

# 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 FeO-SiO<sub>2</sub> rich slag to CaO-SiO<sub>2</sub>-FeO-MgO slag under a temperature range from 1200°C to 1750°C and oxygen potential varying from very oxidizing condition to carbon saturation condition are indispensable. In addition, the influence of other components such as Al<sub>2</sub>O<sub>3</sub>, MnO, Na<sub>2</sub>O, etc. on the phosphorus distribution between molten iron and multicomponent slag are important. The phosphorus distribution between molten slag and solid Ca<sub>2</sub>SiO<sub>4</sub> phase which can dissolve a considerable amount of P<sub>2</sub>O<sub>5</sub> under the steelmaking condition are also important issue in particular at low temperature range from 1200 to 1600°C. 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<sub>2</sub>O<sub>5</sub> 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<sub>2</sub>O<sub>5</sub> 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 database<sup>1)</sup>. The FACT oxide database contains the complete description of the CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-MgO-FeO-Fe<sub>2</sub>O<sub>3</sub> system with additional components like MnO<sub>x</sub>, CrO<sub>x</sub>, TiO<sub>x</sub>, etc. However, in the case of P<sub>2</sub>O<sub>5</sub>, 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<sub>2</sub>O<sub>5</sub> containing oxide systems (CaO-FeO-Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-MgO-Al<sub>2</sub>O<sub>3</sub>-Na<sub>2</sub>O-P<sub>2</sub>O<sub>5</sub>) 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<sub>2</sub>O<sub>5</sub> 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-FeO-Fe<sub>2</sub>O<sub>3</sub>-MgO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-Na<sub>2</sub>O-P<sub>2</sub>O<sub>5</sub> 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 P<sub>2</sub>O<sub>5</sub> have not been well-known in literature. Thus, the thermodynamic evaluation of pure P<sub>2</sub>O<sub>5</sub> was for the first time properly carried out based on all available equilibration data for gases P<sub>2</sub>O<sub>5</sub> / solid P<sub>2</sub>O<sub>5</sub> / liquid P<sub>2</sub>O<sub>5</sub>. The well-accepted Gibbs energy of formation ( $\Delta G_f^\circ$ ) for P<sub>2</sub>O<sub>5</sub> liquid from Turkdogan and Pearson (1953) are not consistent with the experimental phase diagram data of P<sub>2</sub>O<sub>5</sub>:



- Turkdogan and Pearson (1953) [2]

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

- Present study

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

In the present study, the new  $\Delta G_f^\circ$  of  $\text{P}_2\text{O}_5(\text{l})$  is evaluated based on all available thermodynamic data of  $\text{P}_2\text{O}_5$  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  $\text{P}_2\text{O}_5$  becomes less than  $300^\circ\text{C}$ , while the experimental data shows the melting temperature to be  $580^\circ\text{C}$ . However, interestingly the difference of the  $\log K$  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  $1700^\circ\text{C}$ .

Binary  $\text{MO-P}_2\text{O}_5$  ( $M = \text{Ca, Mg, Fe, Mn}$ ),  $\text{SiO}_2\text{-P}_2\text{O}_5$ ,

$\text{Al}_2\text{O}_3\text{-P}_2\text{O}_5$ ,  $\text{Fe}_2\text{O}_3\text{-P}_2\text{O}_5$  and  $\text{Na}_2\text{O-P}_2\text{O}_5$  systems were optimized based on all available thermodynamic and phase diagram experimental data. In the case of binary  $\text{CaO-P}_2\text{O}_5$  system, for example, many intermediate compounds of  $x\text{CaO}\cdot y\text{P}_2\text{O}_5$  and a liquid phase exist. Among the solid phases, the thermodynamic properties of  $\text{Ca}_4\text{P}_2\text{O}_9$ ,  $\text{Ca}_3\text{P}_2\text{O}_8$ ,  $\text{Ca}_2\text{P}_2\text{O}_7$  and  $\text{CaP}_2\text{O}_6$  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.

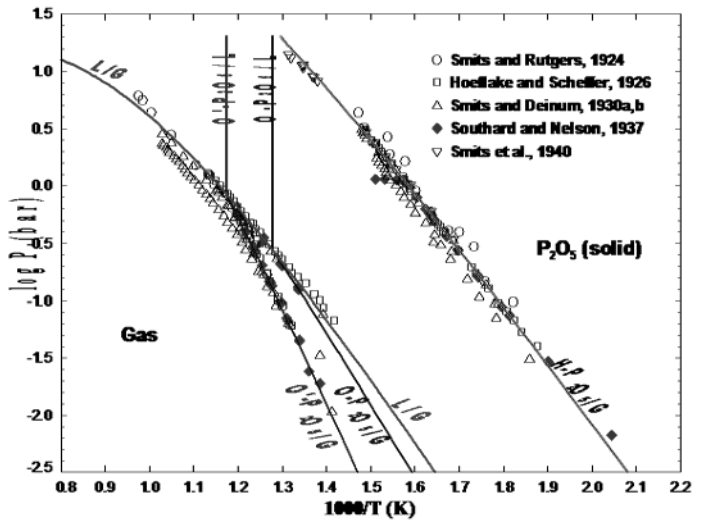


Fig. 1. Log P vs 1000/T diagram of the  $\text{P}_2\text{O}_5$  unary in the present study. O'- $\text{P}_2\text{O}_5$  is the most stable solid phase and its melting temperature is  $580^\circ\text{C}$ .

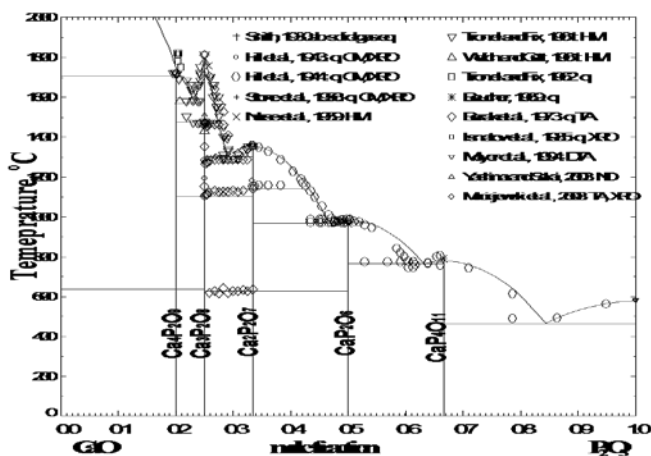


Fig. 2. Optimized binary phase diagram of the  $\text{CaO-P}_2\text{O}_5$  system with experimental data.

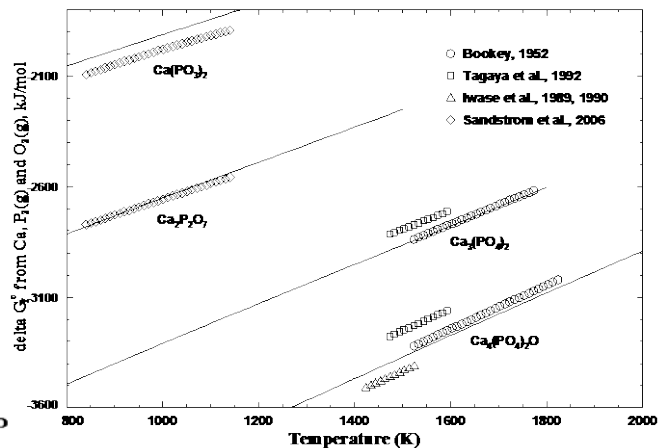


Fig. 3. Optimized Gibbs energy of formation of intermediate compounds in the  $\text{CaO-P}_2\text{O}_5$  system.

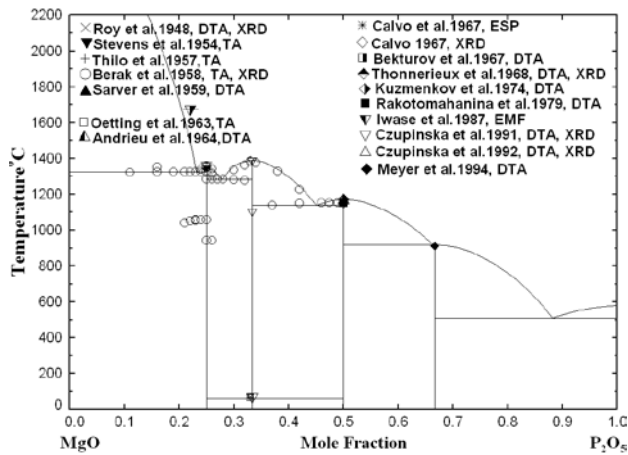


Fig. 4. Optimized binary phase diagram of the MgO-P<sub>2</sub>O<sub>5</sub> system with experimental data.

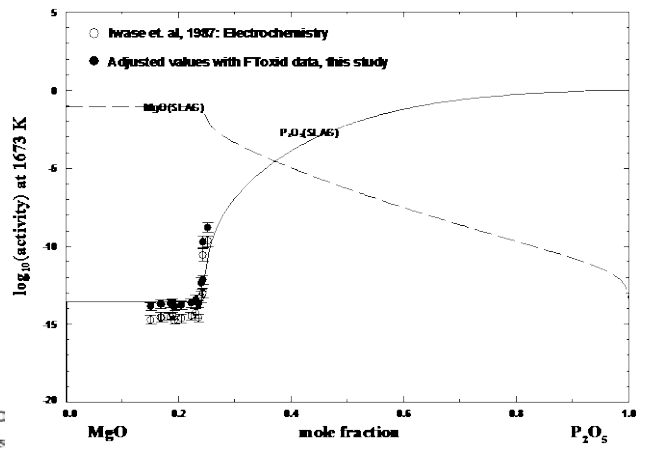


Fig. 5. Calculated activity of P<sub>2</sub>O<sub>5</sub>(l) in the MgO-P<sub>2</sub>O<sub>5</sub> system along with experimental data in literature.

The other optimized thermodynamic results for the MgO-P<sub>2</sub>O<sub>5</sub> 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<sub>2</sub>O<sub>5</sub> systems were critically evaluated and optimized to obtain the binary interactions between oxide components and P<sub>2</sub>O<sub>5</sub> in liquid slag.

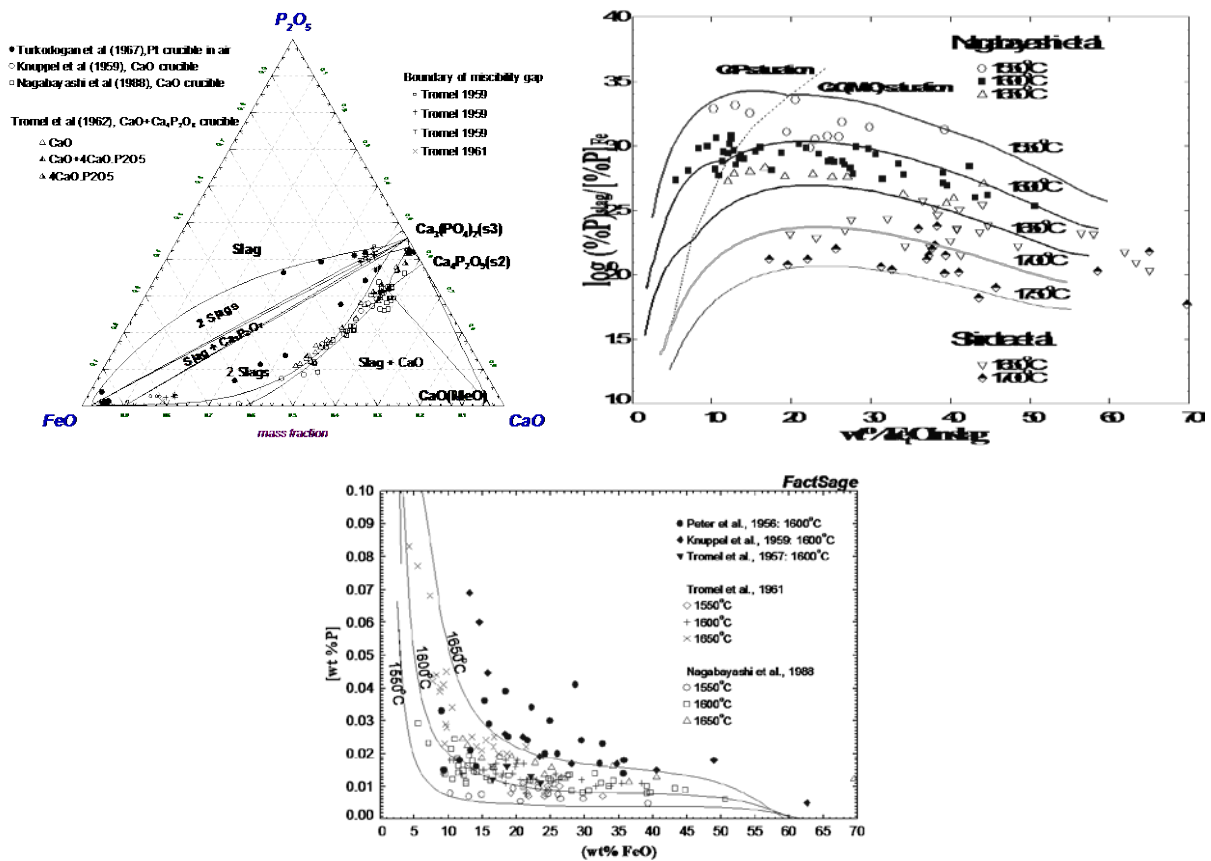


Fig. 6. The calculated phase diagram of the CaO-Fe<sub>1</sub>O-P<sub>2</sub>O<sub>5</sub> system equilibrated with molten Fe at 1600 °C, L<sub>P</sub> between molten iron and the slag along CaO saturation line, and the relationship between [%P] in liquid Fe and FeO content in slag along CaO saturation line in comparison with available experimental data.

The most fundamental system for the BOF De-P slag is the  $\text{CaO-Fe}_t\text{O-P}_2\text{O}_5$  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  $\text{CaO-Fe}_t\text{O-P}_2\text{O}_5$  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  $\text{Fe}_t\text{O}$  concentration in molten slag saturated with CaO or  $4\text{CaO}\cdot\text{P}_2\text{O}_5$  are well reproduced within experimental error limit.

### 3. Application to De-phosphorization in BOF process

BOF slag is typically based on the  $\text{CaO-Fe}_t\text{O-SiO}_2$  system.  $\text{MgO}$  is also intentionally added to protect the refractory lining of the BOF ( $\text{MgO-C}$ ) while small amounts of  $\text{Al}_2\text{O}_3$ ,  $\text{MnO}$ ,  $\text{TiO}_2$ ,  $\text{Na}_2\text{O}$  and  $\text{CaF}_2$  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  $\text{CO}$  or  $\text{CO}_2$  gas by reacting with injected oxygen, the phosphorus in molten Fe ends up as  $\text{P}_2\text{O}_5$  in the molten slag where it can reach several wt. %.

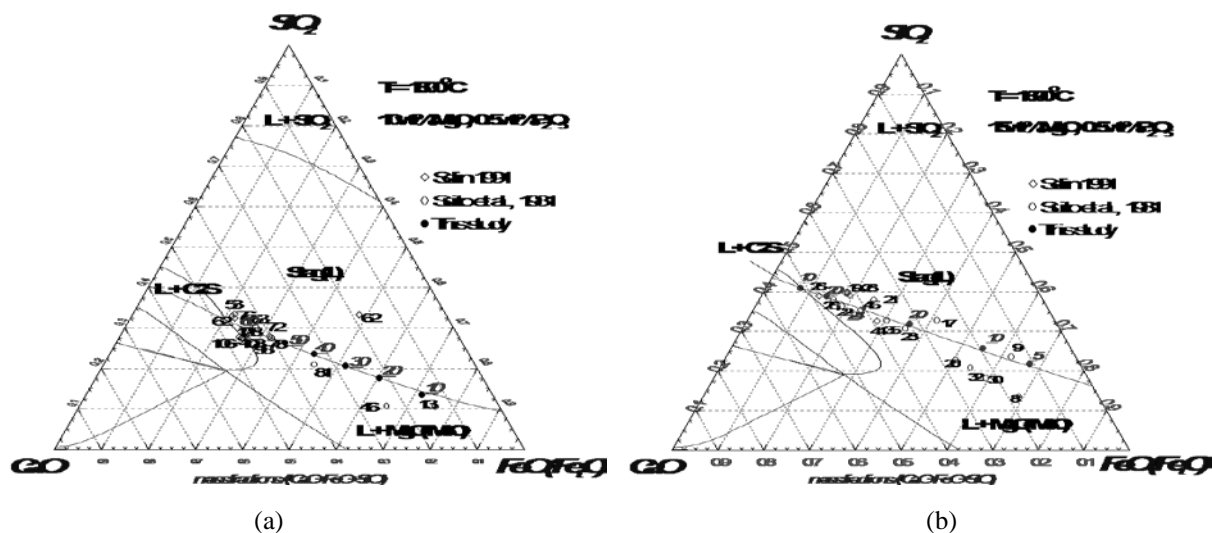


Fig. 7. Calculated phosphorus distribution between slag and molten Fe ( $L_P = (\text{wt. \% P})/[\text{wt. \% P}]$ ) for the  $\text{CaO-Fe}_t\text{O-SiO}_2\text{-MgO}$  slag at 1600 °C in comparison with experimental data. (a)  $\text{CaO-Fe}_t\text{O-SiO}_2\text{-10\% MgO}$  slag and (b)  $\text{CaO-Fe}_t\text{O-SiO}_2\text{-15\% MgO}$  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  $\text{CaO-Fe}_t\text{O-SiO}_2$  slag with 10 and 15 wt. %  $\text{MgO}$  in saturation with molten Fe at 1600°C, which is projected onto the  $\text{CaO-Fe}_t\text{O-SiO}_2$  ternary. In the calculation, 0.5 wt. %  $\text{P}_2\text{O}_5$  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  $\text{MgO}$  crucibles. The  $\text{MgO}$  saturation line (liquidus of  $\text{MgO}_{\text{s.s.}}$ ) from these two experimental studies is rather different especially in the  $\text{FeO}$ -rich corner. The calculated  $\text{MgO}$  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  $\text{Ca}_2\text{SiO}_4$  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<sub>2</sub>-Fe<sub>t</sub>O-Na<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-MnO-P<sub>2</sub>O<sub>5</sub> 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.

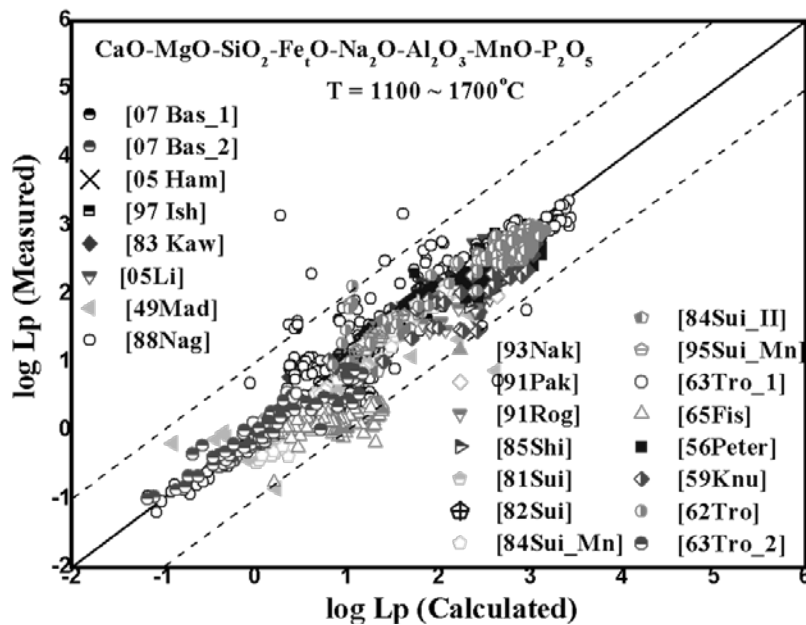


Fig. 8. Comparison between experimental and calculated  $L_P$  values for binary, ternary and multicomponent slags using the present thermodynamic database.

For more detailed examinations for the slag system important for BOF process, the experimental data for the phosphorus distribution between the CaO-MgO<sub>sat</sub>-SiO<sub>2</sub>-Fe<sub>t</sub>O-(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.

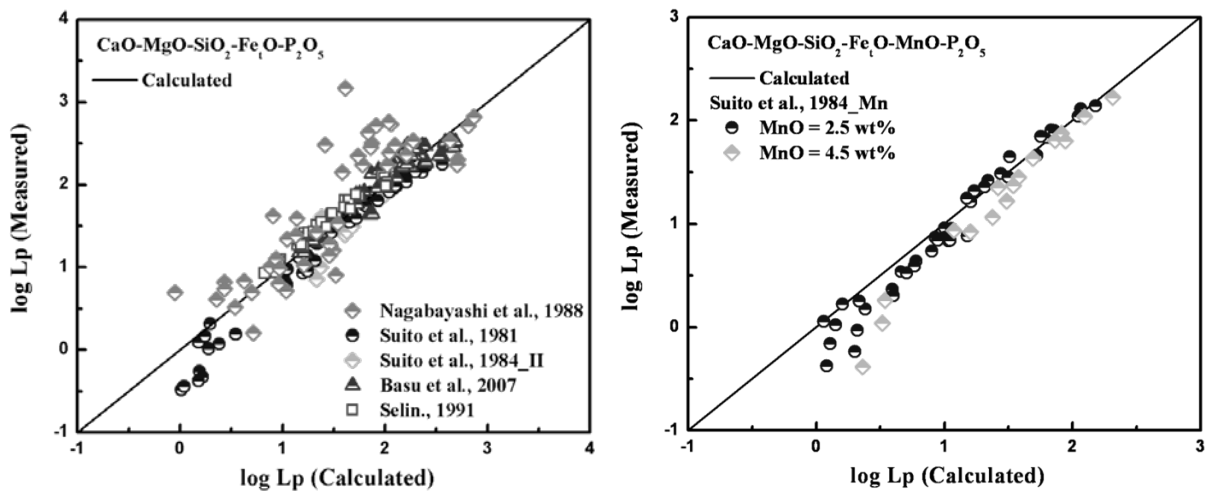


Fig. 9. Comparison between experimental and calculated  $L_P$  values for the CaO-MgO-SiO<sub>2</sub>-Fe<sub>1</sub>O(-MnO) system [3], [4], [5], [6], [7], [8], [9].

#### 4. Summary

In order to meet the strong demands of steelmaking industry, new systematic thermodynamic modeling of the P<sub>2</sub>O<sub>5</sub> containing oxide systems (CaO-FeO-Fe<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-MgO-Al<sub>2</sub>O<sub>3</sub>-Na<sub>2</sub>O-P<sub>2</sub>O<sub>5</sub>) and key phase diagram experiments have been carried out. The phase diagram and thermodynamic properties data available for unary, binary and ternary P<sub>2</sub>O<sub>5</sub> containing systems were critically evaluated and optimized to build up the reliable thermodynamic database. In order to describe the thermodynamic behavior of P<sub>2</sub>O<sub>5</sub> 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 P<sub>2</sub>O<sub>5</sub> 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 sustainable BOF process in the future.

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#### References

- [1] A. D. Pelton, S. A. Degterov, G. Eriksson, C. Robelin, Y. Dessureault. The modified quasichemical model I-binary solutions. *Metall. Mater. Trans. B*, 2000, 31, p651-659.
- [2] E. T. Turkdogan, J. Pearson. Activities of constituents of iron and steelmaking slags. III. Phosphorus pentoxide. *J. Iron Steel Inst. London*, 1953, 175, p398.

- [3] H. Suito, R. Inoue, M. Takada. Phosphorus Distribution between Liquid Iron and Magnesium Oxide Saturated Slags of the System Calcium Oxide-Magnesium Oxide-Iron Oxide-Silicon Oxide ( $\text{CaO-MgO-FeO}_x\text{-SiO}_2$ ). *Trans ISIJ*, 1981, 21(4), p250-259.
- [4] R. Selin. Studies on Magnesia Solubility in Complex Steelmaking Slags in Equilibrium with Liquid Iron and Distribution of Phosphorus and Vanadium between Slag and Metal at MgO Saturation. Part I. Reference System Calcium-Ferrous Oxide-MgO-Silica. *Scand. J. Metall.*, 1991, 20(5), p279-299.
- [5] S. Basu, A. K. Lahiri, S. Seetharaman. Phosphorus Partition between Liquid Steel and  $\text{CaO-SiO}_2\text{-P}_2\text{O}_5\text{-MgO}$  Slag Containing Low FeO. *Metall. Mater. Trans.*, 2007, 38B, p357-366 .
- [6] S. Basu, A. K. Lahiri, S. Seetharaman, Phosphorus Partition between Liquid Steel and  $\text{CaO-SiO}_2\text{-P}_2\text{O}_5\text{-MgO}$  Slag Containing 15 to 25 Pct FeO. *Metall. Mater. Trans.*, 2007, 38B, p623-630.
- [7] R. Nagabayashi, M. Hino, S. Ban-ya. Solubilities of Calcium Oxide, Magnesium Oxide, Silicon Dioxide and  $2\text{CaO}\times\text{SiO}_2$ , and Ferric-Ferrous Equilibrium in  $\text{FeO-(CaO + MgO)-(SiO}_2 + \text{P}_2\text{O}_5)$  Phosphate Slags. *Tetsu to Hagane*, 1988, 74(8), p1577-1584.
- [8] H. Suito, R. Inoue. Effect of Calcium Fluoride on Phosphorus Distribution between MgO Saturated Slags of the System  $\text{CaO-MgO-FeO}_x\text{-SiO}_2$  and Liquid Iron. *Trans ISIJ*, 1982, 22, p869-877.
- [9] H. Suito, R. Inoue, Phosphorus Distribution between MgO-saturated  $\text{CaO-Fe}_t\text{O-SiO}_2\text{-P}_2\text{O}_5\text{-MnO}$  Slags and Liquid Iron *Trans ISIJ*, 1984, 24, p40-46.