

Activity Measurements in Slag Systems by Gas-Equilibration Technique

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ABSTRACT

In the present work experimental measurements of the thermodynamic activities of iron oxide were carried out for some selected compositions in the system CaO-“FeO”-SiO₂ by using a gas equilibration technique at 1873K. The oxides, kept in Pt crucibles, were allowed to come to equilibrium with a CO-CO₂ gas mixture with a defined partial pressure of oxygen at the experimental temperature. A part of the Fe from the “FeO” was reduced and the metal formed dissolved in the Pt phase. The samples were quenched after the required equilibration time and the slag phase as well as the platinum crucible were subjected to chemical analysis. The activities of “FeO” in the slag were calculated from the experimental data using thermodynamic information on the Fe-Pt binary metallic system. To enable this, solid electrolyte galvanic cell measurements of the activities of iron in the Fe-Pt binary metallic system were carried out. The results obtained, together with the literature data were optimised and extrapolated to higher temperatures using a Regular solution model. The experimental results are compared with earlier thermodynamic studies of the slag systems.

INTRODUCTION

In order to meet the customer requirements, the steel industry is often forced to keep the dissolved elements in the steel bath within specified intervals. Furthermore, impurities such as inclusions have to be controlled to satisfy the demands of the material. In steelmaking, final adjustments of the composition take place in the ladle process before the molten metal is cast. During the ladle refining process, the reactions between steel and slag play a significant role on the resulting product. In order to optimise the ladle refining reactions, it is important to have an accurate knowledge of the thermodynamic properties of the slags involved. The present investigation is part of an overall attempt to generate thermodynamic data with respect to ladle slags.

The Division of Metallurgy has developed a slag model that enables the extrapolation of the thermodynamic data of multicomponent slags as functions of composition and temperature. This model, referred to as KTH model, enables the estimation of the thermodynamic activities of higher order systems from the experimental data for lower order systems.

The present work has been initiated as part of a project in the Metallurgy Division in which the “FeO” activities in slags with moderate amounts of “FeO” were to be investigated. The system taken up for the first set of measurements is CaO-“FeO”-SiO₂. Some measurements were also carried out in the binary slag systems “FeO”-SiO₂, “FeO”-Al₂O₃ and CaO-“FeO” in order to make sure that the experimental set-up and the measurement techniques were reliable.

The slags, contained in Pt crucibles, were allowed to come to equilibrium with CO-CO₂-Ar gas mixtures of known oxygen partial pressure at the experimental temperatures. During this procedure, a part of the iron from “FeO” in the slag was found to have dissolved in the thin Pt crucibles used as container materials. In order to determine the “FeO” activities in the slags, it was necessary to have reliable activity data in the binary Fe-Pt system at the experimental temperature. A thermodynamic investigation of the binary system Pt-Fe was carried out using EMF measurements involving calcia-stabilised zirconia solid electrolytes.

PREVIOUS WORK

Fe-Pt system

The thermodynamics of the Fe-Pt alloys have been investigated by several authors earlier using a variety of experimental techniques [1-6]. The three main techniques used were

1. The gas equilibration method where the alloy was equilibrated with a suitable gas mixture of constant and known oxygen partial pressure [1-3],
2. Solid electrolyte galvanic cell method [4, 5]
3. Vapour pressure measurements [6].

There are certain discrepancies between the measurements around 1173 K and those at higher temperatures. One of the aims of the present measurements is to obtain a set of self-consistent values.

CaO-“FeO”-SiO₂

The CaO-“FeO”-SiO₂ ternary system has been investigated by several authors [7-11]. Taylor and Chipman [7] investigated the equilibrium between a complex slag, Al₂O₃-CaO-“FeO”-MgO-SiO₂, and the liquid metal in a rotating induction furnace at 1873 K. Bodsworth [8] performed measurements by equilibrating the slag in a solid iron crucible with a gas mixture of H₂/H₂O in the temperature range 1532-1643 K. Extrapolation of the calculated activities to 1873 K was performed. Timucin and Morris [9] studied phase equilibria and thermodynamics in the CaO-FeO-Fe₂O₃-SiO₂ system at 1723 and 1823 K. Isothermal sections at different silica content and, isobars at oxygen partial pressures in the range 10⁻¹¹ to 1 atm were constructed. Ogura et al. [10] performed an extensive investigation in the system CaO-“FeO”-SiO₂ at 1673 K. The activity of “FeO” was determined at a variety of compositions by employing solid-state galvanic cell technique. Bygdén et al. [11] performed EMF measurement in the CaO-“FeO”-SiO₂ in the temperature range 1473-1623 K. A comparison of the results reveal that the results of Bodsworth [8] are not in agreement with other work.

EXPERIMENTAL

Principle

The gas-equilibration studies:

In the present work, a gas equilibration technique was used to measure the thermodynamic activities of “FeO” in some iron oxide containing slag systems. The technique involves equilibration between the molten slag kept in a platinum crucible and a gas mixture of CO-CO₂-Ar with well-defined oxygen partial pressure. After the required equilibration time at different temperatures, the crucibles with the slags of different composition were quenched. During the equilibration, Fe from the “FeO” component in the slag would have dissolved in the Pt crucible. The equilibration reaction can be represented as



Assuming that the dissolution of Fe in Pt has reached equilibrium under the experimental duration, the activity of “FeO” in the slag can be calculated with a knowledge of the thermodynamic data for the binary alloy system Fe-Pt. The thermodynamics of the binary alloy system Fe-Pt has also been investigated as part of the present work and the experimental results were extrapolated to higher temperatures. The activity of the iron oxide could be calculated by

$$a_{FeO} = a_{Fe(Pt)} * p_{O_2}^{1/2} * C_1 \quad (2)$$

where $a_{\text{Fe(Pt)}}$ is the activity of iron in platinum, p_{O_2} the partial pressure of oxygen and, C_1 is the equilibrium constant for equation (1).

The galvanic cell measurements of the Fe-Pt system

The galvanic cell method was employed in the present work to measure the activities of iron in Fe-Pt alloys. Six different alloys, having the compositions $X_{\text{Pt}} = 0.1, 0.3, 0.45, 0.65, 0.85$ and 0.95 were studied in the temperature range $1073\text{--}1273\text{ K}$. The galvanic cell used can be represented as



The net cell reaction would be



The EMF of cell (I) is directly related to the activity of Fe in the alloy by the Nernst relationship

$$E \text{ (V)} = - (RT/2F) \ln a_{\text{Fe}} \quad (4)$$

Materials

The materials used in this investigation with their purity and suppliers are presented in Table I.

In the case of the galvanic cell measurements for the Fe-Pt system, the partially stabilised zirconia solid electrolyte tubes were of 6 mm o.d., 4.5 mm i.d. and 150 mm in length and were closed at one end. High-density alumina crucibles of 20 mm o.d., 15 mm i.d. and 30 mm in height were used for holding the cell. The CoO used for the calibration experiment was prepared by the decomposition of $\text{Co(NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in a stream of nitrogen at 1073 K . The purity of the CoO produced was confirmed by X-ray diffraction analysis.

In the case of the activity measurements, calcium oxide, silica and alumina were calcined at 1273 K for 12 hours to remove H_2O and CO_2 and, then stored at 373 K . Wüstite was prepared by mixing the required amounts of iron powder and Fe_2O_3 (dried previously at 400 K in air) so that the final composition corresponded to that of "FeO" in equilibrium with iron at 1273 K . The mixture was sintered in a sealed iron crucible kept in argon atmosphere at 1273 K over a period of 12 hours, after which the crucible was quenched. The "FeO" thus produced was examined by X-ray diffraction and the absence of both metallic iron and magnetite was confirmed. From the diffraction pattern, the lattice parameter of the "FeO" produced was computed to be 4.30 \AA , which is in agreement with the literature value of 4.3088 \AA [12].

Platinum crucibles were made from platinum sheets. Great care was taken in shaping the crucibles in order to avoid creeping of the samples along the walls. Precautions were taken to avoid contamination by foaming between the different slag samples.

Experimental

Part 1: The galvanic cell measurements

The cell assembly

The cell assembly used in the present work is shown in Fig. 1. The working electrode, consisting of the metal powder mixture and “FeO” in equimolar proportion, was packed inside the zirconia tube with a Pt wire embedded in the same. The reference electrode consisting of pure Fe and “FeO” was packed in the outer alumina crucible with the electrolyte tube in the middle and a Pt lead in contact with the electrode. The Pt-electrode contacts in both the electrodes were in the same horizontal plane in order to reduce any thermal effect on the cell EMF. The zirconia tube was closed with alumina cement in order to prevent gas phase transport of oxygen between the electrodes.

The cell assembly was positioned in the constant temperature (± 1 K) of a vertical tube furnace with KANTHAL A1 heating elements, which was controlled by a Eurotherm 902 programmable temperature regulator with Pt-10 pct Rh / Pt thermocouple as the sensor. A separate thermocouple in contact with the cell arrangement at the bottom enabled accurate measurements of the cell temperature. The thermocouple wires were earlier calibrated against the melting points of pure gold and palladium.

The experimental procedure

Before the furnace was started, the reaction tube with the cell assembly was evacuated and filled repeatedly with argon. When the oxygen partial pressure of the outgoing gas stream was less than 10^{-13} atm, the furnace temperature was raised to 1473 K in one step. The cell was maintained at this temperature for a minimum of 6 hours until the cell EMF value was steady for at least 1 hour within ± 1 mV. The EMF values were monitored by a KEITHLY 199 System DMM/Scanner with an input impedance of 1 G Ω . All the EMF and temperature data were recorded by EASY VIEW PC software. The cell was taken through temperature cycles and the values were found to be reversible within ± 0.4 mV. The reversibility of the cell was confirmed by polarising the cell repeatedly and confirming that the EMF returned to the original value. At the end of the experiment, the contents of the working electrode were subjected to chemical analysis and X-ray diffraction. Iron was analysed by redox titration while Pt was analysed by atomic absorption spectroscopy. The EMF measurements with one high Pt alloy were carried out using Fe₃O₄ as the equilibrating oxide. One experiment was repeated with Fe-Pt premelted alloy in order to confirm the experimental procedure adopted.

Part 2: Gas-equilibration studies:

The experimental set-up

The experimental set-up used in this study is illustrated in Fig. 2. An alumina reaction tube, (60 mm o.d. and 50 mm i.d.) was positioned in a horizontal resistance furnace equipped with KANTHAL SUPER 1800 heating elements with a maximum working

temperature of 1973 K. The platinum cups holding the slags under investigation were placed in an alumina crucible holder with provision for four platinum crucibles. This holder was placed in the even-temperature zone of the furnace. The sample temperature in the furnace was monitored by a calibrated Pt-30 pct Rh/Pt-6 pct Rh thermocouple. Alumina runners were provided inside the reaction tube to enable the quenching of the slags without any damage to the reaction tube. The gas mixture was lead into the reaction zone by a narrow alumina tube of 5 mm i.d. minimising the thermal segregation in the gas mixture. The gas was delivered in the hot zone of the furnace just above the samples. The temperature in the furnace was controlled by a programmable Eurotherm 2408 P4 regulator with a Pt-30 pct Rh/Pt-6 pct Rh thermocouple as the sensor with an accuracy of ± 3 K.

The gas cleaning system

In order to lower the impurity levels, the different gases used were subjected to a number of purification steps. The gas cleaning system used in the present work is presented in Fig. 3. The moisture impurity in the argon gas was removed by passing the gas successively through silica gel as well as $\text{Mg}(\text{ClO}_4)_2$. 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 earlier 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 $\text{Mg}(\text{ClO}_4)_2$.

The flow rates of the different gases were controlled by the Bronkhorst High-Tech B.V. serie E-7000 system. After the purification step, the gases were mixed in a gas chamber at room temperature and introduced into the alumina reaction tube. The partial pressures of the different components in the gas mixture at the experimental temperatures were calculated by using the THERMO CALCTM software. The total flow rate of the gases during the experiments was $0.2 \text{ dm}^3/\text{min}$. The oxygen partial pressure of the outgoing gas mixture was monitored continuously by a $\text{ZrO}_2\text{-CaO}$ galvanic cell kept at 973 K. The data from the oxygen probe was found to be in agreement with the calculated data.

The experimental procedure

The experiments started with heating the furnace to the required temperature under constant Argon flow. When the experimental temperature was reached, the sample holder with the slag samples in the platinum crucibles was introduced into the even temperature zone of the furnace. The $\text{CO-CO}_2\text{-Ar}$ gas mixture was then introduced into the system and the slags were equilibrated with the gas mixture for 8 hours. This time interval was found to be sufficient for the attainment of equilibrium between the gas and the slag phases as found from earlier studies carried out in the present laboratory. The experiments were performed in the temperature range 1823-1923 K. After the equilibration, the samples were quenched by withdrawing the sample holder to the cold part of the furnace. The cold samples were taken out, preserved in

desiccators, and subsequently subjected to chemical analysis. The platinum crucibles were analysed for dissolved iron as well as for silicon and calcium in appropriate cases using atomic absorption spectroscopy. The calcium content was in all cases less than 0.1 wt pct and, therefore not included in the calculations. Maximum silicon content was found to be 0.12 wt pct. Contamination of the crucibles from the sample holder was checked by a blank run and was found to be negligible. The oxides were investigated by X-ray fluorescence spectroscopy and the contents of the di- and trivalent iron in the slag samples were determined by redox titration.

RESULTS

Part I: Galvanic cell measurements:

In order to confirm the proper functioning of the experimental technique, the galvanic cell arrangement was calibrated by measuring the EMF between Fe-FeO and Co-CoO electrodes. From the results, the standard Gibbs energy of formation of CoO was computed from a knowledge of the corresponding value for FeO available in literature [13]. These values are compared with the values available in the literature in Fig.4. It is seen that the values are close to the values reported earlier, confirming thereby the reliability of the present measurements.

The EMF values obtained in the present work with Fe-Pt alloys in the working electrode are presented in Table II. Plots of the EMF with respect to temperature for different compositions of the alloys are presented in Fig. 5. It is seen that the linear behaviour of the EMF values indicates the constancy of the relative partial molar entropies of iron in the alloys.

The activity of Fe in the alloy at 1273 K is presented as a function of composition in Fig. 6. The standard state of iron was taken as pure solid iron at the experimental temperature. The activities indicate that the system shows a strong negative deviation from ideality, which is in agreement with earlier investigations. The activity values at other temperatures were not shown in the figure for the sake of clarity. It should be mentioned that the temperature coefficients of the activities do not differ significantly in the temperature range of the present measurements. The activities of Pt at 1273 K computed by Gibbs-Duhem integration are also presented in the same figure.

The results from the various activity measurements carried out earlier are compared with the present work in Fig. 7, in which the $\log_{10}\gamma_{\text{Fe}}$ is plotted as a function of the molfraction of iron, X_{Fe} . It is seen that most of the values are in fair agreement with each other in the region with high iron concentrations, while in the high Pt region, there is some scatter. While the results of Alcock and Kubik [5] at 1123 K as well as those of Sundaresen et al.[4] at 1123 K fall slightly below the general trend in the high Pt region, the present results at 1123 K are above. The results at 1273 K seem to fall within the general scatter in the entire composition region.

Part 2: Gas equilibration measurements

The reliability of the experimental technique was verified by carrying out activity measurements in the case of the binary systems “FeO”-SiO₂, Al₂O₃-“FeO”, CaO-

“FeO”. The results were found in general to show similar trends as those found in earlier studies.

The results from the present investigation of the CaO-“FeO”-SiO₂ system is presented in Table III. The activities of “FeO” for the different slag compositions were calculated by using the thermodynamic information in the binary Fe-Pt system. Due to small amounts of slag samples, the chemical analysis of di- and trivalent iron was not performed.

DISCUSSION

Part 1: Fe-Pt system

For the values shown in Fig. 7, a polynomial function was fitted to suit the $\log_{10}\gamma_{\text{Fe}}$ as a function of X_{Fe} independent of temperature as the temperature coefficient of the activity coefficients were very small and irregular. The values from the present results at 1273 K, the values of Alcock and Kubik [5] at 1273 K and the data from the measurements of Sundaresen et al. [4] at 923 K in the high platinum region were omitted in the regression calculation. The equation corresponding to this regression analysis is

$$\log_{10}\gamma_{\text{Fe}} = -3.11 + 3.383X_{\text{Fe}} + 10.749X_{\text{Fe}}^2 - 19.647X_{\text{Fe}}^3 + 8.620X_{\text{Fe}}^4 \quad (5)$$

A plot of the $RT \ln \gamma_{\text{Fe}}$ as a function of $(1-X_{\text{Fe}})^2$ is presented in Fig. 8. As can be seen, the plot is a straight line passing through the origin irrespective of the temperature. The equation corresponding to this line is

$$RT \ln \gamma_{\text{Fe}} (\text{kJ/mol}) = -65.6(1-X_{\text{Fe}})^2 \quad (6)$$

The above plot indicates that at temperatures at and above 1273 K, the Fe-Pt solid alloys can be considered to conform to the regular solution model of Hildebrand and Scott [18]. The enthalpies of mixing for the alloys at high temperatures can be estimated using the regular solution model to be $\Omega \cdot X_{\text{A}} \cdot X_{\text{B}}$, where Ω is the slope of the line in Fig. 9 and termed as Hildebrand Interaction parameter in the present work. The value for Ω was found to be -65.6 kJ/mol with a scatter of ± 1.6 kJ/mol. The enthalpies of mixing for Fe-Pt alloys estimated from the regular solution model are compared with those presented by Alcock and Kubik [5] at 1123 K and those of Sundaresen et al. [4] at 1123 K.

The enthalpies of mixing presented by Alcock and Kubik [5] are fairly symmetrical, but the value corresponding to Ω should be somewhat more negative. Sundaresen et al. [4] report a positive enthalpy of mixing at high iron concentrations at 1123 K while the enthalpies at 923 K are negative. This has been attributed by these authors to the large enthalpy of ordering for Fe₃Pt. No evidence of positive enthalpies in this concentration region could be observed in the present measurements.

In Fig. 10, the activity of “FeO” in the CaO-“FeO”-SiO₂ system is presented with previous investigations at different temperatures and basicities. The calculations indicate the behaviour of the system to be near ideal. The results obtained seem to be more in agreement with the work of Ogura et al. [10] than the investigation by Bodsworth [8]. Several slag models based on different approaches have been developed during the years with a variable degree of success. To separate the different models they can be divided into two groups, structural based models and empirical or semi-empirical models. The predictive capacity of the different types of models is only as good as the structural information and experimental data available respectively. One of the attempts, based on Lumsden’s regular solution model, is from the work of Ban-Ya and Hino [19]. They calculated the activities of “FeO” in the CaO-“FeO”-SiO₂ system at 1873. The iso-activity curves proposed by these authors are presented in Fig. 11 together with the results from the present investigation. It can be seen that the results from the present study are in agreement with the model calculation of Ban-ya and Hino.

In order to study the thermodynamic properties of various slag systems the Division of Metallurgy has been developing a slag model that enables the extrapolation of the thermodynamic data of multicomponent slag systems as functions of composition and temperature. This model, referred to as the KTH model, is based on Temkins description of the entropy of ionic melts coupled with Lumsden’s description of complete ionisation of silicates to Si⁴⁺ and O²⁻. The model enables the estimation of the thermodynamic activities of higher order systems using experimental information from lower order systems. In Fig. 12, the activity of “FeO” in the CaO-“FeO”-SiO₂ system calculated by the model is compared with the present experimental data at 1873 K. Considering the uncertainties in the experimental as well as the modelling approaches, the agreement can be considered reasonable.

SUMMARY AND CONCLUSIONS

The present work was carried out with a view to measuring the thermodynamic activities of Fe in Fe-Pt alloys in the temperature range 1073-1273 K using the solid electrolyte galvanic cell method with zirconia partially stabilised with calcia as the solid electrolyte. The cell EMF values were found to be linear functions of composition and the activities showed a strong negative deviation from Raoult’s law. The activity coefficients from the present results showed general agreement with earlier measurements. The experimental activity coefficients of iron were fitted into a Hildebrand regular solution model and the relative integral molar enthalpies of mixing were estimated.

The results of these measurements enable the estimation of the activities of “FeO” in metallurgical slags contained in thin Pt crucibles and equilibrated with gas mixtures of known oxygen partial pressures.

Gas-equilibration measurements of the activities of “FeO” in the ternary system CaO-“FeO”-SiO₂ were carried out at 1873K by equilibrating the slag, kept in Pt crucibles with Ar-CO-CO₂ gas mixtures. The results obtained from the present study at low content “FeO” are compared to earlier investigations.

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REFERENCES

1. H. R. Larson and J. Chipman, *Acta Metall.*, 2, (1954), pp. 1-2.
2. R. W. Taylor and A. Muan, *Trans. Metall. Soc. AIME*, 224, (1962), pp. 500-502.
3. E. F. Heald, *Trans. Metall. Soc. AIME*, 239, (1967), pp. 1337-1340.
4. M. Sundaresen, Ya. I. Gerasimov, V. A. Geiderikh and I. A. Vasil'eva, *Russ. J. Phys. Chem.*, 37, (1963), pp. 1330-1330.
5. C. B. Alcock and A. Kubik, *Acta Metall.*, 17, (1969), pp. 437-442.
6. J. Vrestal, *Kovove Mat.*, 11, (1973), pp. 291-299.
7. C. R. Taylor, J. Chipman, *Trans. Met. Soc. AIME*, 154, (1943), pp. 225-247.
8. Bodsworth, J. *Iron Steel Inst.*, 193, (1959), pp. 13-24.
9. M. Timucin, E. Morris, *Met. Trans.*, 1 (1970), pp. 3193-3201.
10. T. Ogura, R. Fujiwara, R. Mochizuki, Y. Kawamoto, T. Oishi, M. Iwase, *Met. Trans. B*, 23B, (1992), pp. 459-466.
11. J. Bygdén, D. Sichen, S. Seetharaman, *Steel Research*, 10 (1994), pp. 421-428.
12. *Handbook of Chemistry and Physics*, 60:th ed., CRC Press, Cleveland, Ohio, (1974-1979), pp. B-196.
13. O. Sjöden, S. Seetharaman and L.-I. Staffansson, *Metall. Trans.*, 17B, (1986), pp. 179-184.
14. J. D. Tretyakov and H. Schmalzried, *Ber. Bunsenges. Phys. Chem.*, 65, (1965), pp. 396-402.
15. W. G. Bugden and J. N. Pratt, *Trans. Inst. Min. Met. Sec.*, C79, (1970), pp. C221.
16. G. Rog, B. Langanke, G. Borchardt and H. Schmalzried, *J. Chem. Thermodyn.*, 6, (1974), pp. 1113-1119.
17. Vasileva, I. S. Sukhushina, Zh. V. Granovskaya, R. F. Balabaeva and A. F. Maiorova, *Russ. J. Phys. Chem.*, 49, (1975), pp. 1275-1278.
18. J. H. Hildebrand and R. L. Scott, "The Solubility of Nonelectrolytes", Reinhold, New York, (1950).
19. S. Ban-ya and M. Hino, *Tetsu-to-Hagane*, 73 (1987), pp. 476-783.

Table I. Materials used in the present work

Material	Purity	Supplier
Titanium foil	99.7 %	Aldrich, USA
Iron foil	99.5%	Goodfellow, UK
Platinum wire	99.9 %	Jonhson Matthey Inc., UK
Platinum/Rhodium wire		Johnson Matthey Inc., UK
Cobalt powder	99.8	Johnson Matthey Inc., UK
Carbonyl iron powder	pro analysi	E. Merck, Germany
Platinum powder	99.9 %	Chempur, Germany
Copper	99 %	Johnson Matthey Inc., UK
Magnesium	> 99 %	E. Merck, Germany
Hematite	anhydrous	Fisher Scientific, USA
Magnetite	96.7%	LKAB, Sweden
Calcium Oxide		Fischer Scientific, USA
Silicon Oxide	pro analysi	E. Merck, Germany
Aluminum Oxide	anhydrous	E. Merck, Germany
Cobalt(II) nitrate hexahydrate	98%	Aldrich, USA
Silica gel		Kebo, Sweden
Magnesium perchlorate	anhydrous	Kebo, Sweden
Ascarite		Thomas Scientific, USA
Iron crucible	99.9 %	Armco Iron, USA
Platinum sheet	99.998 %	Johnson Matthey Inc., UK
Argon	plus-grade	AGA Gas, Sweden
Carbon Monoxide	plus-grade	AGA Gas, Sweden
Carbon Dioxide	plus-grade	AGA Gas, Sweden
Air, 20 % O ₂	plus-grade	AGA Gas, Sweden
Nitrogen	plus-grade	AGA Gas, Sweden
Calcia stabilized zirconia		Yamari Industries, Japan
Yttria stabilized zirconia		Friatech, Germany
Alumina tubes, Alumina cement	99.7%	Keranova, Sweden

Table II. Experimental results

x_{Pt}	EMF (mV)	T (K)	x_{Pt}	EMF (mV)	T (K)
0.10	5.56	1224	0.85	271.32	1125
	5.72	1275		293.76	1178
				316.51	1229
0.30	22.89	1123	0.95	335.92	1277
	25.35	1176			
	26.40	1222		395.64	1123
	27.78	1273		400.51	1173
0.45				404.16	1223
	46.85	1078		407.96	1273
	52.02	1124			
	56.68	1173			
	60.76	1224			
	64.68	1273			
0.65	149.76	1126			
	161.05	1174			
	169.58	1223			
	176.25	1274			

Table III. Experimental results of the CaO-”FeO”-SiO₂ system (T=1873 K, p_{O2} = 2.83*10⁻⁶ atm)

Heat No.	Final composition of slag (wt%)			wt%CaO/ wt%SiO ₂	a _{FeO}	wt%Fe	Index
	CaO	“FeO”	SiO ₂				
A2:1	46.50	5.49	48.01	0.97	0.0615	11.28	1
A2:2	43.28	1.64	55.08	0.76	0.0061	6.50	2
A2:3	29.34	6.90	63.76	0.46	0.0397	10.18	3
A2:4	22.18	21.60	56.22	0.39	0.1751	14.31	4
A3:1	46.90	5.64	47.46	0.99	0.0592	11.16	5
A3:2	44.34	1.94	53.72	0.82	0.0052	6.26	6
A3:3	30.42	7.07	62.51	0.49	0.0375	10.05	7
A3:4	22.06	21.10	56.84	0.39	0.1963	14.69	8

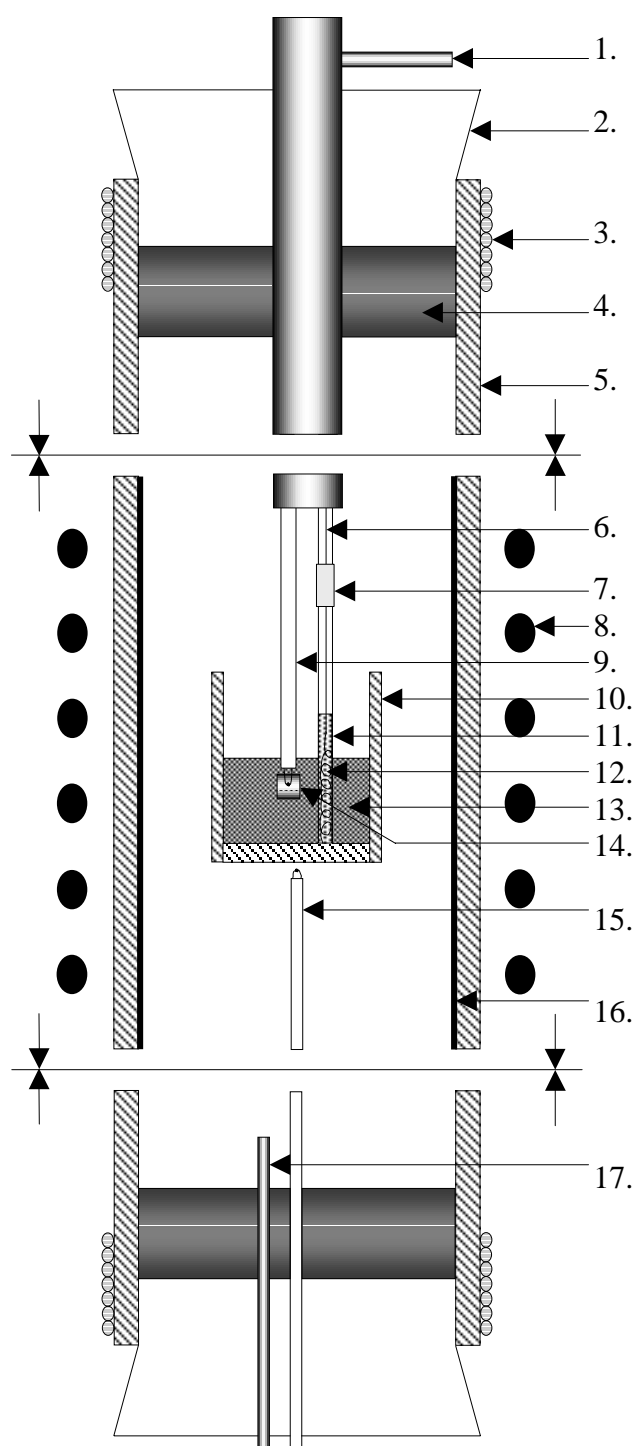


Fig. 1. The experimental assembly: (1) Gas inlet, (2) Silica stopper, (3) Cooling coils, (4) Refractory, (5) Alumina reaction tube, (6) Pt wire, (7) Alumina cement, (8) Heating coil, (9) Thermocouple, (10) Alumina crucible, (11) Solid electrolyte, (12) Working electrode, (13) Reference electrode, (14) Iron foil, (15) Thermocouple, (16) Nickel foil, (17) Gas outlet.

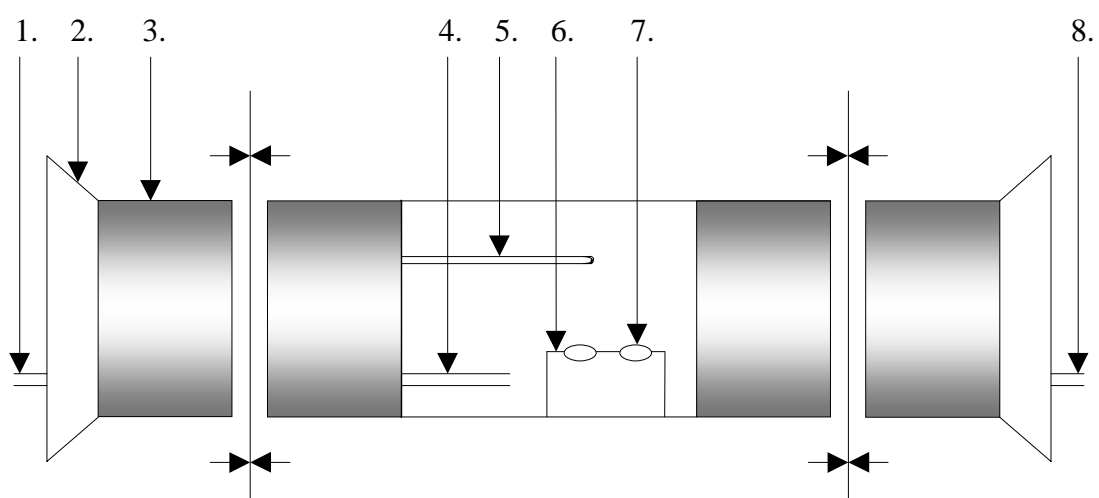


Fig. 2. The furnace assembly: 1. Gas inlet, 2. Silica stopper, 3. Alumina reaction tube, 4. Gas inlet, 5. Thermocouple, 6. Alumina crucible holder, 7. Platinum crucible, 8. Gas outlet.

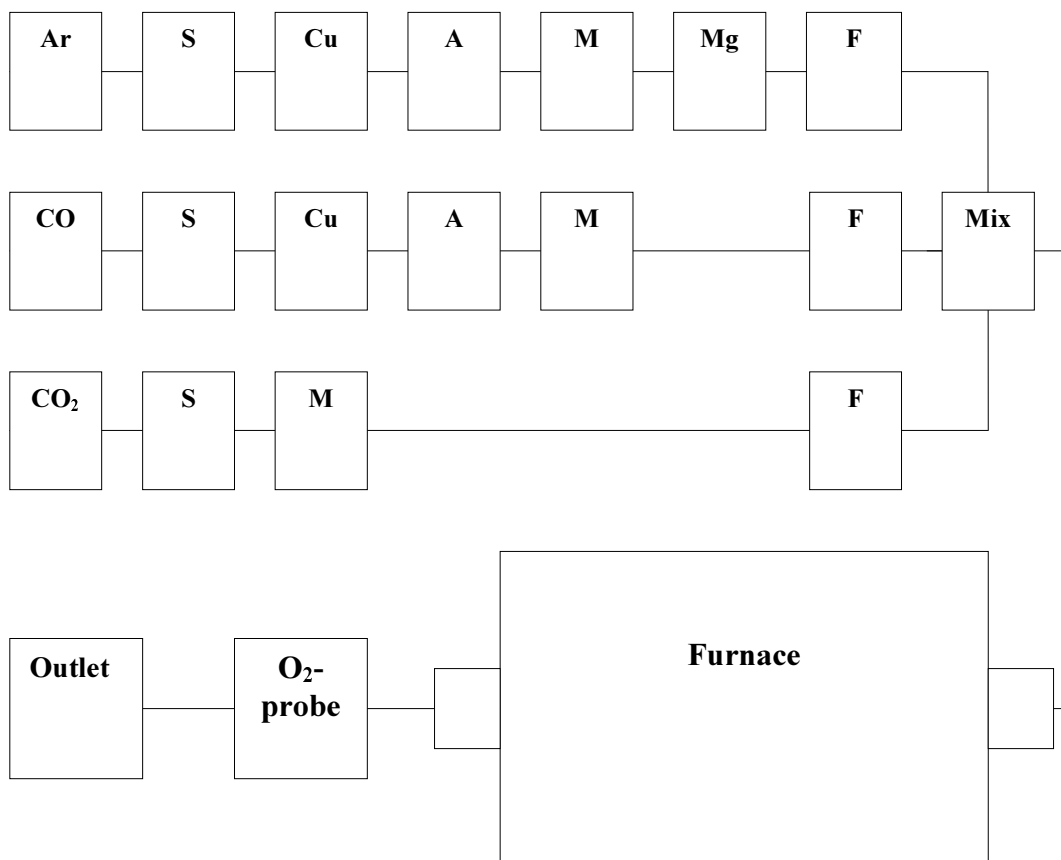


Fig. 3. The gas cleaning system: S = Silica Gel, Cu = Copper turnings, A = Ascarite, M = Magnesium perchlorate, Mg= Magnesium turnings, F = Magnetic flow meters, Mix = Gas mixing chamber.

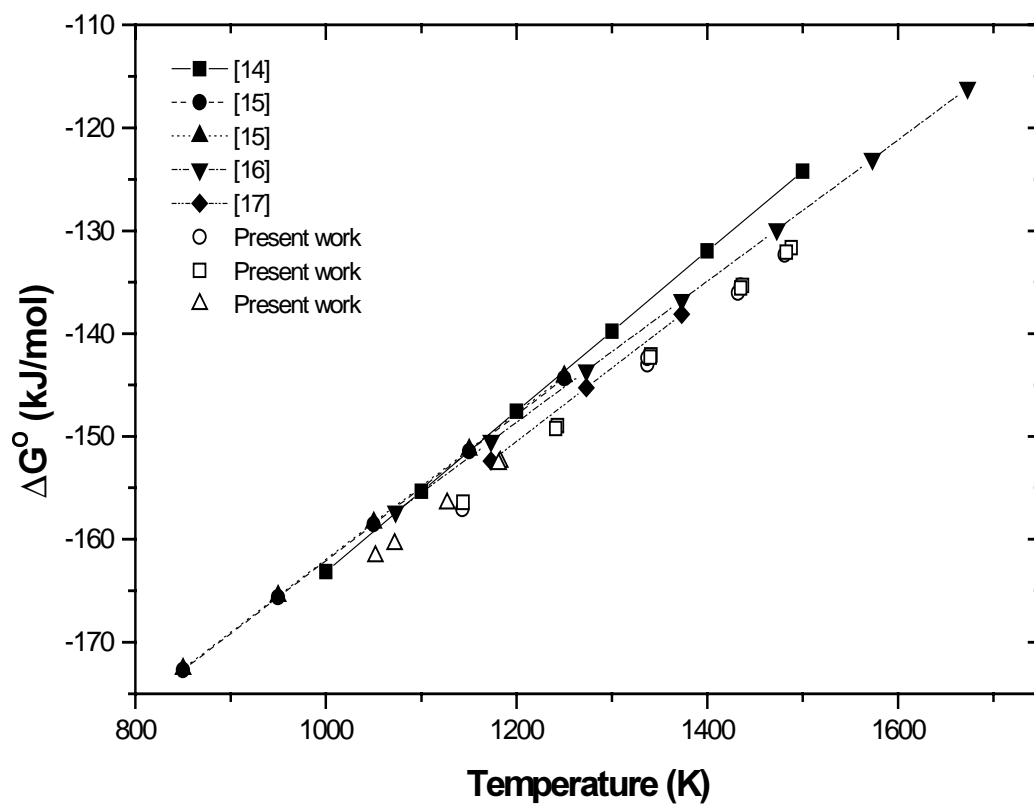


Fig. 4. Gibbs Energy of Formation for Cobalt Oxide. Results from the present work compared with earlier trials.

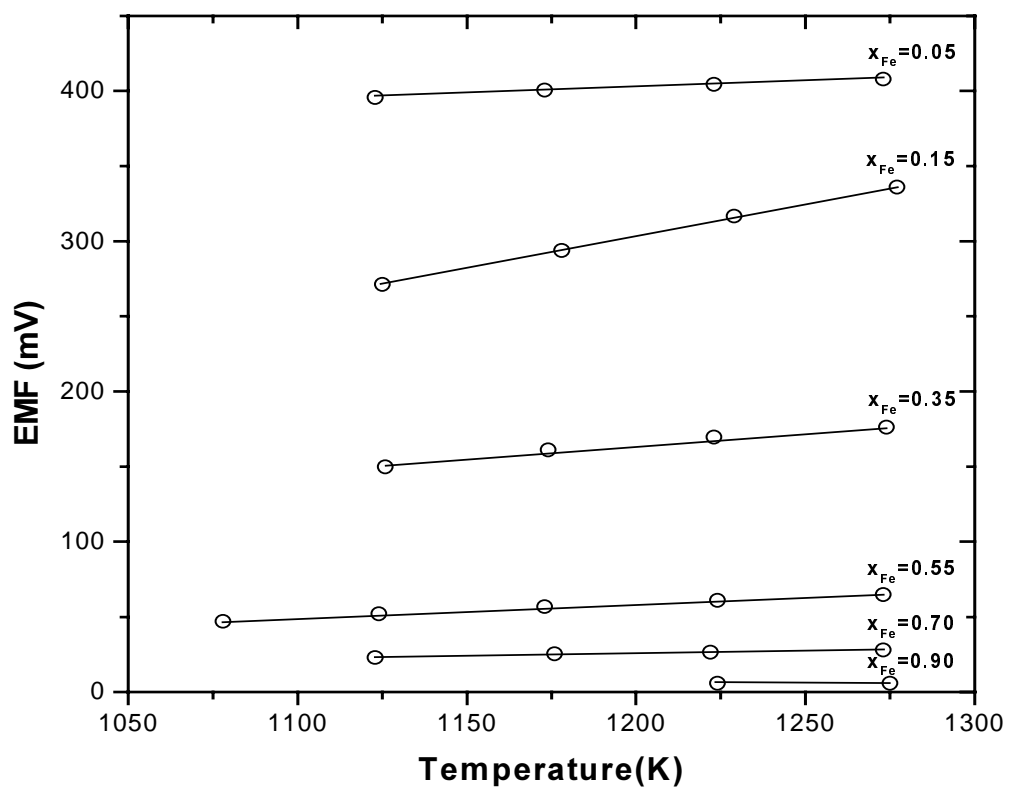


Fig. 5. EMF as a function of temperature.

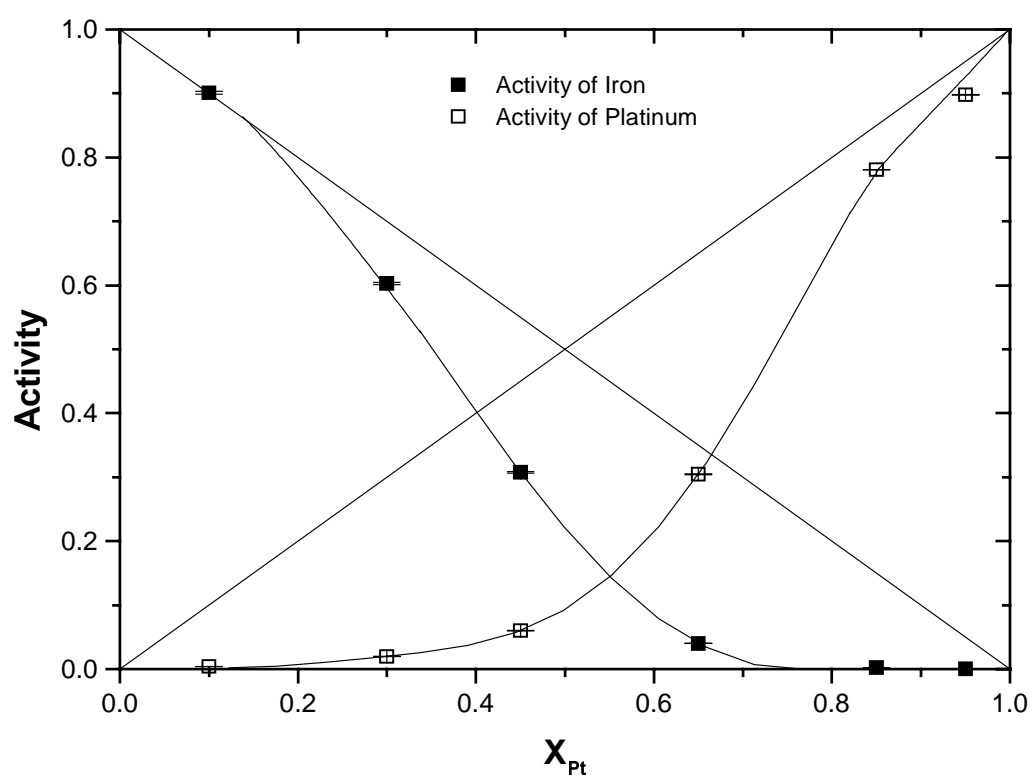


Fig. 6. Activity of Fe and Pt at 1273 K.

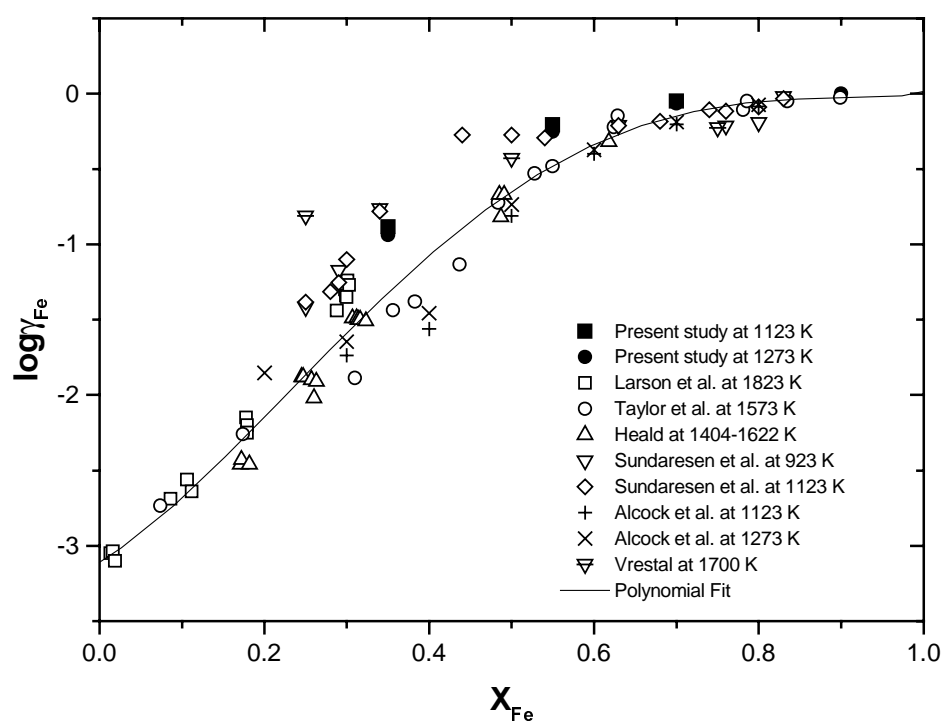


Fig. 7. $\log_{10} \gamma_{\text{Fe}}$ as a function of the mole fraction of Fe.

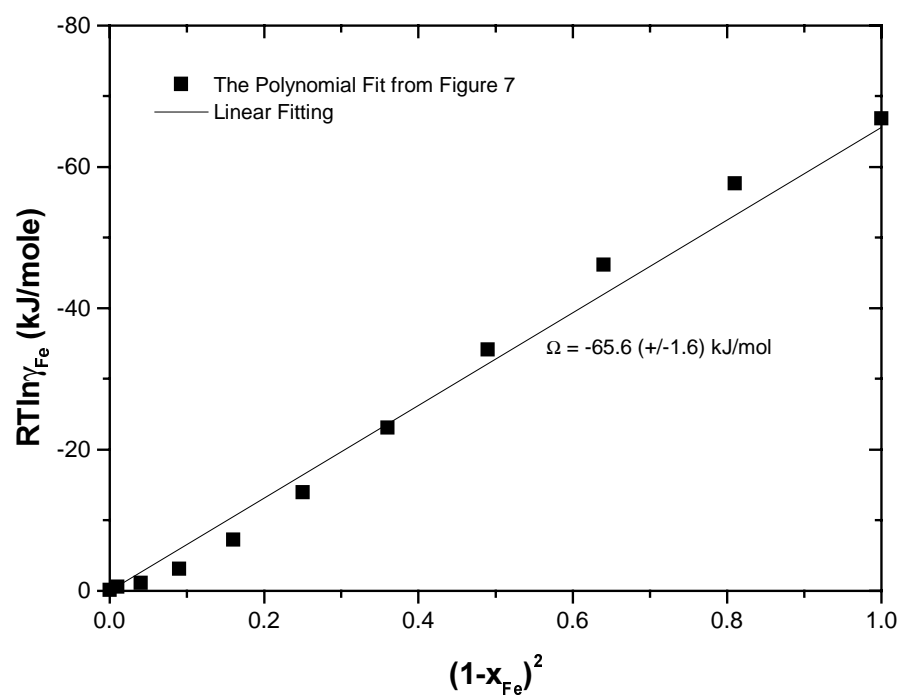


Fig. 8. The Hildebrand Interaction parameter evaluated in the present work.

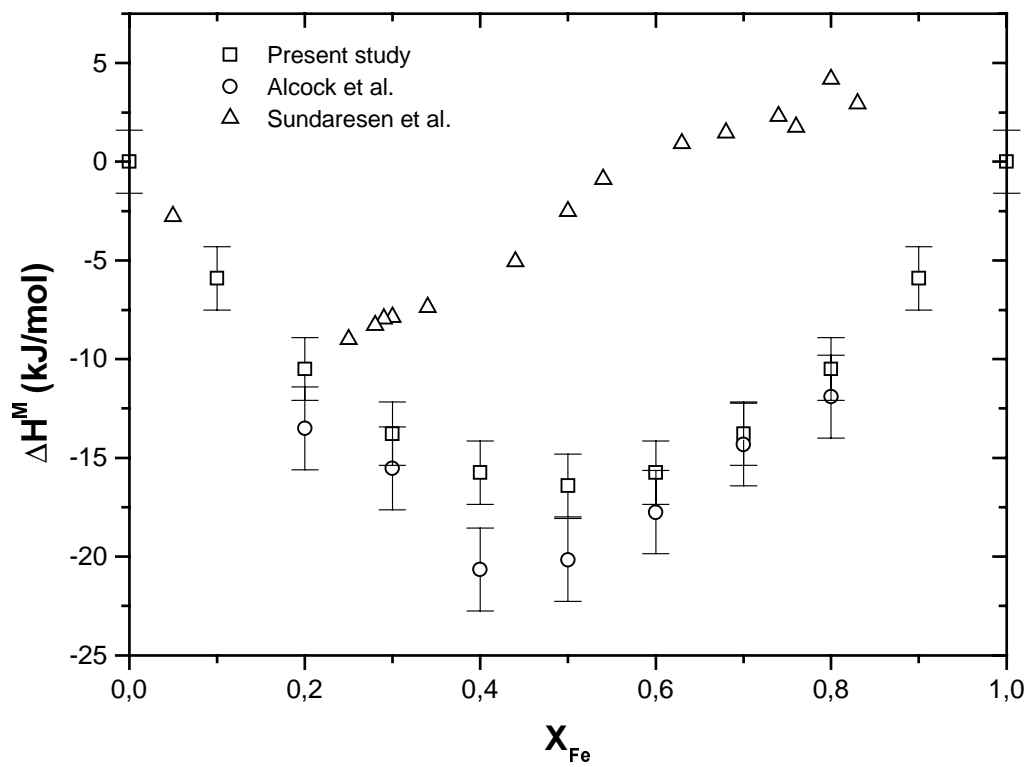


Fig. 9. The Relative Integral Molar Enthalpies of Mixing in the System Fe-Pt.

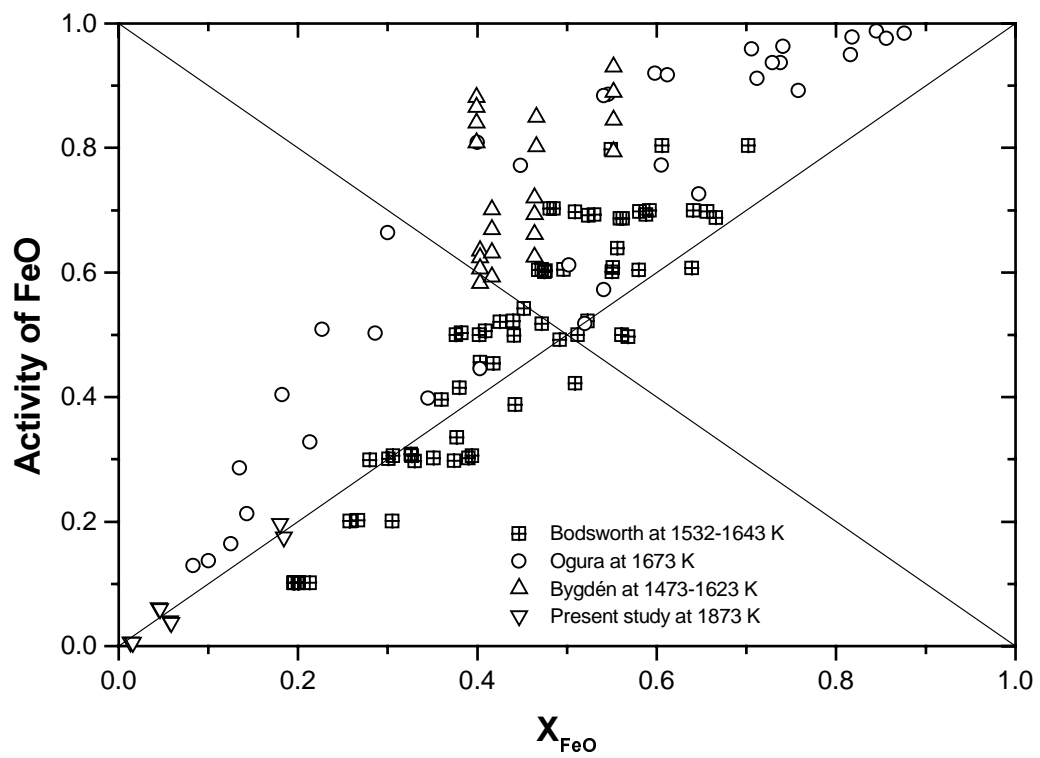


Fig. 10. The activity of "FeO" in the CaO-"FeO"-SiO₂ system.

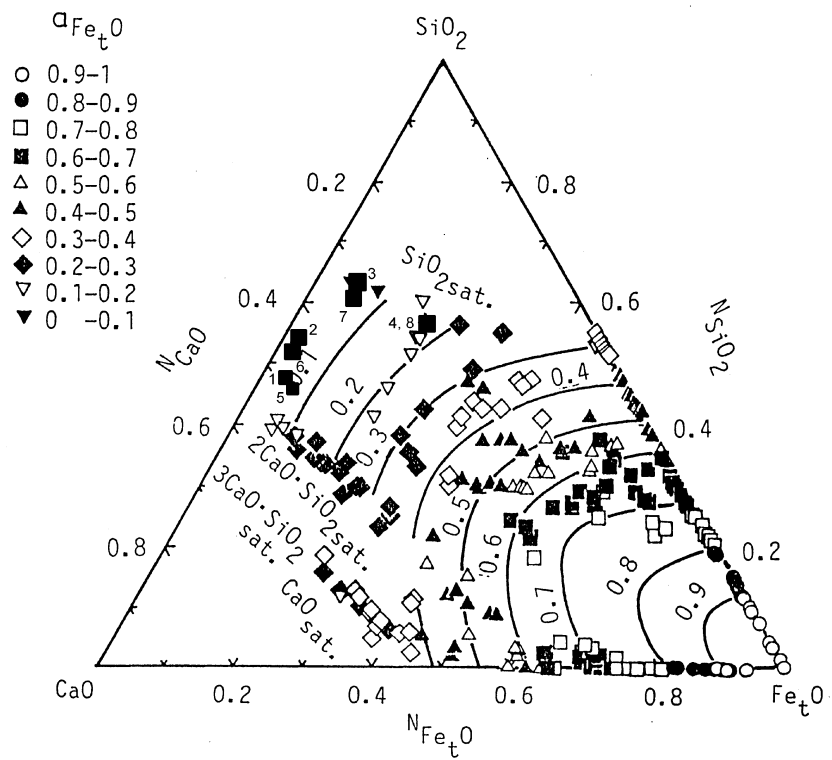


Fig. 11. Iso-activity contours of "FeO" in the CaO-"FeO"-SiO₂ system according to Ban-ya and Hino at 1873 K. Point 1-8 are from the present study.

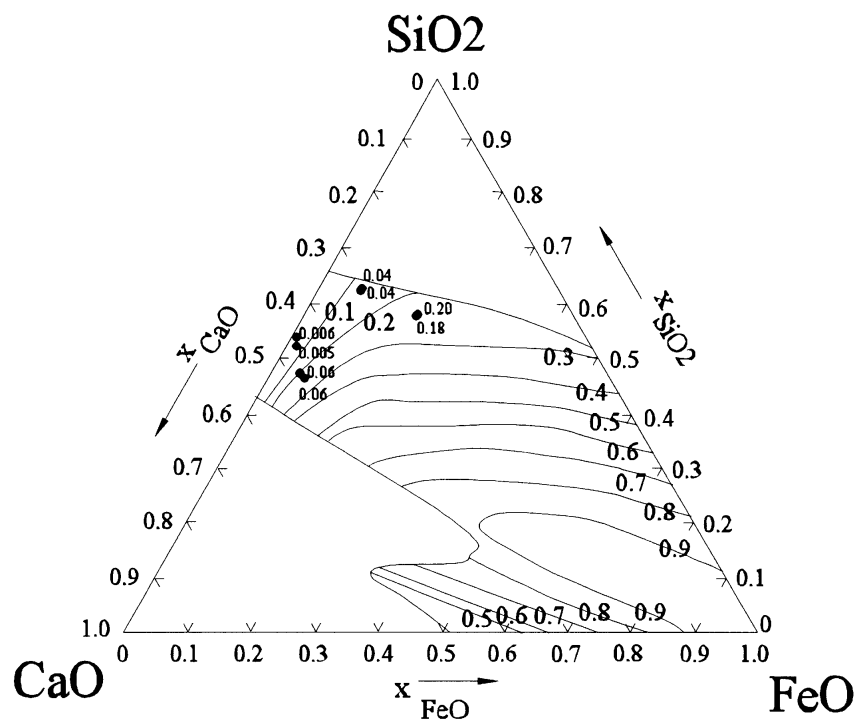


Fig. 12. Activity of "FeO" in the CaO-"FeO"-SiO₂ system from the KTH model at 1873 K.