M. Hasegawa*, Y. Kashiwaya and M. Iwase

Thermodynamic Properties of Solid Solutions between Di-calcium Silicate and Tri-calcium Phosphate

Abstract: For a better understanding of phosphorus removal from hot metal, the Gibbs free energies of solid solutions between di-calcium silicate and tri-calcium phosphate were derived through applications of solutions models. The regular solution model with the parameters determined in this study gave the activities of the components thermodynamically consistent with the literature data and the phase diagrams.

Keywords: di-calcium silicate, tri-calcium phosphate, solid solution, dephosphorization

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*Corresponding author: M. Hasegawa: Department of Energy Science and Technology, Kyoto University, Kyoto 606-8501, Japan E-mail: hasegawa@energy.kyoto-u.ac.jp
Y. Kashiwaya: Department of Energy Science and Technology, Kyoto University, Kyoto 606-8501, Japan
M. Iwase: Department of Energy Science and Technology, Kyoto University, Kyoto 606-8501, Japan

1 Introduction

The ternary system, calcium oxide-silicon oxide-phosphorus oxide, constitutes one of the most fundamental steelmaking slags. Figure 1(a) gives the iso-thermal section of the ternary system CaO-SiO2-P2O5 near the CaO apex at 1573 K, determined by the present authors /1/. As can be seen in Figure 1(a), this system has the following double oxides;

di-calcium silicate $Ca_2SiO_4 = 2CaO \cdot SiO_2 = C_2S$
tri-calcium silicate $Ca_3SiO_5 = 3CaO \cdot SiO_2 = C_3S$
tri-calcium phosphate $CaP_2O_8 = 3CaO \cdot P_2O_5 = C_3P$
tetra-calcium phosphate $CaP_2O_9 = 4CaO \cdot P_2O_5 = C_4P$

It has been known that solid solutions form between di-calcium silicate, $Ca_2SiO_4$, and tri-calcium phosphate, $CaP_2O_8$. Figure 1(b) shows the pseudo-binary phase diagram of $Ca_2SiO_4$-$CaP_2O_8$ based upon the work of Fix et al. /2/ and includes the following triple oxides;

$CaP_SiO_{16} = 7CaO \cdot P_2O_5 \cdot 2SiO_2 = C_7PS_2$
$CaP_{2SiO_{12}} = 5CaO \cdot P_2O_5 \cdot SiO_2 = C_5PS$

Figure 1(b) illustrates that the temperatures of the phase transformations from $\alpha'-C_2S$ to $\alpha-C_2S$ and from $\alpha-C_3P$ to $\bar{\alpha}-C_3P$ are 1693 K and 1743 K, respectively, and solid solutions $(C_2S-C_3P)_{ss}$ form between $\alpha-C_2S$ and $\bar{\alpha}-C_3P$. As seen in Figure 1(a), $(C_2S-C_3P)_{ss}$ can coexist with solid CaO at 1573 K although the stoichiometric compounds of $C_2S$ and $C_3P$ can not. This is consistent with the observation that, during phosphorus removal from hot metal, phosphorus would often be present in $(C_2S-C_3P)_{ss}$ coexisting with...
solid CaO /3/. A better understanding of dephosphorization process would rely on the knowledge of the thermodynamic properties of \( \langle C_{2}S\cdot C_{3}P \rangle_{ss} \), whereas there has been a definite lack of such data. The present study is aimed at deriving the activities of the components at 1573 K by applying solution models to \( \langle C_{2}S\cdot C_{3}P \rangle_{ss} \).

2 Calculation

2.1 Solution models

Figure 1(b) reported by Fix et al. /2/ shows that solid solutions \( \langle C_{2}S\cdot C_{3}P \rangle_{ss} \) could form between higher-temperature forms of \( \text{Ca}_2\text{SiO}_4 \) and \( \text{Ca}_3\text{P}_2\text{O}_8 \), represented by \( \alpha\cdot C_{3}S \) and \( \tilde{\alpha}\cdot C_{3}P \). The lattice structures of these solid phases have not been clarified /2/. As illustrated schematically in Figure 2, however, it is not unacceptable that electrically neutral molecules of “(1/2)\( \text{Ca}_3\text{P}_2\text{O}_8 \)” would replace with those of “\( \text{Ca}_2\text{SiO}_4 \)”, depending on compositions of solid solutions. Such a simple assumption derives the definition of the substitution ratio \( Y \), given as

\[
y = n_{(1/2)\text{Ca}_3\text{P}_2\text{O}_8}/(n_{\text{Ca}_2\text{SiO}_4} + n_{(1/2)\text{Ca}_3\text{P}_2\text{O}_8}) \quad (1)
\]

where \( n_i \) denotes the number of moles of component \( i \) in solid solutions. The consideration that the molecular mass of “(1/2)\( \text{Ca}_3\text{P}_2\text{O}_8 \)” is half of that of \( \text{Ca}_3\text{P}_2\text{O}_8 \) leads to equation (2).

\[
n_{(1/2)\text{Ca}_3\text{P}_2\text{O}_8} = 2n_{\text{Ca}_3\text{P}_2\text{O}_8} \quad (2)
\]

Inserting equation (2) into equation (1), we have

\[
y = 2n_{\text{Ca}_3\text{P}_2\text{O}_8}/(n_{\text{Ca}_2\text{SiO}_4} + 2n_{\text{Ca}_3\text{P}_2\text{O}_8}) \quad (3)
\]

The present study is aimed at deriving the relative partial molar Gibbs free energies of \( \text{Ca}_2\text{SiO}_4 \) and \( \text{Ca}_3\text{P}_2\text{O}_8 \) within \( \langle C_{2}S\cdot C_{3}P \rangle_{ss} \) at 1573 K. Towards this objective, the ideal solution model and the regular solution model were applied to solid solutions \( \langle C_{2}S\cdot C_{3}P \rangle_{ss} \) between \( \alpha\cdot C_{3}S \) and \( \tilde{\alpha}\cdot C_{3}P \). The activities of \( \text{Ca}_2\text{SiO}_4 \) and \( \text{Ca}_3\text{P}_2\text{O}_8 \) referred to the most stable forms at 1573 K as standard states, i.e., \( \alpha\cdot C_{3}S \) and \( \tilde{\alpha}\cdot C_{3}P \), could be formulated as follows.

Ideal Solution Model

\[
RT \ln a_{\text{Ca}_2\text{SiO}_4} = \Delta G^\circ(\text{Ca}_2\text{SiO}_4) + RT \ln(1 – Y) \quad (4)
\]

\[
RT \ln a_{\text{Ca}_3\text{P}_2\text{O}_8} = 2RT \ln a_{(1/2)\text{Ca}_3\text{P}_2\text{O}_8} = \Delta G^\circ(\text{Ca}_3\text{P}_2\text{O}_8) + 2RT \ln Y \quad (5)
\]

Regular Solution Model

\[
RT \ln a_{\text{Ca}_2\text{SiO}_4} = \Delta G^\circ(\text{Ca}_2\text{SiO}_4) + RT \ln(1 – Y) + \Omega Y^2 \quad (6)
\]

\[
RT \ln a_{\text{Ca}_3\text{P}_2\text{O}_8} = 2RT \ln a_{(1/2)\text{Ca}_3\text{P}_2\text{O}_8} = \Delta G^\circ(\text{Ca}_3\text{P}_2\text{O}_8) + 2RT \ln Y + 2\Omega(1 – Y)^2 \quad (7)
\]

where \( R \) is the gas constant, \( \Delta G^\circ(\text{Ca}_2\text{SiO}_4) \) and \( \Delta G^\circ(\text{Ca}_3\text{P}_2\text{O}_8) \) represent the Gibbs free energy changes of the phase transformations of \( \text{Ca}_2\text{SiO}_4 \) and \( \text{Ca}_3\text{P}_2\text{O}_8 \), respectively, and \( \Omega \) is the interaction parameter independent of composition and temperature.

2.2 Thermodynamic data used for calculations and necessary conditions

Kubashevski, Alcock and Spencer listed the thermal data on \( \text{Ca}_2\text{SiO}_4 \), i.e., heat capacities of \( \alpha\cdot C_{3}S \) and \( \tilde{\alpha}\cdot C_{3}S \), and heat of the phase transformation /4/. By extrapolating the data for heat capacity of \( \alpha\cdot C_{3}S \) at temperature below 1693 K, the value for \( \Delta G^\circ(\text{Ca}_2\text{SiO}_4) \) at 1573 K could be calculated as

\[
\Delta G^\circ(\text{Ca}_2\text{SiO}_4) = G^\circ(\alpha\cdot C_{3}S) – G^\circ(\tilde{\alpha}\cdot C_{3}S)
\]

\[
= 1,132 \text{ J} \cdot \text{mol}^{-1} \text{ at } 1573 \text{ K} \quad (8)
\]

where \( G^\circ(i) \) is the standard Gibbs free energy of substance \( i \). On the other hand, the literature data have been lacking for the calculation of \( \Delta G^\circ(\text{Ca}_3\text{P}_2\text{O}_8) \). Therefore, the following formula was assumed in this study.

\[
\Delta G^\circ(\text{Ca}_3\text{P}_2\text{O}_8) = G^\circ(\tilde{\alpha}\cdot C_{3}P) – G^\circ(\alpha\cdot C_{3}P)
\]

\[
= \Delta H^\circ(\text{Ca}_3\text{P}_2\text{O}_8) (1 – T/1743) \quad (9)
\]

where \( \Delta H^\circ(\text{Ca}_3\text{P}_2\text{O}_8) \) is the heat of the phase transformation from \( \alpha\cdot C_{3}P \) to \( \tilde{\alpha}\cdot C_{3}P \) at the transition temperature of 1743 K.
The reactions of the formations of Ca$_2$SiO$_4$ and Ca$_3$SiO$_3$ from CaO and SiO$_2$ are expressed as

\[ 2 \text{CaO} + \text{SiO}_2 = \text{Ca}_2\text{SiO}_4 \]  
\[ 3 \text{CaO} + \text{SiO}_2 = \text{Ca}_3\text{SiO}_3 \]  

The present authors assessed the thermal data by Kubaschewski et al. /4/ to derive the equilibrium constants of reactions (10) and (11) thermodynamically consistent with phase diagrams; the results could be given as follows /5/.

\[ \log K(10) = \log a_{\text{Ca}_2\text{SiO}_4} - 2 \log a_{\text{CaO}} - \log a_{\text{SiO}_2} = 4.78 \text{ at } 1573 \text{ K} \]  
\[ \log K(11) = \log a_{\text{Ca}_3\text{SiO}_3} - 3 \log a_{\text{CaO}} - \log a_{\text{SiO}_2} = 4.80 \text{ at } 1573 \text{ K} \]

where \(a_i\) represents the activities of substance \(i\) referred to pure \(i\) of the most stable form at 1573 K. For the standard Gibbs free energy changes of the formations of Ca$_2$P$_2$O$_8$ and Ca$_3$P$_2$O$_8$ from CaO and P$_2$O$_5$, the following literature data were accepted.

\[ 3 \text{CaO} + 2 \text{P}_2\text{O}_5 = \text{Ca}_3\text{P}_2\text{O}_8 \]  
\[ \Delta G(14) = -RT \ln K(14) = -776,300 + 18.6 \times (T/K) (J \cdot \text{mol}^{-1}) /6, 7/ \]

\[ \log K(14) = \log a_{\text{Ca}_3\text{P}_2\text{O}_8} - 3 \log a_{\text{CaO}} - \log a_{\text{P}_2\text{O}_5} = 24.80 \text{ at } 1573 \text{ K} \]

\[ 4 \text{CaO} + \text{P}_2\text{O}_5 = \text{Ca}_4\text{P}_2\text{O}_9 \]  
\[ \Delta G(17) = -RT \ln K(17) \]

\[ = -781,500 + 14.8 \times (T/K) (J \cdot \text{mol}^{-1}) /7/ \]

\[ \log K(17) = \log a_{\text{Ca}_4\text{P}_2\text{O}_9} - 4 \log a_{\text{CaO}} - \log a_{\text{P}_2\text{O}_5} = 25.18 \text{ at } 1573 \text{ K} \]

In this study, \(a_{\text{P}_2\text{O}_5}\) represents the activity of P$_2$O$_5$ referred to hypothetical pure liquid P$_2$O$_5$ /8/.

As shown in Figure 1(a), the iso-thermal section of the CaO-SiO$_2$-P$_2$O$_5$ system near the CaO apex at 1573 K consists of the following three-phase assemblages.

\(\left(C_2\text{S}-\text{C}_3\text{P}\right)_{ss} + \text{Ca}_2\text{SiO}_4 + \text{Ca}_3\text{SiO}_3; \text{triangle } b-a-\text{Ca}_2\text{SiO}_4\)  
\(\left(C_2\text{S}-\text{C}_3\text{P}\right)_{ss} + \text{CaO} + \text{Ca}_3\text{SiO}_3; \text{triangle } c-\text{CaO}-\text{Ca}_3\text{SiO}_3\)  
\(\left(C_2\text{S}-\text{C}_3\text{P}\right)_{ss} + \text{CaO} + \text{Ca}_2\text{P}_2\text{Si}_2\text{O}_{16}; \text{triangle } d-\text{CaO}-e\)  
\(\left(C_2\text{S}-\text{C}_3\text{P}\right)_{ss} + \text{CaO} + \text{Ca}_3\text{P}_2\text{O}_8; \text{triangle } g-\text{CaO}-f\)  
\(\left(C_3\text{S}-\text{C}_3\text{P}\right)_{ss} + \text{CaO} + \text{Ca}_3\text{P}_2\text{SiO}_{12}; \text{triangle } h-\text{CaO}-i\)  
\(\text{CaO} + \text{Ca}_2\text{P}_2\text{O}_5 + \text{Ca}_3\text{P}_2\text{Si}_2\text{O}_{16}; \text{triangle } j\)  
\(\left(C_2\text{S}-\text{C}_3\text{P}\right)_{ss} + \text{Ca}_4\text{P}_2\text{O}_9 + \text{Ca}_2\text{P}_2\text{Si}_2\text{O}_{16}; \text{triangle } k\)  
\(\left(C_2\text{S}-\text{C}_3\text{P}\right)_{ss} + \text{Ca}_3\text{P}_2\text{O}_8 + \text{Ca}_4\text{P}_2\text{O}_9; \text{triangle } l\)  
\(\text{Ca}_3\text{P}_2\text{O}_8 + \text{Ca}_4\text{P}_2\text{O}_9 + \text{Ca}_2\text{P}_2\text{Si}_2\text{O}_{16}; \text{triangle } m\)  

It should be noticed here that the compounds of Ca$_2$SiO$_4$, Ca$_3$SiO$_3$, Ca$_2$P$_2$SiO$_{16}$, Ca$_3$P$_2$SiO$_{12}$ and Ca$_3$P$_2$O$_8$ included in these three-phase regions were non-stoichiometric. The compositions of points \(a, b, d, e, f, g, h, i, k, l, m\) and \(n\) could be read off by using the scales of the mole fractions of SiO$_2$ and P$_2$O$_5$ in Figure 1(a), while those of points \(c\) and \(j\) have not been determined precisely /1/. Table 1 summarizes the values for \(Y\) in \(\left(C_2\text{S}-\text{C}_3\text{P}\right)_{ss}\) at compositions \(b, h, l\) and \(m\). Based on

<table>
<thead>
<tr>
<th>Region</th>
<th>(Y) in (\left(C_2\text{S}-\text{C}<em>3\text{P}\right)</em>{ss})</th>
<th>(a_{\text{Ca}_2\text{SiO}_4})</th>
<th>(a_{\text{Ca}_3\text{P}_2\text{O}_8})</th>
<th>(\log a_{\text{CaO}})</th>
<th>(\log a_{\text{SiO}_2})</th>
<th>(\log a_{\text{P}_2\text{O}_5})</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\left(C_2\text{S}-\text{C}<em>3\text{P}\right)</em>{ss} + \text{Ca}_2\text{SiO}_4 + \text{Ca}_3\text{SiO}_3)</td>
<td>(0.088)</td>
<td>(0.995^{(a)})</td>
<td>0.016</td>
<td>-0.02</td>
<td>-4.75</td>
<td>-26.53</td>
<td>(\log a_{\text{P}_2\text{O}<em>5} = -26.53; \text{Eq. (28)}) (a</em>{\text{Ca}_2\text{SiO}_4} &lt; 1; \text{Eq. (20)})</td>
</tr>
<tr>
<td>(\left(C_2\text{S}-\text{C}<em>3\text{P}\right)</em>{ss} + \text{CaO} + \text{Ca}_2\text{P}_2\text{Si}<em>2\text{O}</em>{16})</td>
<td>(0.592)</td>
<td>0.445</td>
<td>0.745</td>
<td>0.00</td>
<td>-5.13</td>
<td>-24.93</td>
<td>(\log a_{\text{Ca}_3\text{P}_2\text{O}_8} &lt; 0.417; \text{Eq. (25)})</td>
</tr>
<tr>
<td>(\left(C_2\text{S}-\text{C}<em>3\text{P}\right)</em>{ss} + \text{Ca}_4\text{P}_2\text{O}_9 + \text{Ca}_3\text{P}_2\text{O}_8)</td>
<td>(0.748)</td>
<td>0.274</td>
<td>1.193</td>
<td>-0.46</td>
<td>-4.43</td>
<td>-23.35</td>
<td>(0.417 &lt; a_{\text{Ca}_3\text{P}_2\text{O}_8} &lt; 1; \text{Eq. (26)})</td>
</tr>
<tr>
<td>(\left(C_2\text{S}-\text{C}<em>3\text{P}\right)</em>{ss} + \text{Ca}_3\text{P}_2\text{O}_8 + \text{Ca}_4\text{P}_2\text{O}_9)</td>
<td>(0.841)</td>
<td>0.173</td>
<td>1.507</td>
<td>-0.56</td>
<td>-4.33</td>
<td>-22.95</td>
<td>(a_{\text{Ca}_3\text{P}_2\text{O}_8} &lt; 1; \text{Eq. (21)})</td>
</tr>
</tbody>
</table>

\(a\) The values with superscript "a" satisfied the necessary conditions.  
\(b\) The values with superscript "b" did not satisfy the necessary conditions.

Table 1: Calculation results of the ideal solution model with \(\Delta F^\circ(\text{Ca}_2\text{P}_2\text{O}_5) = 101 \text{kJ} \cdot \text{mol}^{-1}\).
the thermodynamic considerations of the phase relations, the conditions which the solution models should satisfy were mentioned below.

As seen in Figure 1(b), Ca₃P₂O₈ is soluble in α·C₃S; point a represents the solubility limit at 1573 K. Such a solubility requires that the Ca₅SiO₄ activity at point a is to be less than unity. According to the Condensed Phase Rule, when three phases coexist in a three-component system, there is only one degree of freedom. This implies that for a particular temperature, there are zero degrees of freedom; the Ca₅SiO₄ activity is independent of the bulk composition. Namely, the Ca₅SiO₄ activity within (C₃S·C₃P)ss at point a is equivalent to that at point a and hence to be less than unity.

\[ a_{\text{Ca₅SiO₄}} < 1 \] (at point b; \( Y = 0.088 \), \( T = 1573 \) K) (20)

In analogy with this, for the three-phase region of (C₃S·C₃P)ss + Ca₅P₂O₈ + Ca₃P₂O₈ (triangle b - a - Ca₃SiO₅), the solubility of Ca₃SiO₅ in α·C₃P requires that the Ca₃P₂O₈ activity within (C₃S·C₃P)ss at composition m is less than unity.

\[ a_{\text{Ca₃P₂O₈}} < 1 \] (at point m; \( Y = 0.841 \), \( T = 1573 \) K) (21)

The P₂O₅ activity within the three-phase assemblage of CaO + Ca₃P₂O₈ + Ca₅P₂O₈ (triangle CaO - Ca₃P₂O₈ - C₃S) can be calculated from equation (19) with the unit activities of CaO and Ca₃P₂O₈.

\[ \log a_{\text{P₂O₅}} = -\log K(17) = -25.18 \text{ at } 1573 \text{ K} \] (22)

Inserting equation (22) into equation (16), the activity of hypothetical solid Ca₅P₂O₈ in the three-phase region of CaO + Ca₃P₂O₈ + Ca₅P₂O₈ can be evaluated as

\[ \log a_{\text{Ca₅P₂O₈}} = \log K(14) - \log K(17) = -0.38 \text{ at } 1573 \text{ K} \] (23)

\[ a_{\text{Ca₅P₂O₈}} = 0.417 \text{ at } 1573 \text{ K} \] (24)

Along the Ca₃SiO₅ - Ca₅P₂O₈ edge in Figure 1(a), the Ca₅P₂O₈ activity should increase with an increase in the Ca₅P₂O₈ concentration. Therefore, the Ca₅P₂O₈ activity in the three-phase region of CaO + Ca₃P₂O₈ + Ca₅P₂O₈ is to be greater than that at point h and is to be smaller than that at point l. Thus, we obtain the following inequalities.

\[ a_{\text{Ca₅P₂O₈}} < 0.417 \] (at point h; \( Y = 0.592 \), \( T = 1573 \) K) (25)

\[ 0.417 < a_{\text{Ca₅P₂O₈}} < 1 \] (at point l; \( Y = 0.748 \), \( T = 1573 \) K) (26)

The P₂O₅ activity in (C₃S·C₃P)ss at composition b was determined by the present authors through a gas equilibrium method /9/. Molten copper containing phosphorus was brought to equilibrium with mixtures of (C₃S·C₃P)ss + Ca₅SiO₄ + Ca₅SiO₄ in a stream of Ar + H₂ + H₂O gas mixtures. The results were expressed as

\[ RT \ln a_{\text{P₂O₅}} = -1,106,000 + 194.7 \times (T/K) \] (J mol⁻¹) (27)

\[ \log a_{\text{P₂O₅}} = -26.53 \text{ at point } b, T = 1573 \text{ K} \] (28)

On the other hand, by using equations (12), (13) and (16) with the unit activity of Ca₅P₂O₈, \( a_{\text{P₂O₅}} \) in the three-phase region of (C₃S·C₃P)ss + Ca₅SiO₄ + Ca₅SiO₄ can be expressed as

\[ \log a_{\text{P₂O₅}} = 3 \log a_{\text{Ca₅SiO₄}} + \log a_{\text{Ca₅P₂O₈}} - 3 \log K(10) + 3 \log K(11) - \log K(14) + 24.74 \text{ at } 1573 \text{ K} \] (29)

Combining equations (28) and (29), we have

\[ 3 \log a_{\text{Ca₅SiO₄}} + \log a_{\text{Ca₅P₂O₈}} = -1.79 \text{ at point } b; \ Y = 0.088, \ T = 1573 \text{ K} \] (30)

Equation (30) should hold when the values for \( a_{\text{Ca₅SiO₄}} \) and \( a_{\text{Ca₅P₂O₈}} \) at composition b evaluated with the solution models are inserted.

### 3 Calculation results

When the ideal solution model was applied to solid solutions (C₃S·C₃P)ss, combining equations (4), (5), (8) and (9) gave the following formulae for the activities of Ca₂SiO₄ and Ca₃P₂O₈ at 1573 K.

\[ \log a_{\text{Ca₂SiO₄}} = 3.76 \times 10^{-2} + \log(1 - Y) \] (31)

\[ \log a_{\text{Ca₃P₂O₈}} = 2 \log a_{\text{Ca₂SiO₄}} = 3.24 \times 10^{-6} + \Delta H°,_{Ca₃P₂O₈} + 2 \log Y \] (32)

The ideal solution model used in this study had one undetermined parameter, viz., \( \Delta H°,_{Ca₃P₂O₈} \). Inserting equations (31) and (32) into equation (30), the value for \( \Delta H°,_{Ca₃P₂O₈} \) could be determined as

\[ \Delta H°,_{Ca₃P₂O₈}/[\text{J mol}^{-1}] = 1.01 \times 10^5 \] (33)

Thus, the activities of Ca₃P₂O₈ at 1573 K could be expressed as
\[ \log a_{\text{Ca}_3\text{P}_2\text{O}_8} = 2 \log a_{\text{(1/2)Ca}_3\text{P}_2\text{O}_8} - 3.28 \times 10^{-1} + 2 \log Y \]  
(34)

Rewriting equations (31) and (34), we had

\[ a_{\text{Ca}_3\text{SiO}_4} = 1.09 \times (1 - Y) \]  
(35)

\[ a_{\text{(1/2)Ca}_3\text{P}_2\text{O}_8} = 1.46 \times Y \]  
(36)

\[ a_{\text{Ca}_3\text{P}_2\text{O}_8} = (a_{\text{(1/2)Ca}_3\text{P}_2\text{O}_8})^2 = (1.46 \times Y)^2 \]  
(37)

The numbers of 1.09 in equation (35) and 1.46 in equation (36), respectively, indicated the activities of \( \alpha\text{-Ca}_3\text{SiO}_4 \) with reference to \( \alpha\text{-Ca}_3\text{SiO}_4 \) as the standard state and that of \( (1/2)\text{Ca}_3\text{P}_2\text{O}_8 \) with reference to \( (1/2)\text{Ca}_3\text{P}_2\text{O}_8 \) as the standard state at 1573 K. Dotted lines in Figure 3(b) shows \( a_{\text{Ca}_3\text{SiO}_4} \) and \( a_{\text{(1/2)Ca}_3\text{P}_2\text{O}_8} \) at 1573 K based on equations (35) and (36). As seen in this figure, \( a_{\text{Ca}_3\text{SiO}_4} \) and \( a_{\text{(1/2)Ca}_3\text{P}_2\text{O}_8} \) within \( (C_3S-C_3P)_{SS} \) were proportional to \( (1 - Y) \) and \( Y \), respectively. Figure 3(a) is the redrawn pseudo-binary phase diagram of \( \text{Ca}_3\text{SiO}_4-\text{Ca}_3\text{P}_2\text{O}_8 \), in which compositions are shown by the values for \( Y \). According to the Condensed Phase Rule, the activities were constant within the two-phase regions of \( a-b, \; d-e, \; f-g, \; h-i, \; k-l \) and \( m-n \). The values for \( a_{\text{Ca}_3\text{P}_2\text{O}_8} \) were obtainable from equation (37) and could be read off by using the subsidiary scale added to Figure 3(b). Table 1 summarizes \( a_{\text{Ca}_3\text{SiO}_4} \) and \( a_{\text{Ca}_3\text{P}_2\text{O}_8} \) at compositions \( b, \; h, \; l \) and \( m \). As seen in Table 1, the values for \( a_{\text{Ca}_3\text{P}_2\text{O}_8} \) at points \( h, \; l \) and \( m \) did not satisfy inequalities (25), (26) and (21), respectively. These results led to the conclusion that the ideal solution model could not give the relative partial molar Gibbs free energies of the components within \( (C_3S-C_3P)_{SS} \).

On the other hand, the regular solution model gave the following equations by combining equations (6), (7), (8) and (9).

\[ \log a_{\text{Ca}_3\text{SiO}_4} = 3.76 \times 10^{-1} + \log(1 - Y) + 3.32 \times 10^{-3} \times \Omega Y^2 \]  
(38)

\[ \log a_{\text{Ca}_3\text{P}_2\text{O}_8} = 2 \log a_{\text{(1/2)Ca}_3\text{P}_2\text{O}_8} = 3.24 \times 10^{-6} \times \Delta H^0(\text{Ca}_3\text{P}_2\text{O}_8) + 2 \log Y + 6.64 \times 10^{-3} \times \Omega(1 - Y)^2 \]  
(39)

These formulae included undetermined parameters, \( \Omega \), \( \Delta H^0(\text{Ca}_3\text{P}_2\text{O}_8) \) and \( \Omega \). Inserting equations (38) and (39) into equation (30), the relation between \( \Delta H^0(\text{Ca}_3\text{P}_2\text{O}_8) \) and \( \Omega \) was obtained as

\[ \Omega = 5.86 \times 10^{-1} - 5.79 \times 10^{-2} \times \Delta H^0(\text{Ca}_3\text{P}_2\text{O}_8) \]  
(40)

Substituting equation (40) into equations (38) and (39), the activities of \( \text{Ca}_3\text{SiO}_4 \) and \( \text{Ca}_3\text{P}_2\text{O}_8 \) could be expressed as functions of \( \Delta H^0(\text{Ca}_3\text{P}_2\text{O}_8) \) and \( Y \).

\[ \log a_{\text{Ca}_3\text{SiO}_4} = 3.76 \times 10^{-1} + \log(1 - Y) + [1.95 \times 10^{-1} - 1.92 \times 10^{-6} \times \Delta H^0(\text{Ca}_3\text{P}_2\text{O}_8)] \times Y \]  
(41)

\[ \log a_{\text{Ca}_3\text{P}_2\text{O}_8} = 2 \log a_{\text{(1/2)Ca}_3\text{P}_2\text{O}_8} = 3.24 \times 10^{-6} \times \Delta H^0(\text{Ca}_3\text{P}_2\text{O}_8) + 2 \log Y + [3.90 \times 10^{-1} - 3.84 \times 10^{-6} \times \Delta H^0(\text{Ca}_3\text{P}_2\text{O}_8)] \times (1 - Y)^2 \]  
(42)

Under the conditions that the values calculated from equations (41) and (42) satisfied inequalities (20), (21), (25) and (26), \( \Delta H^0(\text{Ca}_3\text{P}_2\text{O}_8) \) was determined as

\[ \Delta H^0(\text{Ca}_3\text{P}_2\text{O}_8)/\text{mol}^{-1} = (2.10 \pm 2.10) \times 10^{3} \]  
(43)

Inserting equation (43) to equation (40), we had

\[ \Omega/\text{mol}^{-1} = (5.74 \pm 0.12) \times 10^{4} \]  
(44)

Combining equations (38), (39), (43) and (44), the activities of \( \text{Ca}_3\text{SiO}_4 \) and \( \text{Ca}_3\text{P}_2\text{O}_8 \) at 1573 K were expressed as

---

![Fig. 3: (a) Phase diagram of the pseudo-binary system Ca$_3$SiO$_4$-Ca$_3$P$_2$O$_8$. (b) Activities of Ca$_3$SiO$_4$ and Ca$_3$P$_2$O$_8$ as functions of the substitution ratio Y.](image-url)
Table 2: Calculation results of the regular solution model with $\Delta H^o(Ca_7P_2Si_2O_{16}) = 2.10 \pm 2.10 \text{k}_\text{j} \cdot \text{mol}^{-1}$ and $\Omega = 5.74 \pm 0.12 \text{k}_\text{j} \cdot \text{mol}^{-1}$.

\[
\log a_{Ca_2SiO_4} = 3.76 \times 10^{-2} + \log(1 - Y) + 1.91 \times 10^{-1} \times Y^2
\]

\[
\log a_{Ca_3P_2O_8} = 2 \log a_{Ca_2SiO_4}^{1/2} \log a_{Ca_3P_2O_8} = 6.80 \times 10^{-3} + 2 \log Y + 3.81 \times 10^{-1} \times (1 - Y)^2
\]

Table 2 gives the present values for $a_{Ca_2SiO_4}$ and $a_{Ca_3P_2O_8}$ calculated from equations (45) and (46). The uncertainties of the activities in Table 2 were based on the inaccuracies of $\Delta H^o(Ca_7P_2Si_2O_{16})$ and $\Omega$ given in equations (43) and (44). As seen in this table, inequalities (20), (25), (26) and (21) held with the present results at compositions $b$, $h$, $l$ and $m$, respectively. Solid curves in Figure 3(b) represent the activity-composition curves evaluated from equations (45) and (46). These curves were slightly convex upward owing to the positive value for the interaction parameter $\Omega$. As already mentioned above, the activities were constant in the two-phase regions. For example, the $Ca_3P_2O_8$ activity at point $h$ was equal to that at point $i$. The hatched areas in Figure 3 denote the composition ranges of non-stoichiometric compounds of $\alpha'$-$Ca_5SiO_3$, $Ca_3P_2Si_5O_{18}$, $Ca_4P_2SiO_7$ and $Ca_3P_2O_8$, in which activity-composition curves could not be obtained in this study.

4 Discussion

Figure 4(a) shows the iso-thermal section of the ternary system $CaO-SiO_2-P_2O_5$ near the $CaO$ apex at 1573 K; this figure is identical to Figure 1(a). By using the present results of the regular solution model, the activities of $CaO$, $SiO_2$ and $P_2O_5$ could be calculated within the following regions.

\[
\begin{align*}
&\langle C_5-C_2P \rangle ss + Ca_5SiO_3 + Ca_3SiO_4; \text{triangle } b-a-Ca_5SiO_3 \\
&\langle C_2-C_2P \rangle ss + Ca_3SiO_4; \text{triangle } b-c-Ca_3SiO_4 \\
&\langle C_2-C_2P \rangle ss + CaO + Ca_3SiO_4; \text{triangle } c-CaO-Ca_3SiO_4 \\
&\langle C_2-C_2P \rangle ss + Ca_2SiO_4; \text{triangle } d-CaO-e \\
&\langle C_2-C_2P \rangle ss + CaO + Ca_3P_2SiO_{16}; \text{triangle } d-CaO-f \\
&\langle C_2-C_2P \rangle ss + CaO + Ca_3P_2SiO_{16}; \text{triangle } g-CaO-f \\
&\langle C_2-C_2P \rangle ss + CaO; \text{region } g-h-CaO \\
&\langle C_2-C_2P \rangle ss + CaO; \text{region } g-h-CaO \\
&\langle C_2-C_2P \rangle ss + CaO + Ca_3P_2O_{12}; \text{triangle } h-CaO-i \\
&\langle C_2-C_2P \rangle ss + Ca_3P_2O_{12} + Ca_3P_2SiO_{12}; \text{triangle } l-Ca_3P_2O_{12} + Ca_3P_2SiO_{12}
\end{align*}
\]
The activities of \( \text{CaO} \) at \( 1573 \text{ K} \) should be unity. Therefore, equation (12) could be rewritten as

\[
\log a_{\text{CaO}} = -0.06 - \log (1 - Y) - 1.91 \times 10^4 \times Y^2 \quad (51)
\]

\[
\log a_{\text{SiO}_2} = -4.63 + 3 \log (1 - Y) + 5.73 \times 10^{-1} \times Y^2 + 3.81 \times 10^{-1} \times (1 - Y)^2 \quad (52)
\]

\[
\log a_{P_2O_5} = -24.62 + 3 \log (1 - Y) + 2 \log Y + 5.73 \times 10^{-1} \times Y^2 + 3.81 \times 10^{-1} \times (1 - Y)^2 \quad (53)
\]

The activities in the three-phase region of \((C_S-C_P)_{ss} + \text{Ca}_3\text{SiO}_5 + \text{Ca}_5\text{P}_2\text{O}_{12}\) (triangle \(b-a-Ca_3\text{SiO}_5\)) could be calculated by inserting \( Y = 0.088 \) at point \(b\) into equations (51), (52) and (53).

\[
\log a_{\text{CaO}} = -0.02 \quad \text{at point b; } Y = 0.088, \ T = 1573 \text{ K} \quad (54)
\]

\[
\log a_{\text{SiO}_2} = -4.74 \quad \text{at point b; } Y = 0.088, \ T = 1573 \text{ K} \quad (55)
\]

\[
\log a_{P_2O_5} = -26.53 \quad \text{at point b; } Y = 0.088, \ T = 1573 \text{ K} \quad (56)
\]

On the other hand, the composition of \((C_S-C_P)_{ss} + \text{Ca}_3\text{SiO}_5 + \text{Ca}_5\text{P}_2\text{O}_{12}\) in equilibrium with \(\text{Ca}_3\text{SiO}_5\) and \(\text{CaO}\), i.e., point \(c\), has not been reported. By solving equation (51) under the condition that \( \log a_{\text{CaO}} = 0 \), this composition could be estimated as

\[
Y = 0.131 \quad \text{at point c; } T = 1573 \text{ K} \quad (57)
\]

Inserting equation (57) to equations (52) and (53), the \(\text{SiO}_2\) and \(P_2O_5\) activities in the three-phase assemblage of \((C_S-C_P)_{ss} + \text{Ca}_3\text{SiO}_5 + \text{Ca}_5\text{P}_2\text{O}_{12}\) (triangle \(c-CaO-Ca_5\text{SiO}_5\)) were obtained as

\[
\log a_{\text{SiO}_2} = -4.80 \quad \text{at point c; } Y = 0.131, \ T = 1573 \text{ K} \quad (58)
\]

\[
\log a_{P_2O_5} = -26.27 \quad \text{at point c; } Y = 0.131, \ T = 1573 \text{ K} \quad (59)
\]

The \(\text{CaO}\) activity in the regions including \(\text{CaO}\) should be unity. Thus, equations (12) and (16), respectively, could be rewritten as

\[
\log a_{\text{CaO}} = \log a_{\text{Ca}_5\text{SiO}_5} - \log K(10) \quad (60)
\]

\[
\log a_{P_2O_5} = \log a_{\text{Ca}_3\text{P}_2\text{O}_8} - \log K(14) \quad (61)
\]

Combining equations (45), (46), (60) and (61), the \(\text{SiO}_2\) and \(P_2O_5\) activities within the two-phase region of \((C_S-C_P)_{ss} + \text{Ca}_3\text{SiO}_5\) (regions \(c-d-CaO\) and \(g-h-CaO\)) were given as

\[
\log a_{\text{SiO}_2} = -4.74 + \log (1 - Y) + 1.91 \times 10^{-1} \times Y^2 \quad (62)
\]

\[
\log a_{P_2O_5} = -24.79 + 2 \log Y + 3.81 \times 10^{-1} \times (1 - Y)^2 \quad (63)
\]

The values for \(a_{\text{SiO}_2}\) and \(a_{P_2O_5}\) in the three-phase regions of \((C_S-C_P)_{ss} + \text{Ca}_5\text{P}_2\text{Si}_2\text{O}_{12}\) (triangles \(d-CaO-e\) and \(g-CaO-f\)) and \((C_S-C_P)_{ss} + \text{Ca}_3\text{SiO}_5 + \text{Ca}_5\text{P}_2\text{Si}_2\text{O}_{12}\) (triangle \(h-CaO-i\)) could be calculated from equations (62) and (63).
Based on the unit Ca₃P₂O₈ activity in the regions including Ca₃P₂O₈, equation (19) was rewritten as

\[ \log K(17) = -4 \log a_{\text{CaO}} - \log a_{\text{P}_2\text{O}_5} \]  

(64)

Solving simultaneous equations (12), (16) and (64), we had

\[ \log a_{\text{CaO}} = -0.39 - 2 \log Y - 3.81 \times 10^{-1} \times (1 - Y)^2 \]  

(68)

\[ \log a_{\text{P}_2\text{O}_5} = -3.97 + 4 \log Y + 1.91 \times 10^{-1} \times Y^2 + 762 \times 10^{-1} \times (1 - Y)^2 \]  

(69)

\[ \log a_{\text{P}_2\text{O}_5} = -23.63 + 8 \log Y + 1.52 \times (1 - Y)^2 \]  

(70)

The values for the activities in the three-phase regions of \((C₂S-C₃P)\text{ss} + \text{Ca}_{3}\text{P}_{2}\text{O}_{8} + \text{Ca}_{5}\text{P}_{2}\text{SiO}_{12}\) (triangle \(l\)-\text{Ca}_{3}\text{P}_{2}\text{O}_{8}-k) and \((C₂S-C₃P)\text{ss} + \text{Ca}_{3}\text{P}_{2}\text{O}_{8} + \text{Ca}_{5}\text{P}_{2}\text{SiO}_{12}\) (triangle \(m\)-\text{Ca}_{5}\text{P}_{2}\text{O}_{8}-n) could be calculated from equations (68), (69) and (70).

The \text{CaO}, \text{SiO}_2, and \text{P}_2\text{O}_5 activities estimated in this study are summarized in Table 2, and illustrated in Figures 4(b) and 4(c). The uncertainties of the values in Table 2 were due to the inaccuracies of \(\Delta H^\circ (\text{Ca}_{3}\text{P}_{2}\text{O}_{8} - k, \Omega)\) and \(\Omega\) determined in this study. Figure 4(b) shows that the \text{CaO} activities are unity between point \(c\) and point \(j\); in this composition range, the two- and three-phase regions include solid \text{CaO} as seen in Figure 4(a). Figure 4(c) illustrates that the \text{P}_2\text{O}_5 activities increase monotonically with an increase in the values for \(Y\) in \((C₂S-C₃P)\text{ss} + \text{Ca}_{5}\text{P}_{2}\text{SiO}_{12}\). It would be worth mentioning here that the \text{P}_2\text{O}_5 activity in the two-phase assemblage of stoichiometric \text{Ca}_{5}\text{P}_{2}\text{O}_{8} + \text{Ca}_{3}\text{P}_{2}\text{O}_{8} at 1573 K can be calculated as

\[ \log a_{\text{P}_2\text{O}_5} = -4 \log K(14) + 3 \log K(17) = -23.66 \text{ at } 1573 \text{ K} \]  

(71)

This value corresponds to the logarithmic activity of \text{P}_2\text{O}_5 at \(Y=1.0\) in Figure 4(c), and would not be incompatible with the activity-composition curves determined in this study. On the other hand, the \text{SiO}_2 activities do not decrease monotonically with an increase in \(Y\). Magnitude correlations of activities strongly depend on phase relations. Therefore, the behaviour of the \text{SiO}_2 and \text{P}_2\text{O}_5 activities will be able to be explained by future work on the \text{SiO}_2-rich and/or \text{P}_2\text{O}_5-rich areas of the \text{CaO}-\text{SiO}_2-\text{P}_2\text{O}_5 ternary iso-thermal section. The present values for \(a_{\text{P}_2\text{O}_5}\) and \(a_{\text{SiO}_2}\) can be recommended at least as tentative estimates for understanding dephosphorization process.

The reaction of phosphorus removal from molten iron can be represented as

\[ 2 [P]_{\text{lg}} + 5 (\text{FeO})_{\text{slag}} = (\text{P}_2\text{O}_5)_{\text{slag}} + 5 \{\text{Fe}\} \]  

(72)

where \([P]_{\text{lg}}\) is phosphorus in liquid iron, \((\text{FeO})_{\text{slag}}\) and \((\text{P}_2\text{O}_5)_{\text{slag}}\) are \text{FeO} and \text{P}_2\text{O}_5 in liquid slag, and \{\text{Fe}\} is liquid iron. For reaction (72), Turkdogan and Pearson derived the following expression /10/.

\[ \log K(72) = \log \{a_{\text{P}_2\text{O}_5}/h_p^c a_{\text{FeO}}\} = -17.7 + 8.490(T/K) \]  

(73)

By rewriting equation (73), we have

\[ \log h_p = -(1/2) \log K(72) + (1/2) \log a_{\text{P}_2\text{O}_5} - (5/2) \log a_{\text{FeO}} \]  

(74)

For carbon-saturated \{Fe-C-P\} liquid alloys, the Henrian activity of phosphorus is given by

\[ \log h_p = \log [%P] + e^c [%C] \]  

(75)

By combining equations (74) and (75), we have

\[ \log [%P] = -e^c [%C] - (1/2) \log K(72) + (1/2) \log a_{\text{P}_2\text{O}_5} 
- (5/2) \log a_{\text{FeO}} 
= -e^c [%C] + (1/2) \log a_{\text{P}_2\text{O}_5} 
- (5/2) \log a_{\text{FeO}} + 8.9 - 4.250(T/K) \]  

(76)

Equation (76) means that the equilibrium phosphorus concentrations can be estimated by using the values for the activities of \text{P}_2\text{O}_5 and \text{FeO}. Figure 5 shows a schematic illustration of the iso-thermal tetrahedron of the pseudo-quaternary system \text{CaO-Ca}_{2}\text{SiO}_3-\text{Ca}_{5}\text{P}_{2}\text{O}_{8}-\text{FeO} at 1573 K, showing the following four-phase assemblages /11/.

\[
\begin{align*}
\text{Ca}_2\text{SiO}_3 + \text{Ca}_3\text{SiO}_4 + (C₂S-C₃P)\text{ss} + \text{Liquid} & : \text{tetrahedron} \\
\text{Ca}_4\text{SiO}_5-d-b-L(1) \\
\text{CaO} + \text{Ca}_2\text{SiO}_3 + (C₂S-C₃P)\text{ss} + \text{Liquid} & : \text{tetrahedron} \\
\text{CaO-Ca}_4\text{SiO}_5-c-L(2) \\
\text{CaO} + \text{Ca}_4\text{P}_2\text{O}_9 + \text{Ca}_5\text{P}_2\text{SiO}_{12} + \text{Liquid} & : \text{tetrahedron} \\
\text{CaO-Ca}_5\text{P}_2\text{O}_{8}-j-L(3)
\end{align*}
\]

According to the Condensed Phase Rule, when four phases coexist in a four-component system, there is only one
degree of freedom. This implies that for a particular temperature, the activities of FeO and P$_2$O$_5$ are fixed and therefore independent of the bulk slag composition. The P$_2$O$_5$ activities in the four-phase assemblages of Ca$_3$SiO$_5$ + Ca$_2$SiO$_4$ + (C$_2$S-C$_3$P)$_{ss}$ + Liquid, CaO + Ca$_3$SiO$_5$ + (C$_2$S-C$_3$P)$_{ss}$ + Liquid and CaO + Ca$_4$P$_2$O$_9$ + Ca$_5$P$_2$SiO$_{12}$ + Liquid are given by equations (27), (59) and (22), respectively. On the other hand, the FeO activities have been reported as follows /11/.

$$\log a_{FeO} = -0.77 + 720/(T/K)$$ Ca$_3$SiO$_5$ + Ca$_2$SiO$_4$ + (C$_2$S-C$_3$P)$_{ss}$ + Liquid \hspace{1cm} (77)

$$\log a_{FeO} = -1.57 + 1,960/(T/K)$$ CaO + Ca$_3$SiO$_5$ + (C$_2$S-C$_3$P)$_{ss}$ + Liquid \hspace{1cm} (78)

$$\log a_{FeO} = 0.90 - 1,810/(T/K)$$ CaO + Ca$_4$P$_2$O$_9$ + Ca$_5$P$_2$SiO$_{12}$ + Liquid \hspace{1cm} (79)

Figure 6 shows the estimated phosphorus contents in molten iron attainable with the four-phase assemblages under consideration. This figure also gives the final phosphorus levels achieved with the industrial slags, given in Table 3 /12/. It is evident from this graph that the phosphorus concentrations attainable by using the heterogeneous slags are four to five orders of magnitude lower than those obtained with the industrial slags. As a consequence of this behavior, the opportunity is available to considerably reduce required slag volume. Recently, phosphorus removal from hot metal in Japanese steelmaking industries has been operated with relatively lower basic slags to aim at reducing consumption of fluorspar, CaF$_2$, which causes emission of hazardous fluoride species. The present results of solid solutions between Ca$_3$SiO$_5$ and Ca$_4$P$_2$O$_9$ would also be applicable to estimate thermodynamic properties of such dephosphorization slags.

### Table 3: Industrial slags of hot metal processing and corresponding hot metal temperature and phosphorus level.

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>Slag composition (mole %)</th>
<th>Hot metal</th>
</tr>
</thead>
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<tr>
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<td>CaO</td>
<td>SiO$_2$</td>
</tr>
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<td>32.2</td>
</tr>
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<td>58.3</td>
<td>11.1</td>
</tr>
<tr>
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<td>60.0</td>
<td>11.6</td>
</tr>
</tbody>
</table>

*"Others" means CaS + MgO + MnO + Al$_2$O$_3"
5 Conclusions

Solution models have been applied to solid solutions between Ca$_2$SiO$_4$ and Ca$_3$P$_2$O$_8$ to aim at deriving their thermodynamic properties at 1573 K. The parameters included in the regular solution model were determined under the conditions that the activities of Ca$_2$SiO$_4$ and Ca$_3$P$_2$O$_8$ were consistent with the literature data and the phase diagrams. The present results suggested the estimations of the activities of the components in the CaO-SiO$_2$-P$_2$O$_5$ ternary system at high CaO contents and the composition of the Ca$_2$SiO$_4$-Ca$_3$P$_2$O$_8$ solid solution in equilibrium with CaO and Ca$_2$SiO$_4$ at 1573 K.

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References