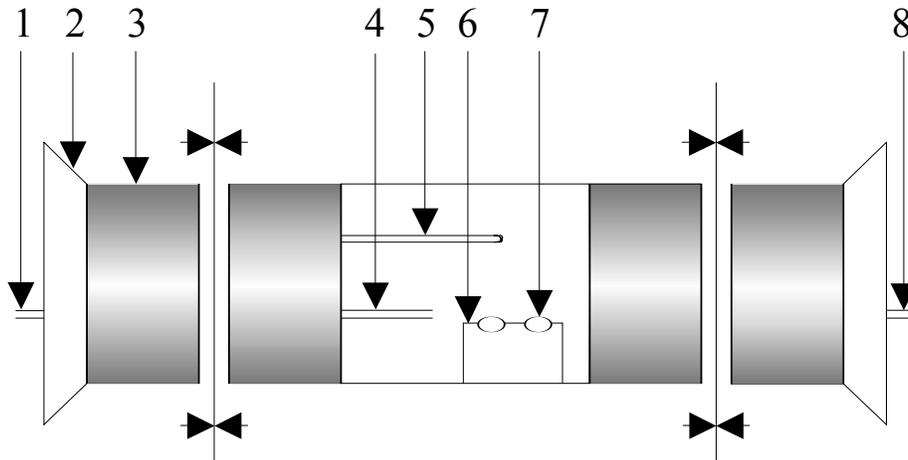


Fig.4. The furnace assembly: 1. Gas inlet, 2. Silica stopper, 3. Alumina reaction tube, 4. Gas inlet, 5. Thermocouple, 6. Alumina crucible holder, 7. Platinum crucible, 8. Gas outlet

3. Results and Discussions

3.1. EMF Measurements

3.1.1. Fe-Pt System

The information regarding the thermodynamics of this system is of great importance in the gas-equilibration measurements of FeO activities in slags contained in Pt crucibles. The present group carried out the experimental investigations of this system by solid-state galvanic cells using partially stabilized zirconia as the solid electrolyte and Fe/FeO as the reference electrode. The buffer oxide at the working electrode was FeO. At high Pt contents, the wüstite, at this electrode was likely to be oxidised to magnetite due to high partial pressure of oxygen prevailing and hence, the electrode was suitably modified. Activities obtained derived from the experimental data are compared with earlier results [7] in Figure 5 (a). Complementary calorimetric studies were also carried out in order to acquire information regarding the enthalpies of phase transformations and specific heats [8]. A thermodynamic assessment [3] of the system was carried out combining the present results with those of earlier measurements available in literature [9]. The phase diagram of the Fe-Pt binary system generated from these studies is presented in Figure 5 (b).

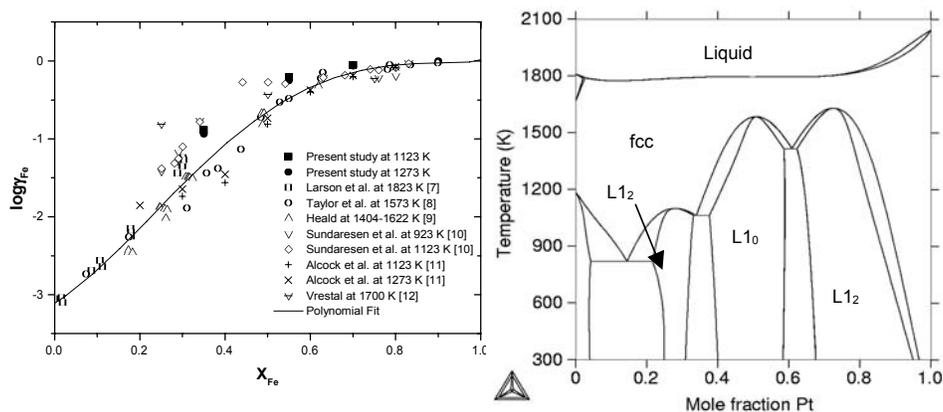


Fig.5. (a) Activity coefficients of Fe in Fe-Pt alloys derived from the present results [7], (b) The assessed phase diagram generated from the experimental data [9]

3.1.2. Ni-W-O System

In the production of tungsten nano-alloys by the reduction route, it is essential to have a thermodynamic understanding of the system Ni-W-O. The system was examined [10] by the solid-state galvanic cell method using ZrO₂-MgO solid electrolyte as in the earlier case. The EMF-temperature lines showed a break point at 1167 K, which has not been reported in earlier measurements. This is shown in Figure 6 (a). The phases corresponding to the various 3-phase regions were confirmed by quenching the samples of corresponding composition and analysing the same by Scanning Electron Microscopy. The experimental information was used to conduct a CALPHAD [3] assessment of this system, leading to a refined phase diagram of the Ni-W-O ternary. A unique feature of this new assessment is the identification of a four-phase equilibrium of class II involving Ni (f.c.c.), NiWO₄(s), WO_{2.72}(s) and WO_{2.9}(s) phases. The isothermal section of the assessed diagram at 1273 K is reproduced in Figure 6 (b).

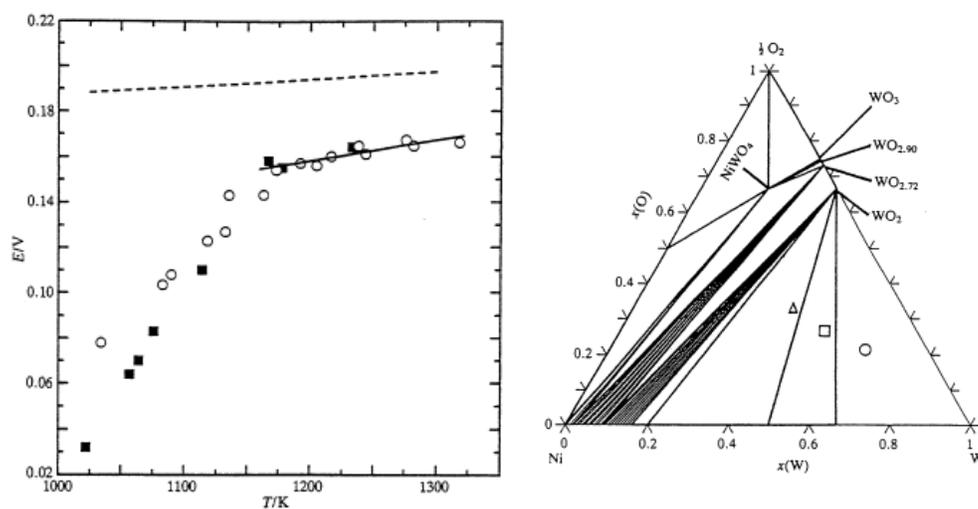


Fig. 6. (a) The EMF vs temperature line for the system Ni-W-O by the galvanic cell method and (b) the isothermal section of the phase diagram at 1273 K [10]

3.1.3. Co-Mn-C System

This system is of special importance to hard materials industry. The thermodynamic properties of this system were not previously known. The thermodynamic activities of Mn in this system were measured by the solid-state galvanic cell method using CaF_2 . The studies were complemented by phase characterization wherein specific alloys were quenched from certain temperatures of interest, and the samples examined by Scanning Electron Microscope and Electron Microprobe analyses. A thermodynamic assessment was carried out using the present results, and a phase diagram was generated. An isothermal section of this diagram is presented in Figure 7 (a) [11].

It is very interesting to note that these results are in agreement with the earlier work carried out in the same research group [12] in the case of the Mn-C binary system. According to this work the system Mn-C exhibits a eutectoidic transformation at 1031 K involving Mn (γ), Mn (α) and Mn_{23}C_6 . This differs from the earlier published phase diagram for this binary system [13] (Figure 7 (b)). This strongly implies that the phase diagram of the system Mn-C need a fresh assessment. Parallely, the thermodynamics of the system Ni-Mn-C is also investigated currently by the present research group. A new assessment of the Mn-C system, and incorporating the same in the Co-Mn-C and Ni-Mn-C systems, are expected to provide new and interesting information regarding the phase relationships in the case of complex carbides containing manganese.

3.2 Gas Equilibration Measurements

3.2.1. Slag Systems Containing FeO

Thermodynamic information regarding the slag systems containing dissolved FeO is very important in the case of iron- and steelmaking processes. The literature data available are often mutually inconsistent. This motivated new investigations by the present group using the gas equilibration method. CO-CO₂-Ar mixtures were used for equilibration. The slag was contained in Pt-crucibles. Part of the iron oxide was reduced to metallic iron and was dissolved in the platinum. From a knowledge of the thermodynamic properties of the system Fe-Pt at the experimental temperatures, the thermodynamic activities of FeO in the slag could be evaluated. A number of binary, ternary and multicomponent slag systems were investigated by this method. The results in the case of the system CaO-FeO-SiO₂ are compared with earlier results in Figure 8 [6]. The results are incorporated in a thermodynamic model developed by the present group [14].

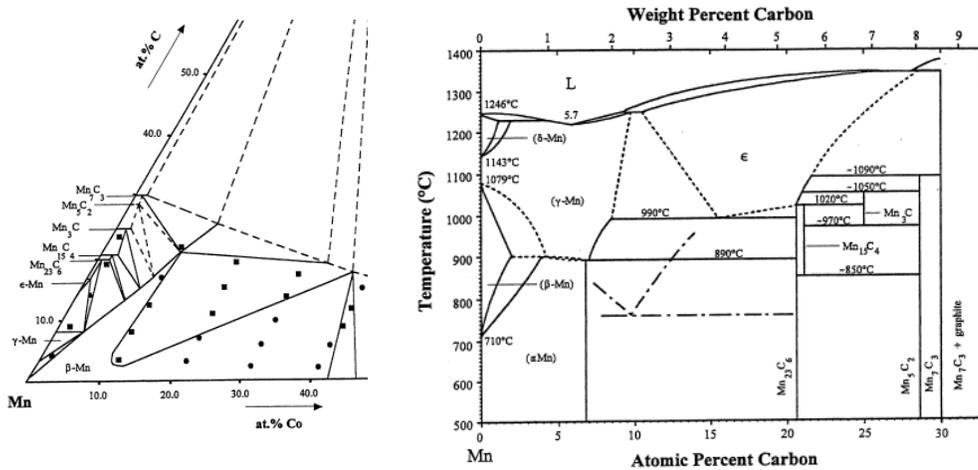


Fig.7. (a) The isothermal section of the Co-Mn-C ternary system at 1273 K and (b) the phase diagram of the system Mn-C with the eutectoid reaction reported at 1031 K reported from this laboratory earlier [11]

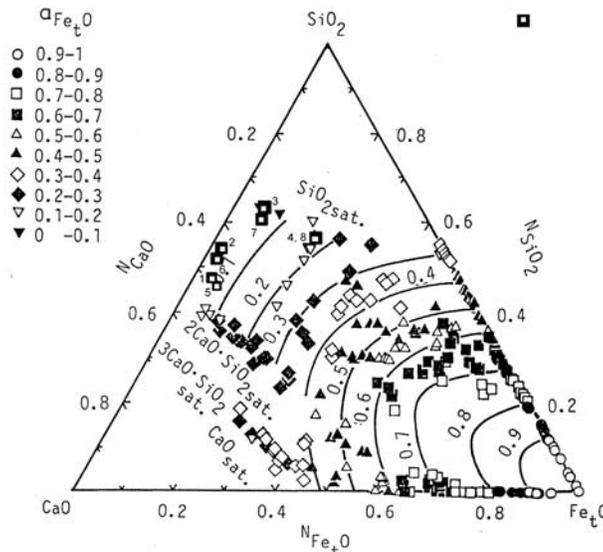


Fig.8. The activities of FeO in CaO-FeO-SiO₂ slags at 1873 K obtained by the present group as well as the iso-activity lines in the ternary [14]

3.2.2. Sulphide Capacities of Multicomponent Slags

The gas equilibration method was used to determine the maximum sulphur absorbing capacity of a metallurgical slag. This is a very important slag property with regard to desulphurisation. The sulphide capacity is a partial molar property corresponding to the sulphide component in the slag and has been shown to be related to the thermodynamic activities of the basic oxides in the slag. The sulphide capacities of a number of binary, ternary, quaternary, quinary and six component slags have been measured. A software was developed that enabled the computation of the sulphide capacities of multicomponent slags from those of binary and ternary systems (THERMOSLAG[®] [14]). Such software is currently being used by Swedish and other steel industries in modelling desulphurisation. The typical iso-sulphide capacity contours in the case of CaO-FeO-SiO₂ slags, developed by the THERMOSLAG[®] [14] software, is presented in Figure 9.

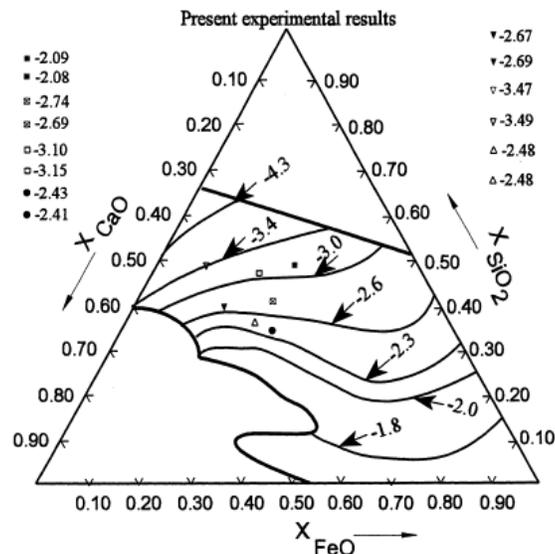


Fig.9. Iso sulphide capacity contours in the case of CaO-FeO-SiO₂ system [14]

3.3. Modelling

Modelling of metallurgical processes require accurate and reliable data on the thermochemical as well as thermophysical properties of metallurgical slags. In industrial

practice, the slags are often complex in nature. The property data necessary for modelling need be reliably extrapolated as functions of temperature and composition. Retrieval of the data and extrapolation with respect to the process conditions need a software that is user-friendly, suitable for use by steel-plant engineers without elaborate training. In addition, the data used must be self-consistent and reliable. A few examples of the computational systems for the thermodynamic properties of slags commercially available today are the Thermo-Calc [1], FACT [2] and MTDATA [15]. These do not include viscosities and other thermophysical properties of slags. In the case of slag viscosities and sulphide capacities, the data available in literature must be tested for consistency constraint. Existing data need be verified experimentally and new data need be generated where the data is lacking. These have motivated the present development work with a view to be of support to the steel industry around the world.

3.3.1. A Unified Composition Description

A unified composition description is adopted in the models for viscosity, sulphide capacity and activity. In the model development [16-18], a silicate melt is considered to consist of cationic and anionic sub-groupings in accordance with the classical Temkin description of ionic liquids. Further, the silicate melt is considered as an oxygen matrix with different cations including Si^{4+} distributed in it, as suggested by Lumsden [19]. Thus, in the present model description, a system containing m different oxides, $\text{C}_{1\text{c}_1}\text{O}_{\text{a}_1}, \text{C}_{2\text{c}_2}\text{O}_{\text{a}_2}, \dots, \text{C}_{i\text{c}_i}\text{O}_{\text{a}_i}, \dots, \text{C}_{m\text{c}_m}\text{O}_{\text{a}_m}$ can be represented as:



where p and q are stoichiometric numbers, $\text{C}_i^{\gamma_i}$ stands for cations, the superscript γ_i represents the electrical charge. The cations are expected to occupy the interstitial positions in the oxygen ion matrix. The electrostatic interactions between the cations and oxygen anion is governed by the electrical charges and the sizes of the cations. Thus, Si^{4+} ion will have a strong influence on the oxygen matrix, while the other cations are expected to be randomly distributed. Even in these cases, the relative size differences of the cations, as for example, Ca^{2+} and Fe^{2+} , would contribute to the non-ideal cation distributions, leading thereby to non-ideal configurational entropies in the cationic sub-grouping. The presence of basic cations such as Ca^{2+} , Fe^{2+} , Mg^{2+} and Mn^{2+} along with Si^{4+} will thus distort the oxygen matrix and determine the configuration of the ionic melt as well as the bond energies between different ions. The configuration of the ions and the bond energies will be functions of composition and

temperature. While there are mutual effects between the cations and oxygen ions, the thermodynamic properties of the solution can be formulated by the consideration of the next- nearest neighbour interactions, namely the interactions between the cations when oxygen ions are present. A detailed description of the viscosity, sulphide capacity and activity features of the software respectively are found in [16-18].

3.3.2. The Software

The present software, THERMOSLAG[®] [14], operates under windows 3.1, win95/98/2000 or Windows NT environment. The computation module is complemented by a databank containing experimental data, data sources and model parameters. It exploits the multi-document feature of windows. An overview of the running software, showing different applications in three opened windows is shown in Figure 10.

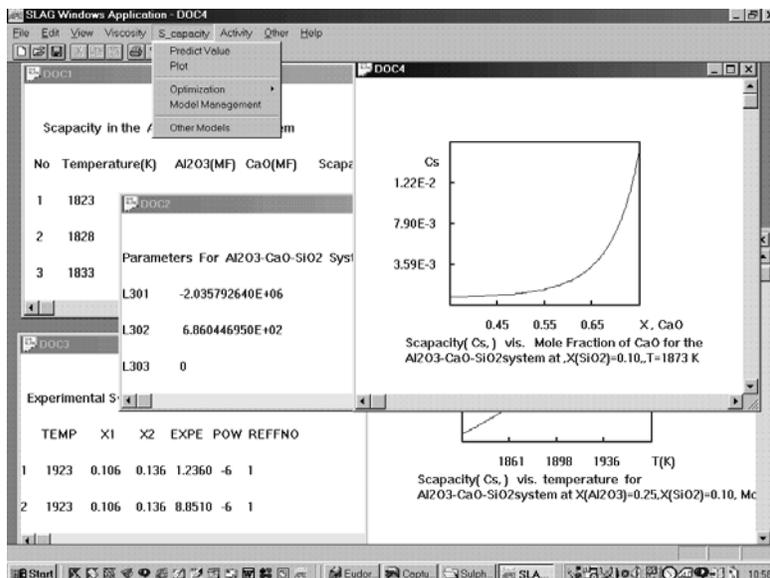


Fig.10. An over view of the running software

In order to utilise each part of the model, a set of self-consistent model parameters are essential. For this purpose, systematic optimisations were carried out using both literature data as well as the experimental values generated in the present laboratory [16-18]. The optimised model parameters are included in the databank. In the present

version, the model parameters enable the estimations of viscosities, sulphide capacities and oxide activities of slags containing up to the following six components, *viz.* Al_2O_3 , CaO , FeO , MgO , MnO and SiO_2 as functions of temperature and composition.

The present software is useful for the ironmaking and steelmaking industry, as it enables the estimations of C_S of any slag in the Al_2O_3 - CaO - FeO - MgO - MnO - SiO_2 system and its sub systems. However, in order to cover the slags in stainless steel making and copper industry, more oxide components, such as Cr_2O_3 and Fe_2O_3 should be included into the databank. Even CaF_2 should be incorporated with appropriate modification of the model in view of its appearance in many metallurgical slags and mould fluxes. Complementation of the C_S databank with these components requires more experimentation in the corresponding binary and ternary systems and careful assessments of the same.

4. Conclusions

The present paper elucidates the importance of experimentation with respect to thermodynamic assessments. The lack of reliable and reproducible data necessitates careful experimentation. Experimental experience is extremely important to the modeller to get an idea as to the errors involved in the various experimental data available in literature. This would minimise the uncertainties in the assessments.

The powerful combination of experimentation with assessment has been illustrated in the case of a number of metallic and slag systems in the present work.

References

1. B. Sundman, B. Jansson and J. O. Andersson, *CALPHAD*, 9 (1985) 153.
2. A. Pelton, C. W. Bale and G. Eriksson, 14th IUPAC Conference on Chemical Thermodynamics, ICCT-96, August 25-30, Osaka, Japan, 1996.
3. N. Saunders and A. P. Miodownik, *CALPHAD, Calculation of Phase Diagrams: A Comprehensive Guide*, *Pergamon Materials Series: Vol. 1*, Elsevier Science Ltd., Oxford, UK, 1998.
4. J. W. Patterson, *J. Electrochem. Soc.*, 18 (1971) 1033.
5. T. Sterneland, Lic. Thesis, Division of Metallurgy, Royal Inst. of Tech., Stockholm, Sweden, 2001.
6. P. Fredriksson, Lic. Thesis, Division of Metallurgy, Royal Inst. of Tech., Stockholm, Sweden, 2000.

7. P. Fredriksson and S. Seetharaman, *Sc. J. of Met.*, 30 (2001) 264.
8. P. Fredriksson, S. Seetharaman and B. Sundman, *CALPHAD XXX*, 27:th May-1:st June, York, England, 2001.
9. P. Fredriksson and B. Sundman, *CALPHAD*, 25 (2001) 535.
10. R. E. Aune, S. Sridhar and Du Sichen, *J. Chem. Thermodyn.*, 26 (1994) 493.
11. R. E. Aune, Ph. D. Thesis, Department of Metallurgy, Royal Institute of Technology, Stockholm, Sweden, 1997.
12. Du Sichen, S. Seetharaman and L. I. Staffansson, *Met. Trans.*, 20B (2002) 747.
13. T. B. Massalski, *Binary Phase Diagrams*, 1st ed., ASM, Metals Park, OH, Oct. 1986, p. 575.
14. THERMOSLAG[®], Division of Metallurgy, Royal Institute of Technology, Stockholm, Sweden.
15. R. H. Davies, A. T. Dinsdale, S. M. Hodson, J. A. Gisby, N. J. Pugh, T. L. Barry and T. G. Chart, in *User Aspects of Phase Diagrams*, ed. F. H. Hayes, Inst. Metals, London, 1997, p.140.
16. F-Z. Ji, Du Sichen and S. Seetharaman, *Int. J. of Thermophys.*, 20 (1999) 309
17. R. Nilsson, Du Sichen and S. Seetharaman, *Scand. J. Metal.*, 25 (1996) 128.
18. J. Björkvall, Du Sichen and S. Seetharaman, *Ironmaking and Steelmaking*, 28 (2001) 250.
19. J. Lumsden, *Physical Chemistry of Process Metallurgy, Part 1*, Interscience, New York, 1961, p.165.