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# Applicability of law of mass action to distribution of manganese between slag melts and liquid iron<sup>①</sup>

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**[Abstract]** According to the law of mass action and the coexistence theory of slag structure, the distribution of manganese between MnO-FeO-SiO<sub>2</sub> and MgO-MnO-FeO-SiO<sub>2</sub> slag melts as well as liquid iron was analyzed. It is shown that  $K'_{Mn}$  and  $K_{MnO}$  are only dependent on temperature and don't change with basicities and compositions of slag melts. So the distribution of manganese between the above mentioned slag melts and molten iron obeys the law of mass action. But analysis of experimental results from other sources shows that  $K'_{Mn}$  and  $K_{MnO}$  really change with basicities of slag, which is probably arisen from not approaching equilibrium under low basicity slag melts.

**[Key words]** manganese distribution; the law of mass action; the coexistence theory of slag structure; mass action concentration

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## 1 INTRODUCTION

Manganese is a widely used alloy element and reducing agent, its distribution between slag melts and liquid steel may serve as indicator of steel bath temperature. Hence, manganese distribution between slag melts and liquid iron provoked great interest on the part of metallurgists to study it.

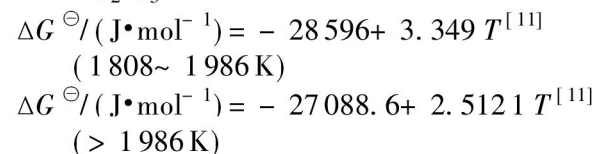
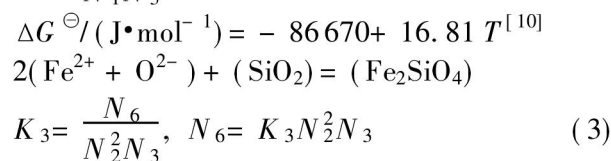
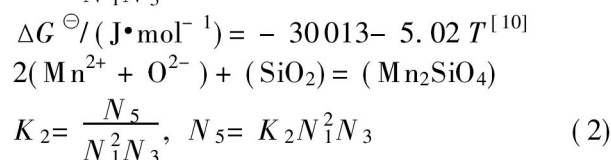
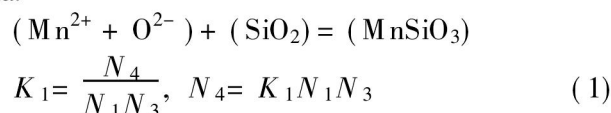
The theoretical results of manganese distribution study between simple slag melts (MnO+ FeO) and molten iron are shown in Table 1. It is seen that there is a certain difference of the calculated values of  $K'_{Mn}$  or  $K_{MnO}$  from various scholars, in spite of the different experimental conditions. But in a word, both  $K'_{Mn}$  and  $K_{Mn}$  change only with temperature (don't change with composition of slag melts and iron) and remain constant as temperature is fixed, hence both obey the law of mass action. However, whether these relationships are applicable to manganese distribution between multicomponent slag melts and liquid iron is still a question to be answered. In order to clarify this problem, using experimental equilibrium data, the manganese distribution between MnO-FeO-SiO<sub>2</sub> and MgO-MnO-FeO-SiO<sub>2</sub> slag melts and liquid iron has been analyzed by the law of mass action in combination with the coexistence theory of slag structure.

## 2 MANGANESE DISTRIBUTION BETWEEN MnO-FeO-SiO<sub>2</sub> SLAG MELTS AND LIQUID IRON

According to the phase diagrams of binary slag

systems FeO-SiO<sub>2</sub> and MnO-SiO<sub>2</sub><sup>[8]</sup>, there are MnSiO<sub>3</sub>, Mn<sub>2</sub>SiO<sub>4</sub> and Fe<sub>2</sub>SiO<sub>4</sub> formed in these melts, so on the basis of the coexistence theory of slag structure<sup>[9]</sup>, their structural units are Mn<sup>2+</sup>, Fe<sup>2+</sup>, O<sup>2-</sup>, MnSiO<sub>3</sub>, Mn<sub>2</sub>SiO<sub>4</sub> and Fe<sub>2</sub>SiO<sub>4</sub>.

Assuming the compositions of reactants as  $b_1 = \Sigma n_{MnO}$ ,  $b_2 = \Sigma n_{FeO}$ ,  $a = \Sigma n_{SiO_2}$ ; the mass action concentration of every structural unit after normalization as  $N_1 = N_{MnO}$ ,  $N_2 = N_{FeO}$ ,  $N_3 = N_{SiO_2}$ ,  $N_4 = N_{MnSiO_3}$ ,  $N_5 = N_{Mn_2SiO_4}$ ,  $N_6 = N_{Fe_2SiO_4}$ ,  $\Sigma n =$  sum of moles of ions and molecules in equilibrium. In the light of the law of mass action, it gives chemical equilibria:



mass balance:

$$N_1 + N_2 + N_3 + K_1 N_1 N_3 + K_2 N_1^2 N_3 + K_3 N_2^2 N_3 - 1 = 0 \quad (4)$$

**Table 1** Theoretical results of manganese distribution between simple slag melts and molten iron

$\lg K'_{Mn}$ or $\lg K_{MnO}$	$\Delta G^\ominus / (\text{J} \cdot \text{mol}^{-1})$	Crucible	Temperature range/ K	Source
$\lg K'_{Mn} = 6440/T - 2.95$ $\lg K_{MnO} = 12760/T - 5.684$	$\Delta G^\ominus = -123385 + 53.884 T$ $\Delta G^\ominus = -244413 + 108.87 T$	MgO	1841~2016	[1]
$\lg K'_{Mn} = 7572/T - 3.599$ $\lg K_{MnO} = 12670/T - 5.617$	$\Delta G^\ominus = -145038.7 + 68.94 T$ $\Delta G^\ominus = -242689 + 107.59 T$	MnO & CaO	1793~2093	[2~5]
$\lg \frac{x_{MnO}}{x_{FeO} w_{Mn}} = 6086/T - 2.76$	$\Delta G^\ominus = -116575 + 52.87 T$	Levitation	1923~2143	[6]
$\lg \frac{x_{MnO}}{x_{FeO} w_{Mn}} = 7452/T - 3.478$	$\Delta G^\ominus = -142740 + 66.62 T$	Using data of [1]	1841~2016	[7]
$\lg \frac{x_{MnO}}{w_{Mn} [a_0]} = 13182/T - 5.875$	$\Delta G^\ominus = -252380 + 112.48 T$			

$$b_1 = \sum n(0.5N_1 + K_1N_1N_3 + 2K_2N_1^2N_3) \quad (5)$$

$$b_2 = \sum n(0.5N_2 + 2K_3N_2^2N_3) \quad (6)$$

$$a = \sum n(N_3 + K_1N_1N_3 + K_2N_1^2N_3 + K_3N_2^2N_3) \quad (7)$$

From Eqs. (5) and (7) as well as Eqs. (6) and (7), Eqs. (8) and (9) are obtained respectively as follows:

$$0.5aN_1 - (b_1 + K_3N_2^2)N_3 + (a - b_1)K_1N_1N_3 + (2a - b_1)K_2N_1^2N_3 = 0 \quad (8)$$

$$0.5aN_2 - b_2(N_3 + b_2K_1N_1 + K_2N_1^2)N_3 + (2a - b_2)K_3N_2^2N_3 = 0 \quad (9)$$

Eqs. (4), (8) and (9) are the calculating model of mass action concentrations for these slag melts. The chemical equilibrium of manganese distribution is  $[Mn] + (Fe^{2+} + O^{2-}) = [Fe] + (Mn^{2+} + O^{2-})$

$$K_{Mn} = \frac{N_{MnO} w_{Fe}}{N_{FeO} w_{Mn}}, \quad K'_{Mn} = \frac{N_{MnO}}{N_{FeO} w_{Mn}} \quad (10)$$

$$[Mn] + [O] = (MnO) \quad K_{MnO} = \frac{N_{MnO}}{w_{Mn} w_O} \quad (11)$$

The manganese distribution coefficient between slag melts and liquid iron is

$$L_{Mn} = \frac{w_{MnO}}{w_{Mn}} = \frac{70.9375 \sum n(0.5N_{MnO} + N_{MnSiO_3} + 2N_{Mn_2SiO_4})}{w_{Mn}} \quad (12)$$

The manganese content of liquid iron becomes

$$w_{Mn} = \frac{N_{MnO}}{N_{FeO} K'_{Mn}} \quad (13)$$

The oxygen content of liquid iron is given by

$$w_O = \frac{N_{MnO}}{w_{Mn} K_{MnO}} \quad (14)$$

Eqs. (10) ~ (14) are the main relationships of manganese distribution between slag melts and liquid

iron. Using equilibrium data of manganese distribution between MnO-FeO-SiO<sub>2</sub> slag melts and liquid iron at 1803~1973 K from Ref. [4], the calculated relations of  $K'_{Mn}$  and  $K_{MnO}$  with temperature are shown in Fig. 1. It is seen from the figure that the temperature dependence of  $K'_{Mn}$  and  $K_{MnO}$  is very evident, in spite of some scatter of data due to ignorance of Fe<sub>2</sub>O<sub>3</sub> analysis in the original experimental results. The relations of  $K'_{Mn}$  and  $K_{MnO}$  with temperature are respectively

$$\lg K'_{Mn} = \frac{5612.1}{T} - 2.557 \quad (r = 0.8895, F = 462.26) \quad (15)$$

$$\Delta G^\ominus / (\text{J} \cdot \text{mol}^{-1}) = -107497.43 + 48.978 T$$

$$\lg K_{MnO} = \frac{11359.8}{T} - 4.955 \quad (r = 0.9456, F = 1029.82) \quad (16)$$

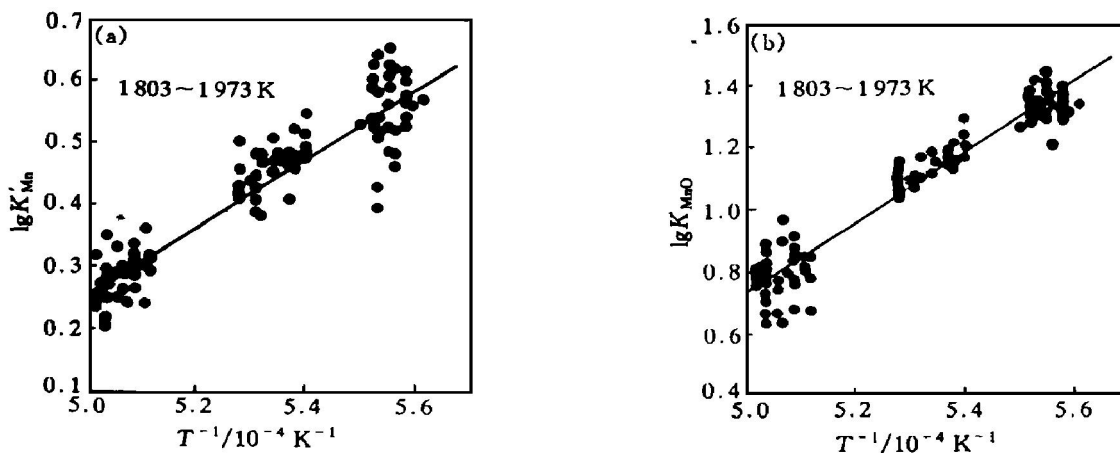
$$\Delta G^\ominus / (\text{J} \cdot \text{mol}^{-1}) = -217593.3 + 94.9 T$$

Table 2 shows the comparison of calculated  $K'_{Mn}$  and  $K_{MnO}$  by equations from literature as well as by manganese partition between MnO-FeO-SiO<sub>2</sub> slag melts and liquid iron at different temperatures. As shown in the table, though the calculated  $K'_{Mn}$  and  $K_{MnO}$  in the present paper are not completely identical with those calculated from literature equations, the difference between them is not considerable indeed.

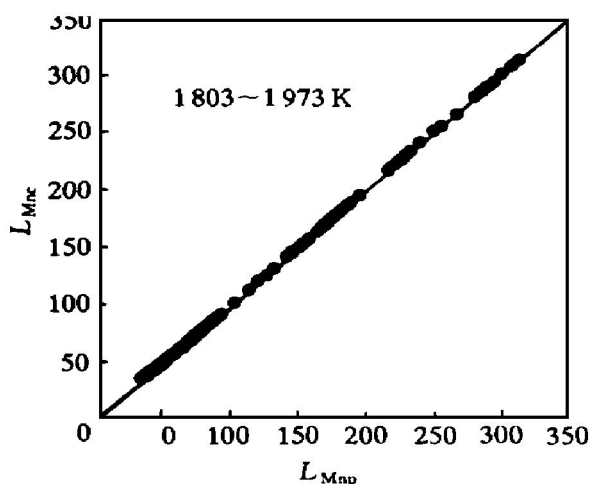
Hence, the manganese distribution between MnO-FeO-SiO<sub>2</sub> slag melts and liquid iron obeys the law of mass action. The comparison of calculated and measured coefficients of manganese distribution  $L_{Mn}$  is shown in Fig. 2. It ought to be pointed out that the agreement between them is excellent. Fig. 3 shows the comparison of calculated and observed values of manganese  $w_{Mn}$  and oxygen  $w_O$  in liquid iron. It is also seen that the agreement between them is satisfactory. In a word, according to the law of mass action in combination with the coexistence theory of slag structure, it is practical to formulate the model of manganese distribution between slag melts and liquid iron which can reflect the characteristics of melts structure.

**Table 2** Comparison of  $K'_{Mn}$  and  $K_{MnO}$  calculated by equations from literature as well as by equations from present paper at different temperatures

Source of equation	$K'_{Mn}$			$K_{MnO}$		
	1773 K	1873 K	1973 K	1773 K	1873 K	1973 K
[1]	4.8113	3.0785	2.0609	32.5718	13.4462	6.0717
[2] ~ [5]	4.6960	2.7779	1.7330	32.5718	13.4462	6.0717
[6]	4.7054	3.0856	2.1118			
[7]	5.3094	3.1670	1.9906	36.2958	14.5515	6.4002
Present paper	4.0580	2.7499	1.9384	28.3208	12.8834	6.3479



**Fig. 1** Relations of  $K'_{Mn}$  and  $K_{MnO}$  with temperature



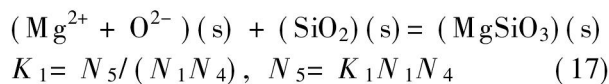
**Fig. 2** Comparison of  $L_{Mnc}$  calculated and  $L_{Mnp}$  observed for equilibrium between MnO-FeO-SiO<sub>2</sub> and liquid iron

### 3 MANGANESE DISTRIBUTION BETWEEN MgO-MnO-FeO-SiO<sub>2</sub> SLAG MELTS AND LIQUID IRON

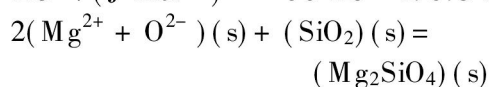
According to the phase diagrams<sup>[8]</sup> and considering that in MgO-MnO-FeO-SiO<sub>2</sub> slag system, there isn't any complex compound formed from three or four simple oxides, so based on the coexistence theory of slag structure<sup>[9]</sup>, the structural units of these slag

melts are Mg<sup>2+</sup>, Mn<sup>2+</sup>, Fe<sup>2+</sup>, O<sup>2-</sup> simple ions as well as SiO<sub>2</sub>, MgSiO<sub>3</sub>, Mg<sub>2</sub>SiO<sub>4</sub>, MnSiO<sub>3</sub>, Mn<sub>2</sub>SiO<sub>4</sub> and Fe<sub>2</sub>SiO<sub>4</sub> molecules.

Assuming the compositions of reactants as  $b_1 = \sum n_{MgO}$ ,  $b_2 = \sum n_{MnO}$ ,  $b_3 = \sum n_{FeO}$  and  $a = \sum n_{SiO_2}$ ; the mass action concentration of every structural unit after normalization as  $N_1 = N_{MgO}$ ,  $N_2 = N_{MnO}$ ,  $N_3 = N_{FeO}$ ,  $N_4 = N_{SiO_2}$ ,  $N_5 = N_{MgSiO_3}$ ,  $N_6 = N_{Mg_2SiO_4}$ ,  $N_7 = N_{MnSiO_3}$ ,  $N_8 = N_{Mn_2SiO_4}$ ,  $N_9 = N_{Fe_2SiO_4}$ ,  $\sum n =$  sum of moles of ions and molecules in equilibrium. In the light of the law of mass action, it gives chemical equilibria:

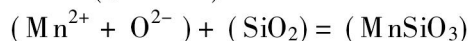


$$\Delta G^\ominus / (J \cdot mol^{-1}) = -36425 - 1.675 T^{[12]}$$



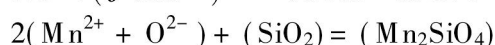
$$K_2 = \frac{N_6}{N_1^2 N_4}, N_6 = K_2 N_1^2 N_4 \quad (18)$$

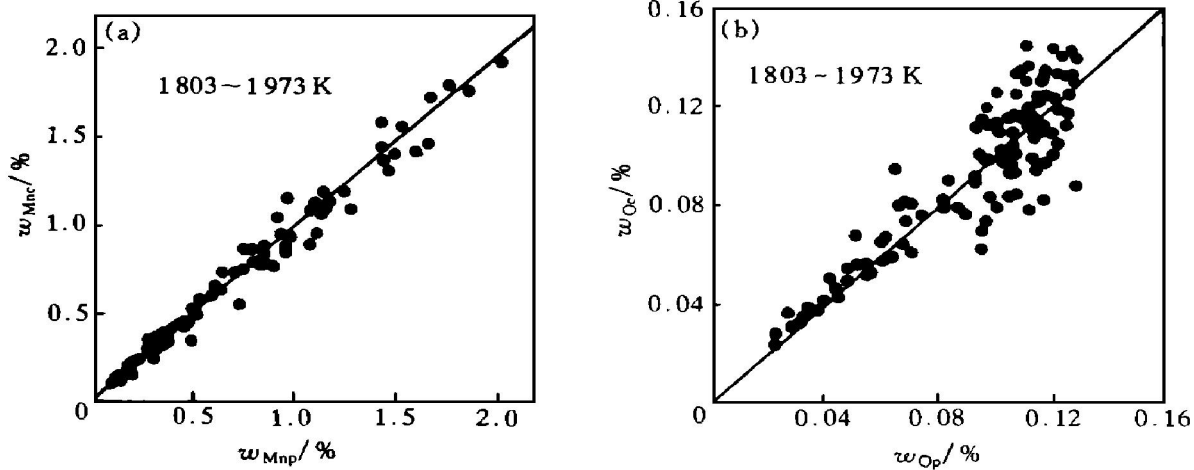
$$\Delta G^\ominus / (J \cdot mol^{-1}) = -63220 + 1.884 T^{[12]}$$



$$K_3 = \frac{N_7}{N_2 N_4}, N_7 = K_3 N_2 N_4 \quad (19)$$

$$\Delta G^\ominus / (J \cdot mol^{-1}) = -30013 - 5.02 T^{[10]}$$





**Fig. 3** Comparison of calculated and observed values of manganese and oxygen contents in liquid iron

$$K_4 = \frac{N_8}{N_2^2 N_4}, \quad N_8 = K_4 N_2^2 N_4 \quad (20)$$

$$\Delta G^\ominus / (\text{J} \cdot \text{mol}^{-1}) = -86670 + 16.81 T^{[10]}$$

$$2(\text{Fe}^{2+} + \text{O}^{2-}) + (\text{SiO}_2) = (\text{Fe}_2\text{SiO}_4)$$

$$K_5 = \frac{N_9}{N_3^2 N_4}, \quad N_9 = K_5 N_3^2 N_4 \quad (21)$$

$$\Delta G^\ominus / (\text{J} \cdot \text{mol}^{-1}) = -28596 - 3.349 T^{[11]}$$

Mass balance:

$$N_1 + N_2 + N_3 + N_4 + N_5 + N_6 + N_7 + N_8 + N_9 - 1 = 0 \quad (22)$$

$$b_1 = \sum n(0.5N_1 + N_5 + 2N_6) \quad (23)$$

$$b_2 = \sum n(0.5N_2 + N_7 + 2N_8) \quad (24)$$

$$b_3 = \sum n(0.5N_3 + 2N_9) \quad (25)$$

$$a = \sum n(N_4 + N_5 + N_6 + N_7 + N_8 + N_9) \quad (26)$$

Combining Eqs. (23) and (26) gives

$$0.5aN_1 + (a - b_1)N_5 + (2a - b_1)N_6 - b_1(N_7 + N_8 + N_9) = 0 \quad (27)$$

Combining Eqs. (24) and (26) gives

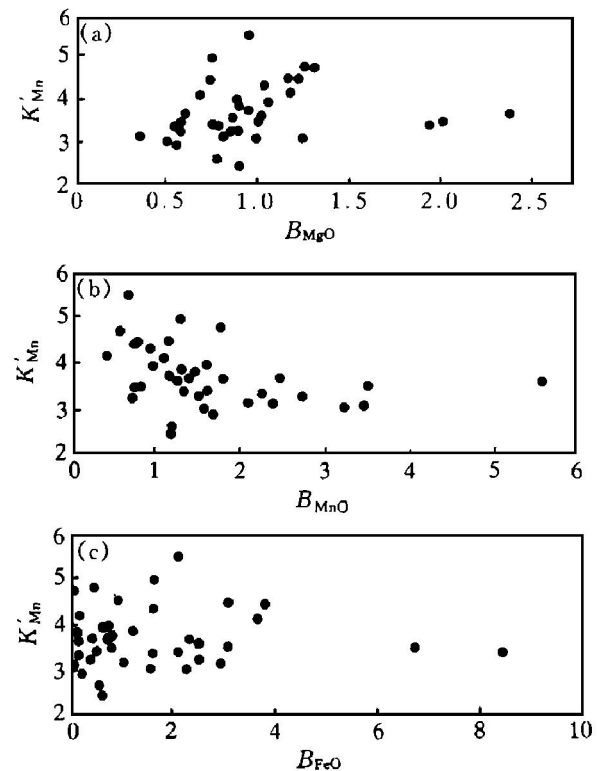
$$0.5aN_2 + (a - b_2)N_7 + (2a - b_2)N_8 - b_2(N_5 + N_6 + N_9) = 0 \quad (28)$$

Combining Eqs. (25) and (26) gives

$$0.5aN_3 + (2a - b_3)N_9 - b_3(N_5 + N_6 + N_7 + N_8) = 0 \quad (29)$$

Eqs. (22), (27), (28) and (29) are the calculating model of mass action concentrations for these slag melts.  $K'_{\text{Mn}}$ ,  $K_{\text{MnO}}$ ,  $L_{\text{Mn}}$ ,  $w_{\text{Mn}}$  and  $w_{\text{O}}$  can be evaluated by Eqs. (10), (11), (12), (13) and (14).

Using literature data of manganese distribution between MgO-MnO-FeO-SiO<sub>2</sub> slag melts and liquid iron at 1823 K<sup>[13]</sup>, the variations of calculated  $K'_{\text{Mn}}$  and  $K_{\text{MnO}}$  with basicities are illustrated respectively in Fig. 4 and Fig. 5. As shown in these figures, irrespective of what way basicities are expressed, there isn't any regular change of  $K'_{\text{Mn}}$  and  $K_{\text{MnO}}$  with basicities. Hence, the arguments about presence of dif-

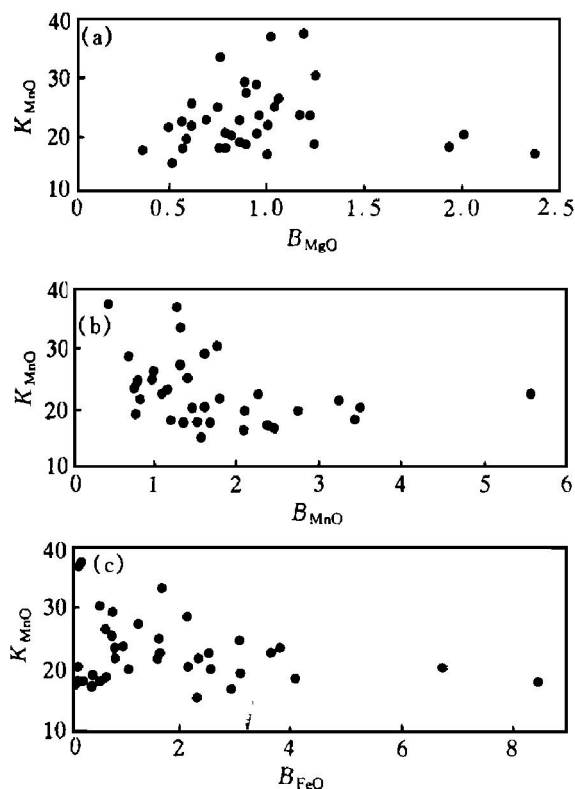


**Fig. 4** Variation of  $K'_{\text{Mn}}$  with basicities

$$(B_{\text{MgO}} = \frac{\sum n_{\text{MgO}}}{\sum n_{\text{SiO}_2}}, B_{\text{MnO}} = \frac{\sum n_{\text{MnO}}}{\sum n_{\text{SiO}_2}}, B_{\text{FeO}} = \frac{\sum n_{\text{FeO}}}{\sum n_{\text{SiO}_2}})$$

ferent values of  $K'_{\text{Mn}}$  and  $K_{\text{MnO}}$  in case of acid and basic slags still need further discussion and consideration. A comparison of average  $K'_{\text{Mn}}$  and  $K_{\text{MnO}}$  evaluated at 1823 K with those calculated from literature equations is shown in Table 3. It is clear from the table that there isn't much difference between them, and a certain fluctuation of  $K'_{\text{Mn}}$  and  $K_{\text{MnO}}$  in Fig. 4 and Fig. 5 may be mainly due to unconsidered Fe<sub>2</sub>O<sub>3</sub> content in the above mentioned slag system.

A comparison of coefficients of manganese distribution  $L_{\text{Mnc}}$  calculated and  $L_{\text{Mnp}}$  observed is given in Fig. 6. It must be said that the agreement is very

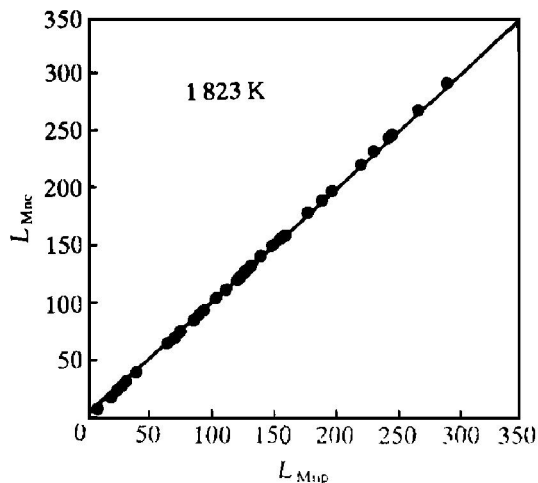


**Fig. 5** Variation of  $K_{MnO}$  with basicities  
 $(B_{MgO} = \frac{\sum n_{MgO}}{\sum n_{SiO_2}}, B_{MnO} = \frac{\sum n_{MnO}}{\sum n_{SiO_2}}, B_{FeO} = \frac{\sum n_{FeO}}{\sum n_{SiO_2}})$

good.

Fig. 7 shows the comparison of calculated and observed values of manganese  $w_{Mn}$  and oxygen  $w_O$  contents in liquid iron. It also can be seen in the figure that the agreement between calculated and observed values is satisfactory.

The above mentioned facts once again confirm that according to the law of mass action in combination with the coexistence theory of slag structure, it is practical to formulate the model of manganese dis-



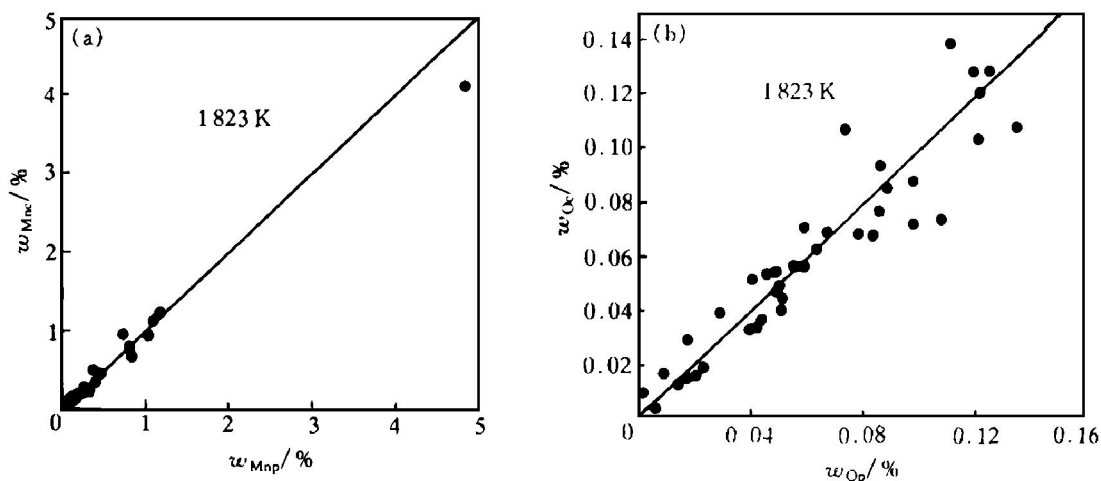
**Fig. 6** Comparison of coefficients of manganese distribution  $L_{Mnc}$  calculated and  $L_{Mnp}$  observed

**Table 3** Comparison of average  $K'_{Mn}$  and  $K_{MnO}$  evaluated at 1823 K by equations of present paper and from literatures

Source of equations	$K'_{Mn}$	$K_{MnO}$
[ 1 ]	3.285	20.675
[ 2 ] ~ [ 5 ]	3.586	21.532
[ 6 ]	3.788	
[ 7 ]	4.072	22.695
Present paper	3.696	22.777

tribution between slag melts and liquid iron which can reflect the characteristics of melts structure.

Finally, it should be pointed out that the increase of  $K'_{Mn}$  and  $K_{MnO}$  with decreasing of basicities during treatment of some literature data<sup>[14,15]</sup> by similar models does not show that the law of mass action is not applicable in this case, but that longer time is required to approach the equilibrium of manganese distribution between slag melts and liquid iron under



**Fig. 7** Comparison of calculated and observed values of manganese and oxygen contents in liquid iron

low basicity slag melts. Recent research of Morales and Fruehan<sup>[16]</sup> shows that 8 h are required to reach equilibrium of manganese distribution between slag melts and liquid iron in case of high manganese content in molten iron, and so the anomaly of Ref. [14, 15] is arisen from not maintaining enough time (the former maintained 3~ 5.5 h for LaCrO<sub>3</sub> heating furnace, the latter 30 min for induction furnace) to attain equilibrium in corresponding experiments.

#### 4 CONCLUSIONS

1) The calculating models of mass action concentrations for MnO-FeO-SiO<sub>2</sub> and MgO-MnO-FeO-SiO<sub>2</sub> slag systems have been formulated according to the law of mass action as well as the coexistence theory of slag structure, and equations for evaluating  $K'_{Mn}$ ,  $K_{MnO}$ ,  $L_{Mn}$ ,  $w_{Mn}$  and  $w_O$  have been deduced in accordance with these models.

2) The calculated  $K'_{Mn}$  and  $K_{MnO}$  are basically identical with equilibrium values obtained from experiments under simple slag melts (MnO + FeO), and don't change with basicities as well as compositions of slag, hence the arguments about the presence of different values of  $K'_{Mn}$  and  $K_{MnO}$  in case of acid and basic slags still need further discussion and consideration.

3) The calculated  $L_{Mn}$ ,  $w_{Mn}$  and  $w_O$  agree well with practice, this in turn shows that the models deduced can reflect the reality of manganese distribution between slag melts and liquid iron.

4) Analysis of experimental results from other sources shows that  $K'_{Mn}$  and  $K_{MnO}$  really change with basicities of slag, which is probably arisen from not approaching equilibrium under low basicity slag melts.

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