Thermodynamic database of P_2O_5-containing oxide system for De-P process in steelmaking

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Abstract: The CaO-FeO-Fe_2O_3-SiO_2-MgO-Al_2O_3-Na_2O-P_2O_5 oxide system is a basic oxide system for the Basic Oxygen Furnace (BOF) process as well as the hot metal de-phosphorization process. Numerous experimental investigations on this oxide system are being carried out to find out the advanced process route for P removal from molten iron. In spite of their industrial importance, however, the phase equilibria of the oxide systems containing P_2O_5 have not been well investigated due to the complexity of their chemistry. No systematic thermodynamic modeling of these systems has been conducted to date, either. In order to meet the strong demands of steelmaking and other industries, new systematic thermodynamic modeling of the P_2O_5 containing oxide systems (CaO-FeO-Fe_2O_3-SiO_2-MgO-Al_2O_3-Na_2O-P_2O_5) and key phase diagram experiments have been carried out over the past several years. In the present study, the results of the thermodynamic modeling of unary, binary and ternary P_2O_5 containing systems and the applications of thermodynamic database to the de-P by multi-component slag in BOF process will be presented in comparison with experimental data. All thermodynamic calculations were performed using FactSage thermodynamic software.

Key words: De-phosphorization, BOF, Thermodynamic database

1. Introduction

The CaO-FeO-Fe_2O_3-MgO-SiO_2-Al_2O_3-P_2O_5 oxide system is a basic oxide system for the Basic Oxygen Furnace (BOF) process as well as the hot metal de-phosphorization process. Great amount of investigations on this oxide system are being carried out to find out the advanced process route for P removal from molten iron. In the modern steelmaking process, the BOF process is a key process for de-phosphorization (De-P) and de-carburization process (De-C). Unfortunately, the deep insight of the process is still in mystery in many aspects because of the complex slag chemistry of the process and the difficulty in the sampling/examination of the process. In particular, there has been a large amount of industrial effort to improve the efficiency of phosphorus removal from hot-metal with minimum loss of Fe during BOF process. Two advanced BOF process technologies recently used in several advanced steel producers are:

- Double slags BOF process technology where the most of molten slag after De-P process at low temperature is discharged and de-C is proceeded afterward with new synthetic slag.
- Double BOF furnaces technology where one furnace dedicated to De-P process at low temperature and the other one dedicated to De-C process at high temperature.

In order to understand the BOF process and improve the process further in particular for De-P reaction, a good thermodynamic understanding of the phosphorus behavior in wide range of slag composition from FetO-SiO2 rich slag to CaO-SiO2-FetO-MgO slag under a temperature range from 1200oC to 1750oC and oxygen potential varying from very oxidizing condition to carbon saturation condition are indispensible. In addition, the influence of other components such as Al2O3, MnO, Na2O, etc. on the phosphorus distribution between molten iron and multicomponent slag are important. The phosphorus distribution between molten slag and solid Ca_2SiO_4 phase which can dissolve a considerable amount of P_2O_5 under the steelmaking condition are also important issue in particular at low temperature range from 1200 to 1600oC. Although many experimental studies have been conducted for the phosphorus distribution between multicomponent slags and molten iron, and phosphate capacity of slag, more accurate knowledge on P_2O_5 containing slags are needed for the improvement of de-phosphorization process. In particular, in order to develop the process simulation model for BOF process, the computerized thermodynamic database for P_2O_5 containing slags are highly required.

Over the past 30 years, advances in thermodynamic modeling have resulted in the development of computer databases containing thermodynamic properties as function of temperature and composition of hundreds of multicomponent oxide phases. One of the most well known and widely used oxide databases is the FACT oxide database1). The FACT oxide database contains the complete description of the $CaO\text{-}Al_2O_3\text{-}SiO_2\text{-}MgO\text{-}FeO\text{-}Fe_2O_3$ system with additional components like MnO_x, CrO_x, TiO_x, *etc*. However, in the case of P_2O_5, the current FACT oxide database is quite restricted within dilute composition and the accuracy of the calculation was less satisfactory.

In order to meet the strong demands of steelmaking and other industries, new systematic thermodynamic modeling of the P_2O_5 containing oxide systems ($CaO\text{-}FeO\text{-}Fe_2O_3\text{-}SiO_2\text{-}MgO\text{-}Al_2O_3\text{-}Na_2O\text{-}P_2O_5$) and key phase diagram experiments have been carried out over the past several years. In the present study, the results of the thermodynamic modeling of unary, binary and ternary P_2O_5 containing systems and the applications of thermodynamic database to the de-P by multi-component slag in BOF process will be presented in comparison with experimental data. All thermodynamic calculations were performed using FactSage thermodynamic software.

2. Thermodynamic modeling

A thermodynamic database for the multicomponent system $CaO\text{-}FeO\text{-}Fe_2O_3\text{-}MgO\text{-}SiO_2\text{-}Al_2O_3\text{-}Na_2O\text{-}P_2O_5$ have been developed in the present research group based on a critical evaluation and optimization of all available phase diagrams and thermodynamic data for unary, binary and ternary systems. In this way, the Gibbs energy of all phases in the given system can be expressed by for each phase and their model parameters can be stored in the computerized data-file. In the present study, the thermodynamic behavior of the liquid phase were described using the Modified Quasichemical Model[1], which considers the short-range-ordering of second nearest neighbor cations.

The thermodynamic properties of even pure P2O5 have not been well-known in literature. Thus, the thermodynamic evaluation of pure P2O5 was for the first time properly carried out based on all available equilibration data for gases P2O5 / solid P2O5 / liquid P2O5. The well-accepted Gibbs energy of formation (ΔG_f^o) for P2O5 liquid from Turkdogan and Pearson (1953) are not consistent with the experimental phase diagram data of P2O5:

$P_2(g) + 5/2O_2(g) = P_2O_5(l)$: ΔG_f^o [1]

- Turkdogan and Pearson (1953) [2]

$\Delta G_f^o = -1534{,}480 + 506.3\,T$ (J/mol); log K = -16.35 at 1873 K [2]

- Present study

$\Delta G_f^o = -1615{,}972 + 539.0\,T$ (J/mol); log K = -16.90 at 1873 K [3]

In the present study, the new ΔG_f^o of P2O5(l) is evaluated based on all available thermodynamic data of P2O5 system. The evaluated Gibbs energy of formation is shown in Eq. [3] and the calculated phase diagram of the present study is shown in Fig. 1. If the previous value by Turkdogan and Pearson is used, the melting temperature of P2O5 becomes less than 300oC, while the experimental data shows the melting temperature to be 580°C. However, interestingly the difference of the logK for reaction (1) between the present study and previous data by Turkdogan and Pearson is just by about 0.5~0.6 in the temperature range between 1300 to 1700°C.

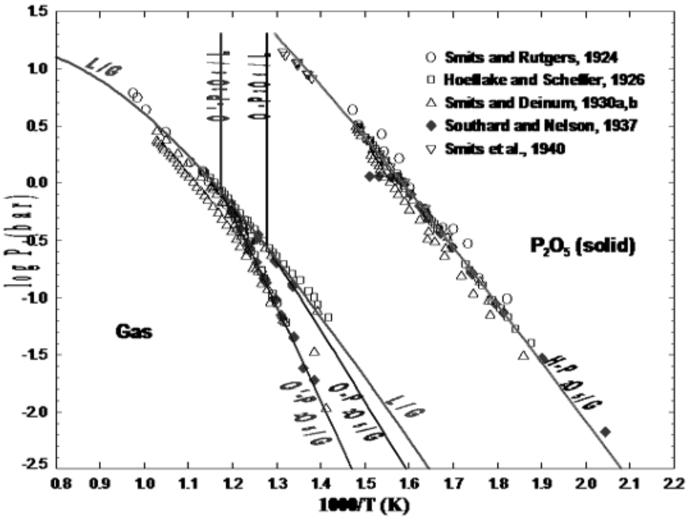


Fig. 1. Log P vs 1000/T diagram of the P_2O_5 unary in the present study. O'-P_2O_5 is the most stable solid phase and its melting temperature is 580°C.

Binary $MO-P_2O_5$ (M = Ca, Mg, Fe, Mn), $SiO_2-P_2O_5$, $Al_2O_3-P_2O_5$, $Fe_2O_3-P_2O_5$ and $Na_2O-P_2O_5$ systems were optimized based on all available thermodynamic and phase diagram experimental data. In the case of binary $CaO-P_2O_5$ system, for example, many intermediate compounds of $xCaO \bullet yP_2O_5$ and a liquid phase exist. Among the solid phases, the thermodynamic properties of $Ca_4P_2O_9$, $Ca_3P_2O_8$, $Ca_2P_2O_7$ and CaP_2O_6 are relatively well investigated by experiments. In thermodynamic modeling, all available and reliable thermodynamic data and phase diagram data were simultaneously optimized to obtain one set of Gibbs energy functions of all phases in the system, as shown in Figs. 2 and 3.

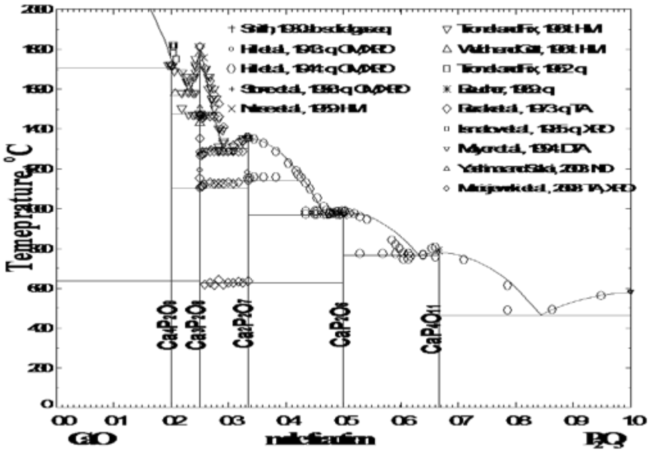


Fig. 2. Optimized binary phase diagram of the $CaO-P_2O_5$ system with experimental data.

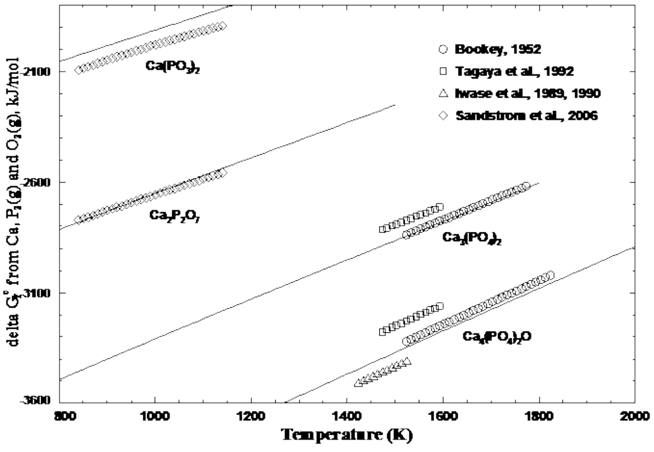
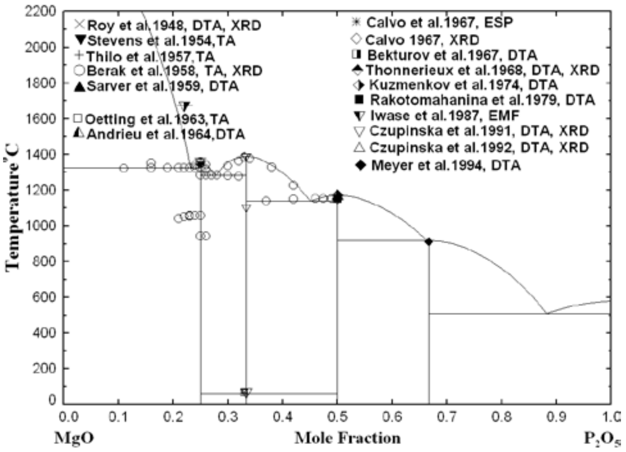


Fig. 3. Optimized Gibbs energy of formation of intermediate compounds in the $CaO-P_2O_5$ system.



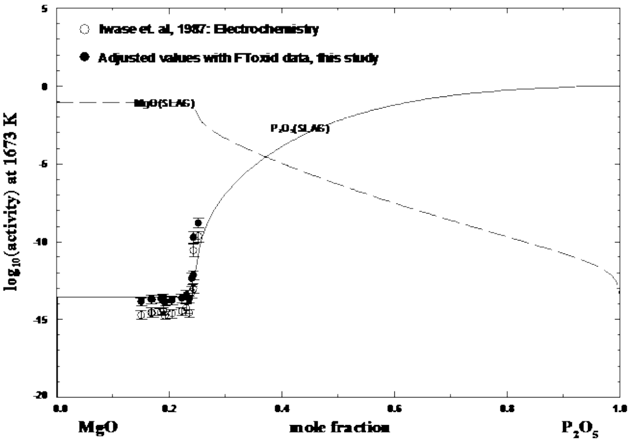


Fig. 4. Optimized binary phase diagram of the MgO-P_2O_5 system with experimental data.

Fig. 5. Calculated activity of P_2O_5(l) in the MgO-P_2O_5 system along with experimental data in literature.

The other optimized thermodynamic results for the MgO-P_2O_5 system are presented in Figs. 4 and 5. In the similar way, all the available phase diagram and thermodynamic properties experimental data in the binary P_2O_5 systems were critically evaluated and optimized to obtain the binary interactions between oxide components and P_2O_5 in liquid slag.

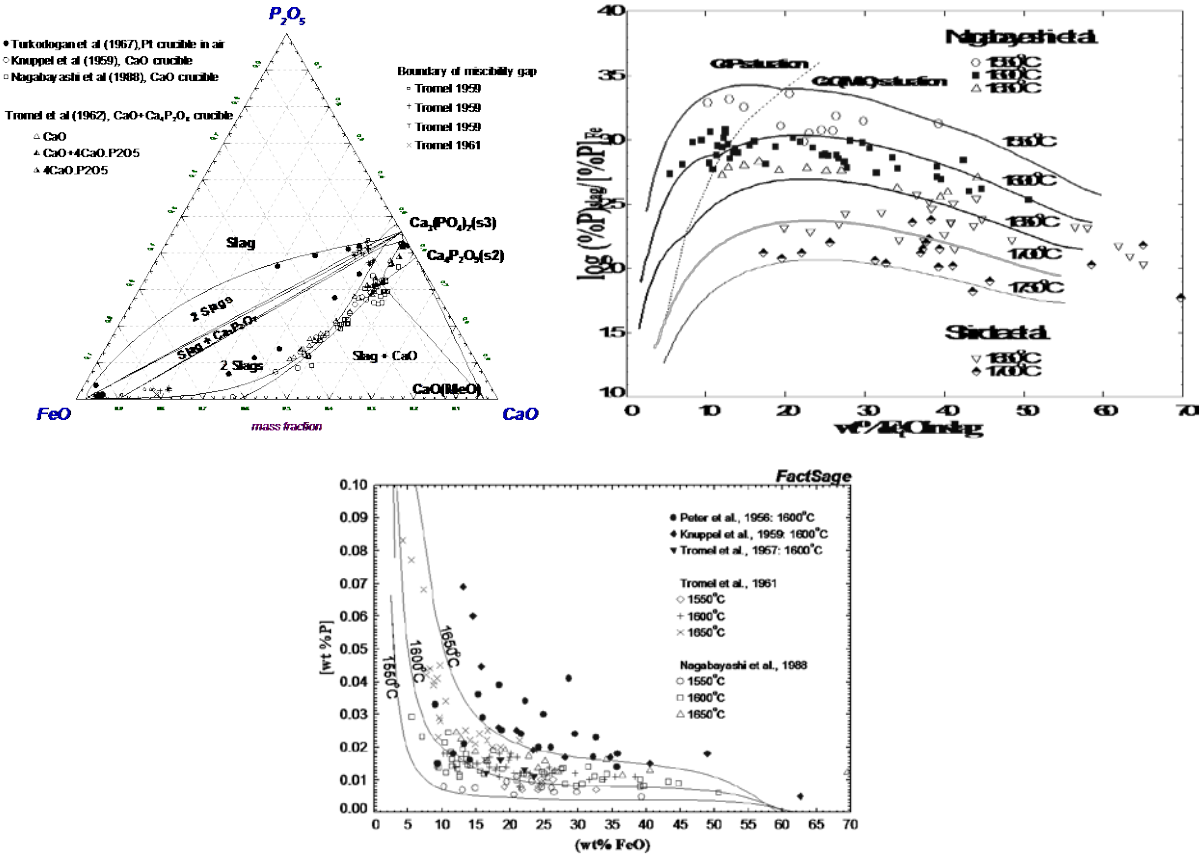
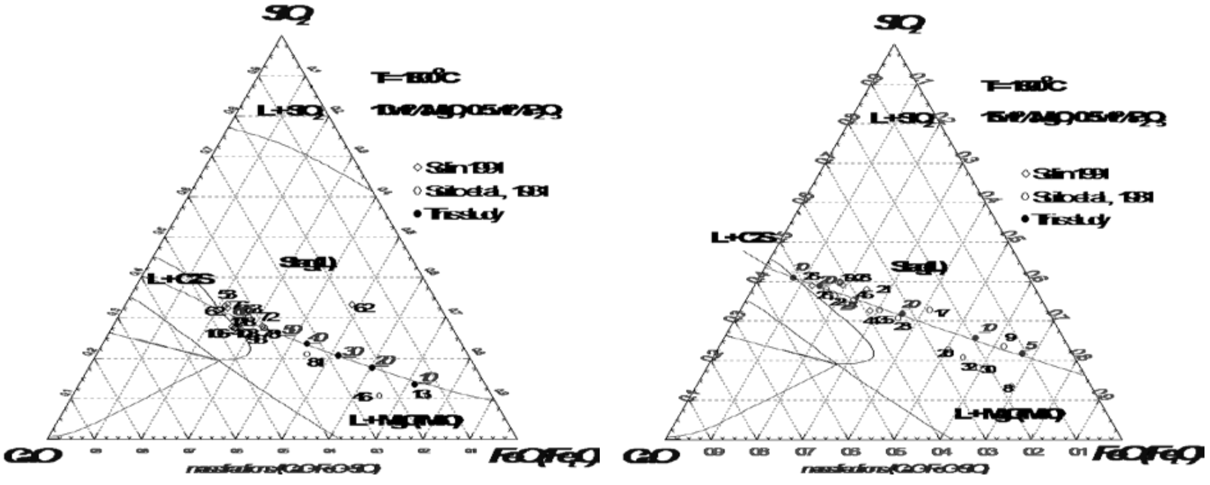


Fig. 6. The calculated phase diagram of the CaO-Fe_tO-P_2O_5 system equilibrated with molten Fe at 1600 °C, L_P between molten iron and the slag along CaO saturation line, and the relationship between [%P] in liquid Fe and FetO content in slag along CaO saturation line in comparison with available experimental data.

The most fundamental system for the BOF De-P slag is the $CaO-Fe_tO-P_2O_5$ system. Many experimental studies have been performed to determine the phase diagram and phosphorus distribution between the slag and molten iron at 1550 to 1750°C. As can be seen in Fig. 6, the phase diagram of the $CaO-Fe_tO-P_2O_5$ system at 1600°C is well reproduced by the thermodynamic modeling. The phosphorus distribution (L_P) and the relationship between [%P] in molten iron along with the Fe_tO concentration in molten slag saturated with CaO or $4CaO \cdot P_2O_5$ are well reproduced within experimental error limit.

3. Application to De-phosphorization in BOF process

BOF slag is typically based on the $CaO-Fe_tO-SiO_2$ system. MgO is also intentionally added to protect the refractory lining of the BOF (MgO-C) while small amounts of Al_2O_3, MnO, TiO_2, Na_2O and CaF_2 are added or naturally formed from molten pig iron during the process. As it is well-known, the main purpose of the BOF process is the de-C and de-P of steel. Although C can be exhausted as CO or CO_2 gas by reacting with injected oxygen, the phosphorus in molten Fe ends up as P_2O_5 in the molten slag where it can reach several wt. %.



(a) (b)

Fig. 7. Calculated phosphorus distribution between slag and molten Fe (L_P = (wt. % P)/[wt. % P]) for the $CaO-Fe_tO-SiO_2-MgO$ slag at 1600 °C in comparison with experimental data. (a) $CaO-Fe_tO-SiO_2$-10% MgO slag and (b) $CaO-Fe_tO-SiO_2$-15% MgO slag. Numbers in the diagram are experimental L_P data and Numbers are the calculated L_P values from the present database.

Figure 7 shows the calculated phase diagram of the $CaO-Fe_tO-SiO_2$ slag with 10 and 15 wt. % MgO in saturation with molten Fe at 1600°C, which is projected onto the $CaO-Fe_tO-SiO_2$ ternary. In the calculation, 0.5 wt. % P_2O_5 was added to calculate the L_P values between slag and molten metal. Suito et al. [3] and Selin [4] investigated the phosphorus distribution in this system using MgO crucibles. The MgO saturation line (liquidus of $MgO_{s.s.}$) from these two experimental studies is rather different especially in the FeO-rich corner. The calculated MgO saturation line from the present database is consistent with that of Selin rather than that of Suito et al. The calculated L_P values from the present thermodynamic database are in good agreement with experimental results near the Ca_2SiO_4 saturation region.

When the FeO concentration is increased in both, Fig. 7 (a) and (b), our L_P values are in good agreement with those of Selin [4]. Because the L_P values are highly dependent on the amount of CaO and FeO, the L_P data from Suito et al. [3] and Selin [4] show more difference in the FeO-rich corner. The L_P data of Suito et al. [3] are in general slightly higher than the values of Selin because the slags of Suito et al. are more CaO-enriched at the same FeO concentration.

A large amount of experimental data for the de-P distributions between multicomponent slags (CaO-MgO-SiO_2-Fe_tO-Na_2O-Al_2O_3-MnO-P_2O_5 system) and liquid iron at temperatures of 1100 to 1700 °C were collected from literature and reviewed in the present study. Thermodynamic calculations between the slag and molten iron were performed using the present thermodynamic database based on each experimental condition. Experimental data and calculated values are compared in Fig. 8. The L_P data for binary, ternary, quaternary and multicomponent systems from the literature were collected and the calculations performed using the same experimental conditions. More than 1000 experimental points are compared in Fig. 8.

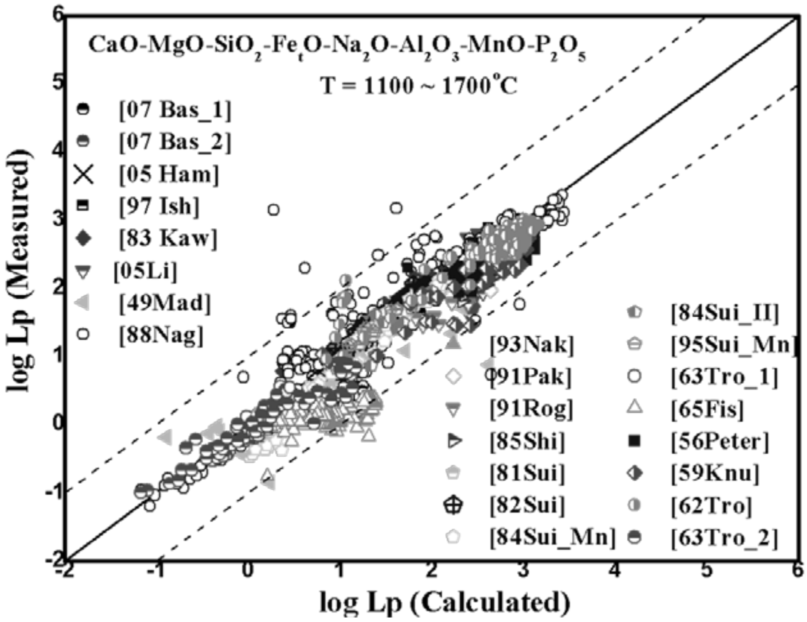


Fig. 8. Comparison between experimental and calculated L_P values for binary, ternary and multicomponent slags using the present thermodynamic database.

For more detailed examinations for the slag system important for BOF process, the experimental data for the phosphorus distribution between the CaO-MgO_{sat}-SiO_2-Fe_tO-(MnO) slag and molten iron are compared with calculations in Fig. 9. The L_P data were determined at the temperature between 1550oC and 1700oC by many researchers under Ar gas with MgO crucibles [3], [4], [5], [6], [7], [8], [9]. The comparison between the measured L_P data and calculated L_P values shows an excellent agreement each other.

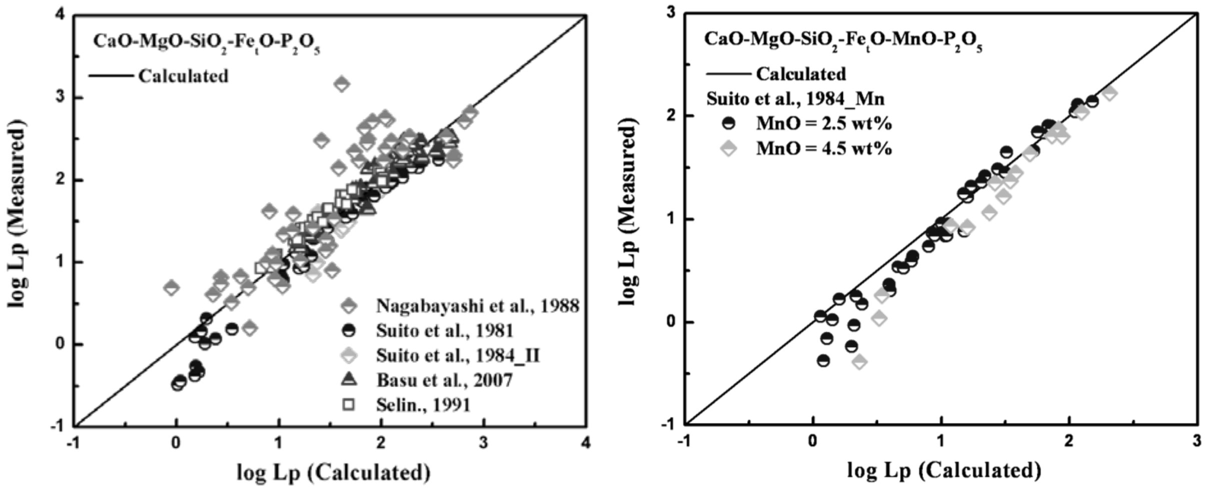


Fig. 9. Comparison between experimental and calculated L_P values for the CaO-MgO-SiO_2-Fe_tO(-MnO) system [3], [4], [5], [6], [7], [8], [9].

4. Summary

In order to meet the strong demands of steelmaking industry, new systematic thermodynamic modeling of the P_2O_5 containing oxide systems (CaO-FeO-Fe_2O_3-SiO_2-MgO-Al_2O_3-Na_2O-P_2O_5) and key phase diagram experiments have been carried out. The phase diagram and thermodynamic properties data available for unary, binary and ternary P_2O_5 containing systems were critically evaluated and optimized to build up the reliable thermodynamic database. In order to describe the thermodynamic behavior of P2O5 in slag, the Modified Quasichemical Model taking into account the short-range-ordering of cations in molten slag is used explicitly in the present study. The optimized model parameters for binary and ternary P2O5 system can be used to predict the phosphorus distribution between multicomponent slag and molten iron at wide range of temperature and oxygen partial pressure. The calculated L_P values from the present thermodynamic database are in good agreement with experimental L_P data within experimental error limit. We believe that the present thermodynamic database can be used for the complex BOF process simulation, which can be helpful to understand the chemical reactions in BOF and eventually be an important tool for the development of environmentally more stainable BOF process in the future.

Acknowledgement

Financial support from TataSteel Europe, Posco, RIST, Hyundai Steel, Nucor steel, RTIT, Nippon Steel Corp., JFE steel, Sumitomo metals, and the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

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