Thermodynamic Aspects of Steel Reoxidation Behavior by the Ladle Slag System of $CaO-MgO-SiO_2-Al_2O_3-Fe_tO-MnO-P_2O_5$

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The reoxidation behavior of steels by slag in the secondary steelmaking process was addressed by investigating the thermodynamic equilibria between the liquid iron containing Mn and P and $CaO-MgO-SiO_2-Al_2O_3-P_2O_5-MnO-Fe_tO$ ladle slag at 1873 K. The activity coefficient of Fe_tO shows a maximum value in the vicinity of the basicity $((X_{CaO} + X_{MgO} + X_{MnO})/(X_{SiO_2} + X_{Al_2O_3} + X_{P_2O_5})) = 2.5$ at the specific mole fraction range of Fe_tO, while that of MnO seems to increase gradually with increasing the basicity. However, the values of γ_{Fe_tO} and γ_{MnO} showed minima with respect to P_2O_5 content of slag. In addition, the values of γ_{Fe_tO} and γ_{MnO} increased as (pct CaO)/(pct Al_2O_3) ratio increased at given SiO_2, MgO, and P_2O_5 contents. The conversion equations between the Fe_tO and MnO activities and their calculated activities *via* regular solution model were derived by the correlation between the measured and calculated activities over the limited ranges of Fe_tO and MnO contents. The regular solution model was used to estimate the oxygen potential in the slag. For MgO saturated slags, $a_{Fe_tO(l)} = 0.864a_{FeO(R.S.)}$, $a_{MnO(l)} = 6.38a_{MnO(R.S.)}$. For Al_2O_3 saturated slags, $a_{Fe_tO(l)} = 2.086a_{FeO(R.S.)}$, $a_{MnO(l)} = 14.39a_{MnO(R.S.)}$

I. INTRODUCTION

RECENTLY, the demand for ultra-low-carbon steel with high cleanliness has been progressively increasing. To obtain high-purity steel, the deoxidized products should be completely removed and the reoxidation of aluminum with air, slag (reducible oxides such as Fe_tO, MnO, and SiO_2), and refractory in ladle and tundish should be prevented effectively. The high oxygen potential in the ladle slag may cause reoxidation of the elements in liquid iron such as Al and Ti, resulting in contamination of steel. Especially, in the case of ultra-low-carbon steel produced by decarburization and subsequent deoxidation processes in RH vessel, the oxygen content in liquid iron is extremely low. Therefore, Fe_tO and MnO in the refining slag can bring about reoxidation of Al easily. Therefore, it is necessary to avoid reoxidation reaction by the ladle slag for the stable production of ultra-low-carbon steel with high cleanliness.

The oxygen potential of slag is related directly to the activity of Fe_tO in slag, but it has been estimated so far by the amount of Fe_tO and MnO in slag for convenience. The slag components such as CaO, MgO, Al_2O_3, SiO_2, P_2O_5, *etc.* may affect the activities of Fe_tO and MnO by the interaction, and the activity coefficients of Fe_tO and MnO may also be dependent on the basicity and other properties of slag. Therefore, it is not accurate to describe the oxygen potential of slag only in terms of the amount of Fe_tO and MnO in slag.

In this work, the thermodynamic equilibria between the liquid iron containing Mn and P and $CaO-MgO-SiO_2-Al_2O_3-P_2O_5-MnO-Fe_tO$ slag system have been carried out in a MgO or Al_2O_3 crucible at 1873 K. The activities of Fe_tO and MnO were discussed from the standpoint of steel cleanliness and calculated by using the regular solution model proposed by Lumsden.[1] The comparison between the measured and calculated activities of Fe_tO and MnO was discussed in order to derive a conversion equation related to the measured and calculated activities.

II. EXPERIMENTALS

The master slags were prepared by premelting the mixture of reagent grade $CaCO_3$, Al_2O_3, SiO_2, and MgO in a graphite crucible, then crushed and baked at 1100 °C for 24 hours for decarburization. A vertical resistance furnace with heating elements of $LaCrO_3$ was used. The experimental apparatus is shown in Figure 1. The metal/slag equilibria with respect to P and Mn were approached from the slag to metal side in the experiments; P was added to the slag as a form of $NH_4H_2PO_4$. An argon gas flow rate of 200 mL/min was used in the furnace. The argon was passed through, in order, sulfuric acid, P_2O_5, $Mg(ClO_4)_2$, sponge Ti heated at 620 °C, and $Mg(ClO_4)_2$ again. Thirty or forty grams of high-purity electrolytic iron containing approximately 500 to 1000 ppm oxygen initially and 8 or 12 g of the mixture of master slag, MnO, $FeC_2O_4 \cdot 2H_2O$, and $NH_4H_2PO_4$ were melted in a MgO or Al_2O_3 crucible at 1873 K under an Ar atmosphere. An appropriate amount of Fe-Mn alloy was introduced to the melt by dropping afterward to adjust the composition of liquid iron. Thereafter, the melts were stirred twice over a period of 4 hours by an Al_2O_3 rod for 30 seconds at 2-hour intervals for the Al_2O_3 crucible experiment to facilitate the dissolution of alumina into the slag. In the case of the MgO crucible experiment, the melts were unstirred because MgO is more quickly dissolved into the slag than Al_2O_3. The temperature was measured by a thermocouple of (Pt-6 pct Rh)/(Pt-30 pct Rh) placed on the crucible bottom with an accuracy of ±2 K. Figure 2 shows the variation of slag and metal compositions as a function of reaction time in the case of Al_2O_3 crucible experiment. The compositions did not vary beyond 5 hours and, thus, the reaction time was chosen as

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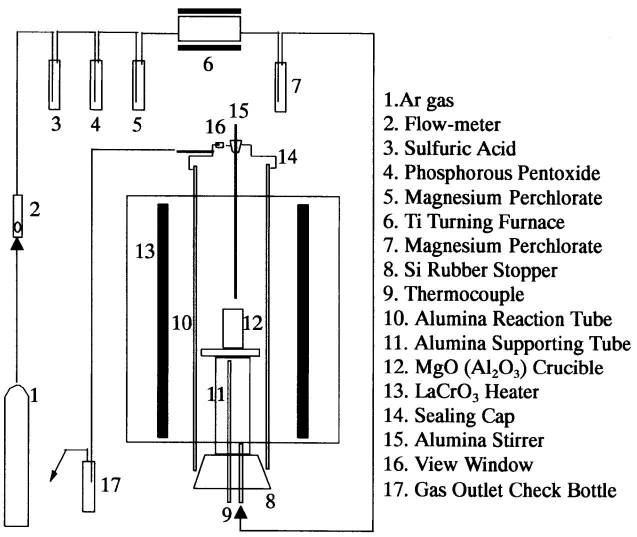

Fig. 1—Schematic diagram of experimental apparatus.

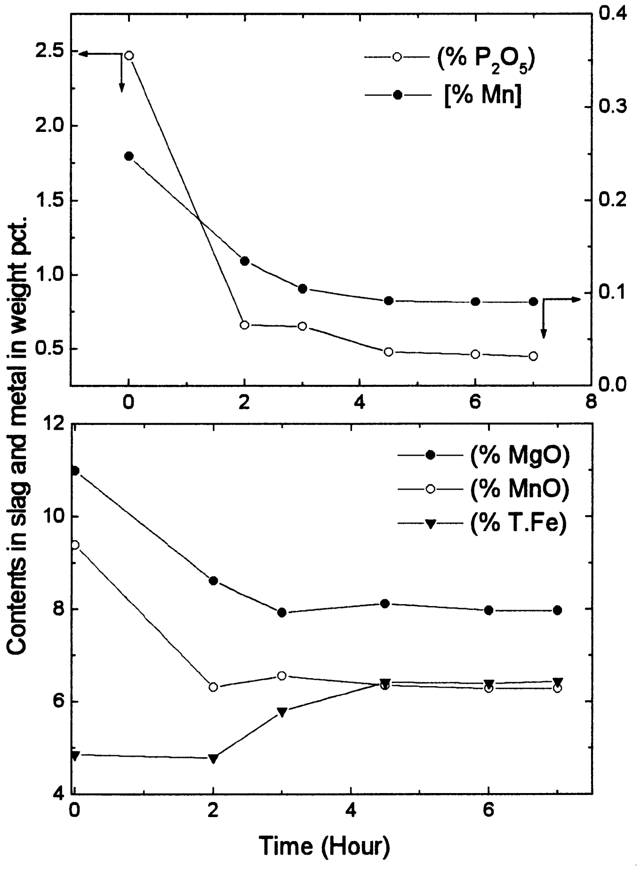

Fig. 2—Variation of slag and metal compositions as function of reaction time.

6 hours to ensure the reaction equilibrium. After reaching equilibrium, the crucible was withdrawn quickly out of the furnace and quenched rapidly in an ice-water bath.

The slag compositions were determined by the X-ray fluorescence spectroscopy method. The manganese content of the metal was analyzed by atomic absorption spectroscopy. Inert-gas fusion-infrared absorptiometry was used for the oxygen analysis in the metal. The phosphorus content of the metal was determined using the molybdenum blue colorimetry method.

III. RESULTS AND DISCUSSION

The various equilibrium compositions of CaO-MgO-SiO_2-Al_2O_3-Fe_tO-MnO-P_2O_5 slags and metals obtained in this work are summarized in Table I.

The activity of Fe_tO in the slag can be calculated using the following reaction:

$$Fe_{(l)} + \underline{O} = Fe_tO_{(l)} \qquad [1]$$

$$\Delta G_1^\circ = -27{,}740 + 11.66T \text{ (cal/mole)}^{[2]}$$

Using the equilibrium constant,

$$K_1 = a_{Fe_tO_{(l)}}/a_O = a_{Fe_tO_{(l)}}/f_O[\text{pct O}] \qquad [2]$$

where $a_{Fe_tO_{(l)}}$ is the activity of total iron oxide in slag with respect to pure liquid standard state; a_O is the activity of oxygen in metal relative to 1 wt pct standard state. The activity of oxygen dissolved in the metal can be determined by the chemically analyzed oxygen content. The activity coefficient of oxygen was calculated from the available thermodynamic data and chemical results of solutal elements. The following interaction parameters[3] listed in Table II were used for the calculation.

Figure 3 exhibits the values of $a_{Fe_tO_{(l)}}$ plotted in the (CaO + MgO + MnO)-(Al_2O_3 + SiO_2 + P_2O_5)-(Fe_tO) pseudoternary system on a mole fraction basis. The isoactivity lines of $a_{Fe_t\,O_{(l)}}$ show the increasing tendency with approaching the corner of (Fe_tO), which is in good agreement with the result by Turkdogan and Pearson[4] for the slag system of (CaO + MgO + MnO)-(SiO_2 + P_2O_5)-(Fe_tO).

Figure 4 shows the activity coefficients of Fe_tO as a function of the basicity $((X_{CaO} + X_{MgO} + X_{MnO})/(X_{SiO_2} + X_{Al_2O_3} + X_{P_2O_5}))$ suggested by Elliott and Luerssen[5] at the various mole fractions of Fe_tO. As shown in Figure 4, the value of $\gamma_{Fe_t\,O_{(l)}}$ does initially increase as the basicity increases to a value of about 2.5, and then it may start to decrease beyond the extreme value at the given mole fraction of Fe_tO. In other words, the maximum value of the Fe_tO activity coefficient exists in the vicinity of $(X_{CaO} + X_{MgO} + X_{MnO})/(X_{SiO_2} + X_{Al_2O_3} + X_{P_2O_5}) = 2.5$. It is further shown that the maximum value of $\gamma_{Fe_tO_{(l)}}$ generally tends to decrease with the increasing mole fraction of Fe_tO. Therefore, in order to prevent the reoxidation by ladle slag in the practical process, the slag basicity should be selected not to be in the vicinity of the value of 2.5, which is likely to avoid increasing the oxygen potential in slag induced by the increase of activity coefficient of Fe_tO. On the other hand, it was reported that the high basicity could act favorably for the elimination of alumina inclusions by increasing the dissolution rate of alumina into slag.[6] Therefore, as expected from these results, it can be suggested that a careful consideration in selecting the suitable basicity of the ladle slag system is required for the steel cleanliness.

Figure 5 represents the values of log $\gamma_{Fe_tO_{(l)}}$ obtained from the experimental data with MgO-saturated slags at 1873 K with respect to the molar fraction of P_2O_5. As the P_2O_5 content increases, the activity coefficient of Fe_tO decreases until it reaches a minimum value at around 0.8 pct P_2O_5; thereafter, it tends to increase. Such a tendency can be approximately expressed by the following equation:

Table I. The Equilibrium Compositions of Slag and Metal at 1873 K

Number*	Metal (Mass Pct) [Mn]	[P]	[O]	Slag (Mass Pct) CaO	MgO	SiO_2	Al_2O_3	Fe_tO	MnO	P_2O_5	Activity Coefficient γ_{FetO}	γ_{MnO}
M11	0.410	0.079	0.002	31.14	22.73	10.47	34.19	0.29	0.33	0.005	3.14	4.48
M12	0.210	0.090	0.035	27.53	15.08	5.17	33.32	9.88	7.77	0.426	1.88	1.97
M13	1.020	0.211	0.007	30.81	20.78	12.77	27.53	1.48	5.98	0.018	2.84	2.83
M14	0.330	0.045	0.020	37.92	13.54	6.43	32.42	4.14	4.52	0.204	2.60	3.09
M15	0.790	0.050	0.008	51.08	16.76	16.97	5.36	4.09	3.44	1.469	1.21	4.49
M16	0.140	0.017	0.050	37.40	13.22	16.93	9.35	14.38	7.26	0.658	1.99	2.16
M17	0.240	0.017	0.051	40.08	9.14	6.28	16.51	16.13	9.93	1.122	1.70	2.59
M18	0.150	0.269	0.037	13.32	28.01	12.88	26.10	11.44	7.12	0.286	1.92	1.82
M19	0.180	0.354	0.027	15.57	30.32	15.29	24.97	7.55	5.31	0.150	2.22	2.24
M20	0.210	0.076	0.026	32.87	14.97	5.62	33.28	7.20	5.00	0.256	1.94	2.31
M21	0.200	0.098	0.054	25.18	12.53	9.32	23.08	15.50	12.91	0.731	1.85	1.74
M22	0.240	0.066	0.028	35.75	12.96	5.29	30.26	8.27	5.92	0.740	1.81	2.39
M23	0.014	0.133	0.107	7.33	16.69	8.26	33.76	30.58	2.27	0.392	1.75	1.30
M24	0.068	0.009	0.093	36.37	12.14	10.17	6.72	27.22	5.01	1.492	1.89	2.72
M25	0.039	0.085	0.118	18.36	10.87	6.38	27.15	29.67	5.95	0.959	1.96	1.46
M26	0.053	0.007	0.069	41.54	14.71	5.07	6.44	27.27	2.53	1.541	1.45	3.23
M27	0.046	0.160	0.102	9.82	18.31	11.44	20.18	29.55	9.51	0.486	1.86	1.04
M28	0.056	0.040	0.098	27.01	8.92	8.31	20.59	26.66	6.07	1.412	1.87	1.80
M29	0.082	0.060	0.063	35.45	11.07	9.03	24.06	13.59	4.05	1.343	2.45	2.63
M30	0.095	0.027	0.035	47.79	12.81	10.62	14.85	8.82	2.22	2.106	2.51	3.71
M31	0.220	0.039	0.044	45.84	8.38	6.47	19.75	11.09	6.09	1.573	2.16	3.38
A11	0.480	0.382	0.002	23.30	5.00	8.42	61.63	0.23	0.60	0.011	3.69	2.68
A12	0.350	0.118	0.009	19.30	6.18	7.44	57.34	2.39	6.53	0.019	1.72	0.87
A13	1.100	0.218	0.002	22.86	11.53	11.04	51.29	0.54	1.88	0.022	1.53	1.91
A14	0.170	0.121	0.023	16.08	7.48	5.94	55.57	5.37	8.70	0.047	1.97	0.82
A15	0.920	0.341	0.009	18.56	9.19	2.53	61.99	1.68	5.20	0.043	2.33	2.73
A16	0.150	0.071	0.036	13.63	4.88	3.64	55.62	12.52	8.86	0.040	1.26	1.05

*M: MgO crucible, and A: Al_2O_3 crucible.

Table II. The Interaction Parameters Used in This Work[3]

$e_O^O = -1750/T + 0.734$	$e_O^{Mn} = -0.021$	$e_O^P = 0.07$
$e_{Mn}^O = -0.083$	$e_{Mn}^{Mn} = 0$	$e_{Mn}^P = -0.0035$

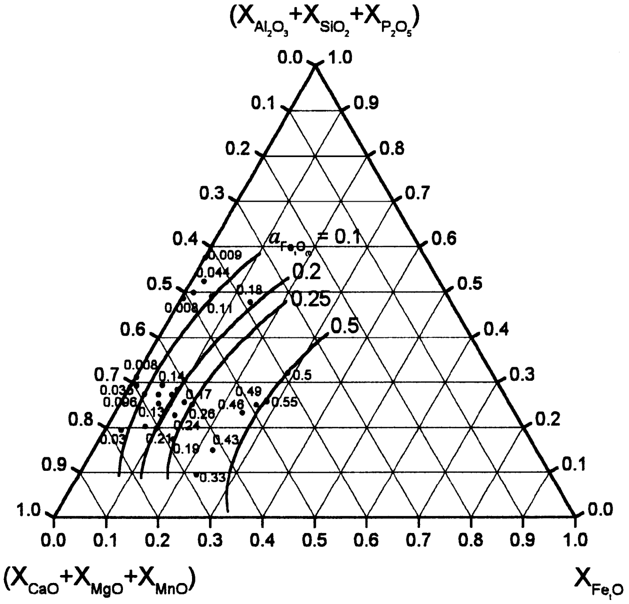

Fig. 3—Plot of isoactivity line of Fe_tO in the (CaO + MgO + MnO)-(SiO_2 + Al_2O_3 + P_2O_5)-Fe_tO pseudoternary system.

$$\log \gamma_{Fe_tO_{(l)}} = 0.00925 \times 10^6 X^2_{P_2O_5} - 0.0833 \times 10^3 X_{P_2O_5} + 0.428 \quad [3]$$

This result indicates that the ladle slag containing an appropriate amount of P_2O_5 is beneficial for the prevention of steel reoxidation by Fe_tO in slag in comparison with the ladle slags containing extremely low or comparatively high P_2O_5 contents. Needless to say, the high P_2O_5 content in slags is harmful for dephosphorization. One would ideally like to have as little P_2O_5 in the ladle slag as possible, as a significant amount of phosphorus could revert to the metal, causing serious chemistry problems.

The activity of MnO is another crucial parameter affecting the oxygen potential in the slag.

$$\underline{Mn} + \underline{O} = MnO_{(l)} \quad [4]$$

$$\Delta G_4^\circ = -59{,}470 + 25.84T \text{ (cal/mole)}^{[2]}$$
$$K_4 = a_{MnO_{(l)}}/a_{Mn}\, a_O \quad [5]$$

where $a_{MnO_{(l)}}$ is the activity of MnO in the slag with respect to pure liquid standard state; a_O and a_{Mn} are the activities of oxygen and manganese in the metal relative to 1 wt pct standard state. The activity of MnO can be also calculated using the chemical analysis results and the thermodynamic data in Table II.

Figure 6 shows the MnO activity plotted in the (CaO + MgO + Fe_tO)-(SiO_2 + Al_2O_3 + P_2O_5)-(MnO) pseudoternary system at 1873 K. It can be seen that the MnO activity

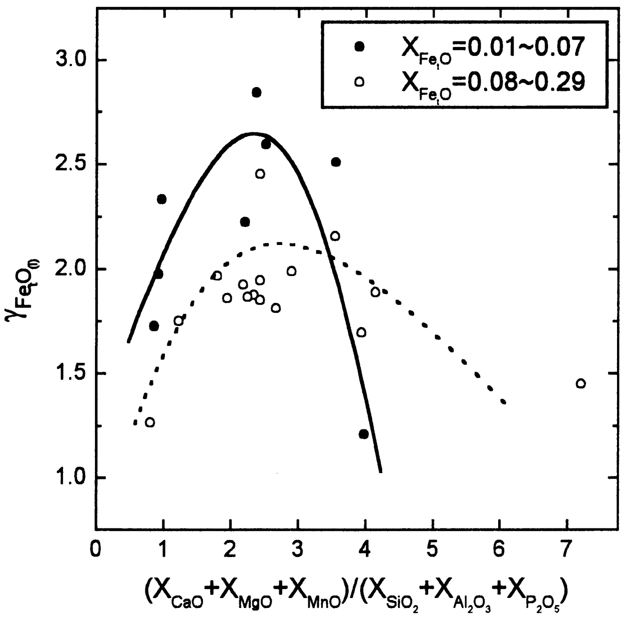

Fig. 4—Relationship between γ_{Fe_tO} and $(X_{CaO} + X_{MgO} + X_{MnO})/(X_{SiO_2} + X_{Al_2O_3} + X_{P_2O_5})$ ratio under the fixed mole fraction of Fe_tO at 1873 K.

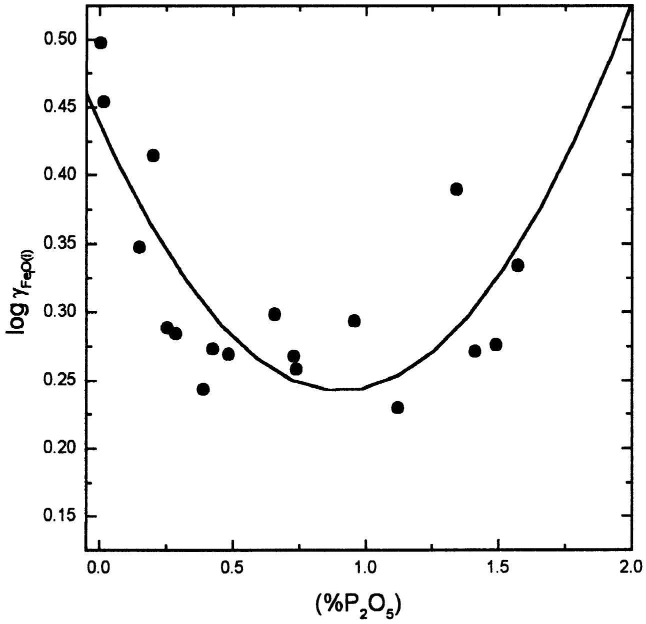

Fig. 5—The effect of P_2O_5 on γ_{Fe_tO} at 1873 K.

shows an increasing tendency with approaching the direction of the (CaO + MgO + Fe_tO)-(MnO) pseudobinary system.

Figure 7 indicates the values for $\gamma_{MnO(l)}$ plotted against the basicity defined by $(X_{CaO} + X_{MgO} + X_{Fe_tO})/(X_{SiO_2} + X_{Al_2O_3} + X_{P_2O_5})$ at 1873 K. The data seem to be somewhat scattered; however, the activity coefficient of $MnO_{(l)}$ statistically appears to increase as the basicity increases, confirming that the high value of the $(X_{CaO} + X_{MgO} + X_{Fe_tO})/(X_{SiO_2} + X_{Al_2O_3} + X_{P_2O_5})$ ratio is not good for the prevention of steel reoxidation by MnO. This result is in fairly good accordance with the previously reported ones.[5,7–9] Elliott and Luerssen[5] plotted the values of $\gamma_{MnO(l)}$ obtained from the actual

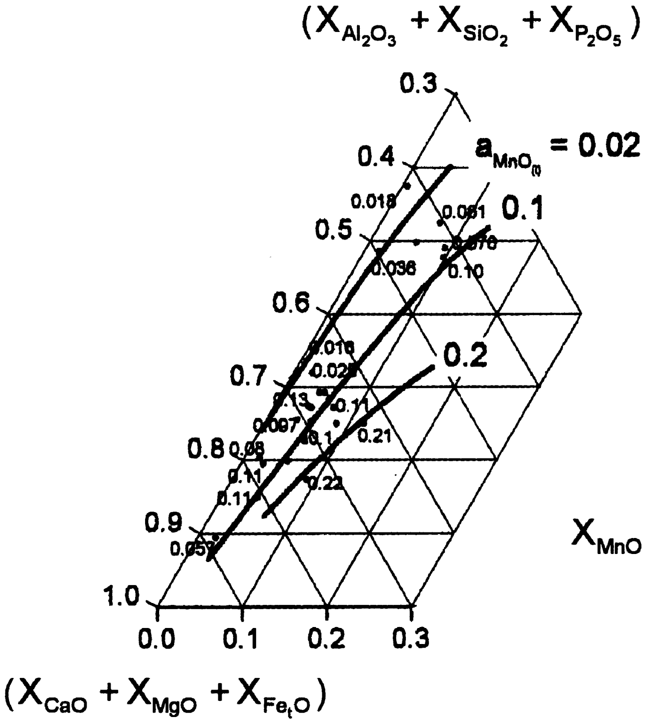

Fig. 6—Plot of isoactivity line of MnO in the (CaO + MgO + Fe_tO)-(SiO_2 + Al_2O_3 + P_2O_5)-MnO pseudoternary system.

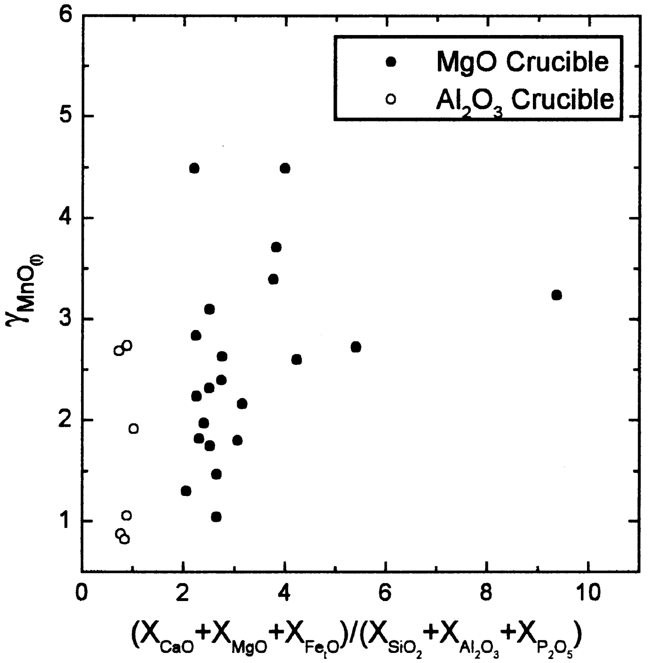

Fig. 7—Relationship between γ_{MnO} and $(X_{CaO} + X_{MgO} + X_{Fe_tO})/(X_{SiO_2} + X_{Al_2O_3} + X_{P_2O_5})$ ratio at 1873 K.

operation data, as well as the previous laboratory data,[7] as a function of the basicity expressed by the $(X_{CaO} + X_{MgO} + X_{MnO})/(X_{SiO_2} + X_{Al_2O_3} + X_{P_2O_5})$ ratio and reported that the maximum value of $\gamma_{MnO(l)}(\cong 3)$ existed on the basicity value of 2.5. It cannot be assured from their plot, however, that the maximum value of $\gamma_{MnO_{(l)}}$ is present at a certain critical basicity ratio, since the data points used by them

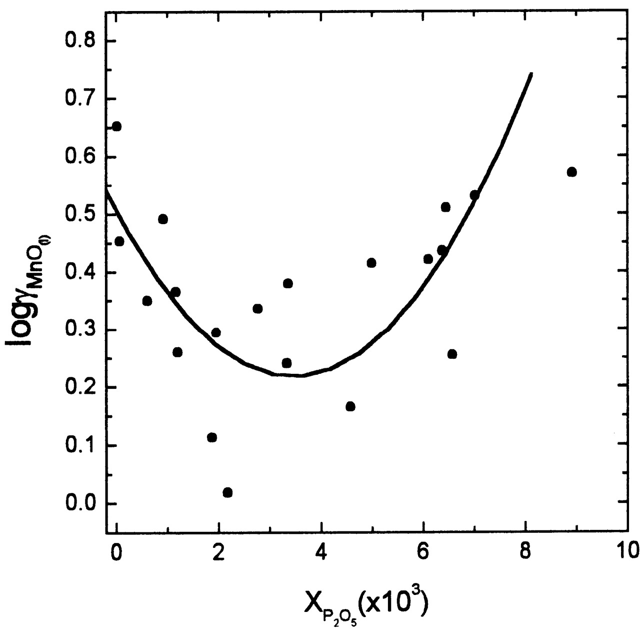

Fig. 8—The effect of P_2O_5 on γ_{MnO} at 1873 K.

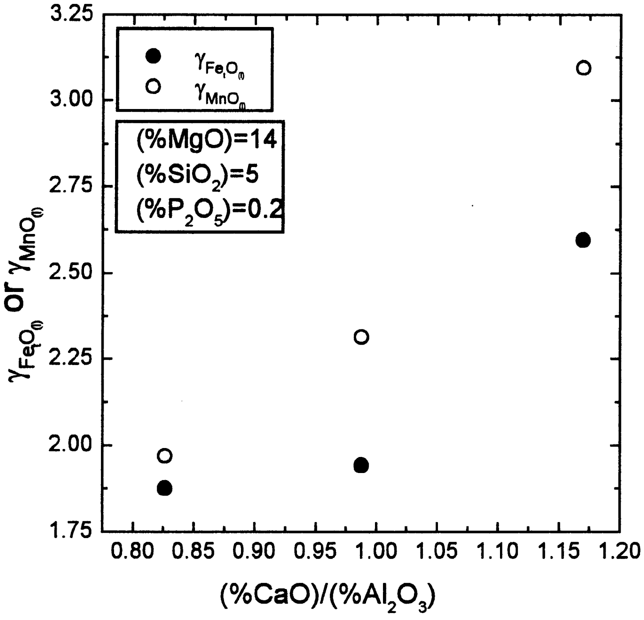

Fig. 9—Variation of γ_{Fe_tO} and γ_{MnO} with respect to (pct CaO)/(pct Al_2O_3) ratio under the fixed (pct MgO), (pct SiO_2), and (pct P_2O_5) at 1873 K.

were scattered to a great extent. Morales and Fruehan[9] recently studied the relationship between $\gamma_{MnO_{(l)}}$ and basicity expressed by (pct CaO + pct MgO)/(pct SiO_2) for the slag system of CaO-$MgO_{sat.}$-SiO_2-Fe_tO-MnO-P_2O_5 at 1873 K and found that the activity coefficient of $MnO_{(l)}$ appeared to increase with the increase of basicity.

The dependence of $\gamma_{MnO_{(l)}}$ on the mole fraction of P_2O_5 is shown in Figure 8. As a result, the value of $\gamma_{MnO_{(l)}}$ represents the same tendency as the variation of Fe_tO in the range of $X_{P_2O_5}$ considered in this work, indicating that the phosphorus oxide in the slag should be controlled critically at around 0.5 pct in order to prevent Al in metal from being reoxidized by MnO in slag. The variation of $\gamma_{MnO_{(l)}}$ with respect to P_2O_5 content could be roughly expressed as the following equation.

$$\log \gamma_{MnO} = 0.0239 \times 10^6 X^2_{P_2O_5} - 0.166 \times 10^3 X_{P_2O_5} + 0.506 \qquad [6]$$

Figure 9 shows the variation of $\gamma_{Fe_tO_{(l)}}$ and $\gamma_{MnO_{(l)}}$ with the (pct CaO)/(pct Al_2O_3) ratio. It demonstrates that at the given MgO, SiO_2, and P_2O_5 contents, the activity coefficients of Fe_tO and MnO tend to increase with an increase of the (pct CaO)/(pct Al_2O_3) ratio. Therefore, the slag compositions with high (pct CaO)/(pct Al_2O_3) ratio seem to be harmful to suppression of steel reoxidation by iron and manganese oxides in slag. From these results, slag compositions with low (pct CaO)/(pct Al_2O_3) ratios are likely to be favorable for the production of high cleanliness steel. In case of very low (pct CaO)/(pct Al_2O_3) ratio of slags, Al_2O_3 content increases inevitably and the capacity of the slag to absorb Al_2O_3 inclusions decreases. Suda *et al.*[10] investigated the elimination amount of Al_2O_3 inclusion in liquid iron by CaO-SiO_2-Al_2O_3-MgO-Fe_tO(<5 pct) slags in terms of the (pct CaO)/(pct Al_2O_3) ratio at the given SiO_2 and MgO contents and reported that the pick-up amount of Al_2O_3 inclusion into slag increases gradually until the ratio reaches a critical value of about 1.8 and then decreases beyond the critical ratio, where the melting temperature of slag increases gradually. Thus, it is suggested that depending on the given specific ladle operation, a moderate (pct CaO)/(pct Al_2O_3) ratio in the corresponding ladle slag should be selected within the ratio of 1.8.

In this work, the regular solution model proposed by Lumsden[1] was adopted to estimate the oxygen potential in the slag. The activity coefficient of component *i* in a multicomponent regular solution is expressed by the following equation:

$$RT \ln \gamma_i = \sum_j \alpha_{ij} X_j^2 + \sum_j \sum_k (\alpha_{ij} + \alpha_{ik} - \alpha_{jk}) X_j X_k \qquad [7]$$

where X_i is cation fraction, and α_{ij} is the interaction energy between cations, *i.e.*, (*i* cation)-O-(*j* cation). The reference state of the activity in this case is taken to be a hypothetical pure liquid.

In the regular solution model, the activity of FeO in the CaO-MgO-SiO_2-Al_2O_3-P_2O_5-MnO-Fe_tO slag can be expressed by the following equations using Eq. [7] and the interaction energy[11] listed in Table III.

$$a_{FeO(R.S.)} = \gamma_{FeO} X_{FeO} \qquad [8]$$

$$\begin{aligned} RT\ln \gamma_{FeO(R.S.)} = {} & 7110X^2_{MnO} - 31{,}380X^2_{CaO} + 33{,}470X^2_{MgO} \\ & - 41{,}840X^2_{SiO_2} - 31{,}380X^2_{PO_{2.5}} - 41{,}000X^2_{AlO_{1.5}} \\ & + 67{,}780X_{MnO}X_{CaO} - 21{,}340X_{MnO}X_{MgO} \\ & + 40{,}580X_{MnO}X_{SiO_2} + 60{,}670X_{MnO}X_{PO_{2.5}} \\ & + 49{,}790X_{MnO}X_{AlO_{1.5}} + 102{,}510X_{CaO}X_{MgO} \\ & + 60{,}670X_{CaO}X_{SiO_2} + 188{,}280X_{CaO}X_{PO_{2.5}} \\ & + 82{,}430X_{CaO}X_{AlO_{1.5}} + 58{,}570X_{MgO}X_{SiO_2} \\ & + 39{,}750X_{MgO}X_{PO_{2.5}} + 63{,}600X_{MgO}X_{AlO_{1.5}} \end{aligned} \qquad [9]$$

Table III. Interaction Energy between Cations of Major Components in the Steelmaking Slag[11]

i^j	Ca^{2+}	Mg^{2+}	Al^{3+}	Mn^{2+}	Si^{4+}	P^{5+}	Fe^{2+}	Fe^{3+}
Ca^{2+}	—	−100,420	−154,810	−92,050	−133,890	−251,040	−31,380	−95,810
Mg^{2+}	−100,420	—	−71,130	61,920	−66,940	−37,660	33,470	−2,930
Al^{3+}	−154,810	−71,130	—	−83,680	−127,610	−261,500	−41,000	−161,080
Mn^{2+}	−92,050	61,920	−83,680	—	−75,310	−84,940	7,110	−56,480
Si^{4+}	−133,890	−66,940	−127,610	−75,310	—	83,680	−41,840	32,640
P^{5+}	−251,040	−37,660	−261,500	−84,940	83,680	—	−31,380	14,640
Fe^{2+}	−31,380	33,470	−41,000	7,110	−41,840	−31,380	—	−18,660
Fe^{3+}	−95,810	−2,930	−161,080	−56,480	32,640	14,640	−18,660	—

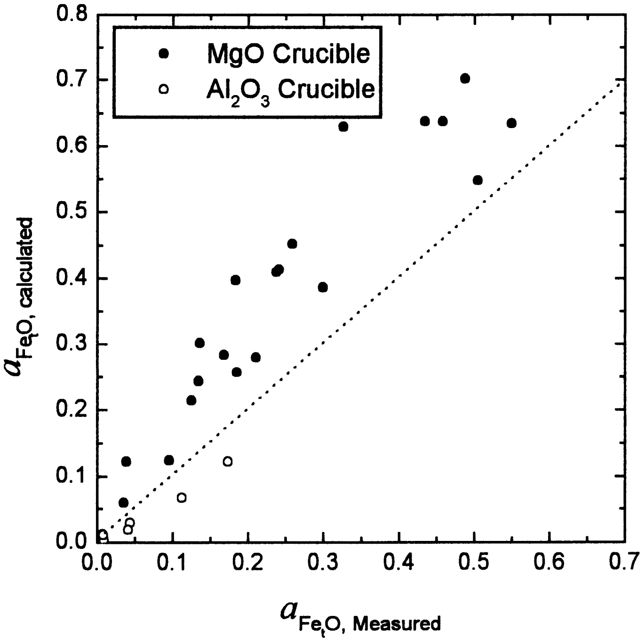

Fig. 10—Comparison of a_{Fe_tO} between the experimentally measured values and calculated ones by the regular solution model using Ban-ya's[11] equation.

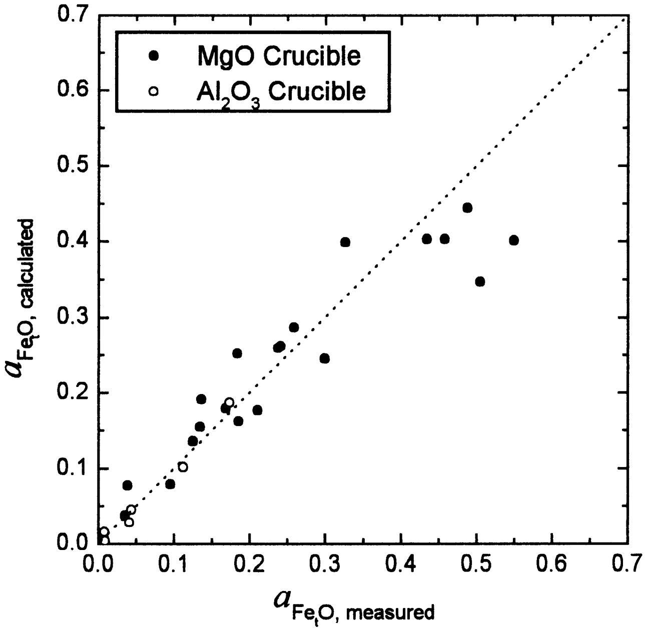

Fig. 11—Linear correlation of a_{Fe_tO} between the measured values and calculated ones by the regular solution model using the new conversion equation.

$$-\,156{,}900X_{SiO_2}X_{PO_{2.5}} + 44{,}770X_{SiO_2}X_{AlO_{1.5}} + 189{,}120X_{PO_{2.5}}X_{AlO_{1.5}}\,(J)$$

It should be noted that in the preceding treatment, all iron in slag is assumed to be present in the form of ferrous oxide and the amount of ferric oxide in the slag can be neglected.

In a regular solution model, the reference state of FeO activity was taken as the hypothetical stoichiometric FeO, even though the reference state for the activity of conventional iron oxide becomes pure iron oxide in equilibration with metallic iron. Ban-ya[11] has reported the thermodynamic data for the conversion reaction of the reference states between activity of FeO in a regular solution and that of Fe_tO in an actual slag.

$$\begin{aligned} &Fe_tO_{(l)} + (1 - t)Fe_{(s\text{ or }l)} = FeO(R.S.) \\ &\Delta G^\circ_{10} = -8540 + 7.142T(\text{J/mole})^{[11]} \end{aligned} \qquad [10]$$

Using Eqs. [8] and [10], the activity of Fe_tO in the slag can be calculated with the aid of a regular solution model. Figure 10 indicates the values for the calculated $a_{Fe_tO_{(l)}}$ using Ban-ya's conversion equation together with the measured values of $a_{Fe_tO_{(l)}}$. It can be seen that in the case of the experimental data using MgO crucibles, the calculated values are greater than the measured ones, while for the data from Al_2O_3 crucibles, the former are smaller than the latter. Therefore, applying the regular solution model to this slag system, it is necessary to find a new Gibbs free energy value for the reaction shown in Eq. [10]. By making respective correlation between the experimentally measured $a_{Fe_tO_{(l)}}$ and the calculated $a_{FeO(R.S.)}$ based on the regular solution model for different slag systems, the activity conversion equation was deduced over the limited concentration range of Fe_tO at 1873 K as follows.

For the $CaO\text{-}MgO_{sat.}\text{-}SiO_2\text{-}Al_2O_3\text{-}P_2O_5\text{-}MnO\text{-}Fe_tO(<30$ pct) slag system,

$$a_{Fe_tO_{(l)}} = 0.864a_{FeO_{(R.S.)}} \qquad [11]$$

For the $CaO\text{-}MgO\text{-}SiO_2\text{-}Al_2O_{3sat.}\text{-}P_2O_5\text{-}MnO\text{-}Fe_tO(<12.5$ pct) slag system,

$$a_{Fe_tO_{(l)}} = 2.086a_{FeO_{(R.S.)}} \qquad [12]$$

Figure 11 shows the comparison between the activity of Fe_tO calculated with the help of the preceding conversion equations and that using the measured one. The two values for the activity of iron oxide coincide fairly well.

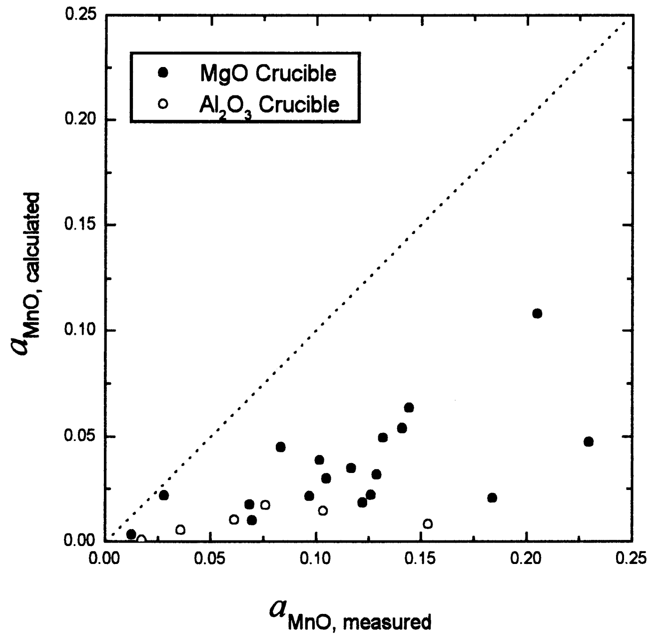

Fig. 12—Comparison of a_{MnO} between the experimentally measured values and calculated ones by the regular solution model using Ban-ya's[11] equation.

Figure 12 indicates an inconsistency of $a_{MnO_{(l)}}$ between the experimentally measured values and the calculated ones by the regular solution model using Ban-ya's conversion equation.

Following the same method as that for $a_{Fe_tO_{(l)}}$, the conversion equation of the activity of MnO between two reference states could be reasonably represented at 1873 K within the specific concentration of MnO as follows.

For the CaO-$MgO_{sat.}$-SiO_2-Al_2O_3-P_2O_5-MnO(<13 pct)-Fe_tO slag system,

$$a_{MnO_{(l)}} = 6.38 a_{MnO_{(R.S.)}} \qquad [13]$$

For the CaO-MgO-SiO_2-$Al_2O_{3sat.}$-P_2O_5-MnO(<9 pct)-Fe_tO slag system,

$$a_{MnO_{(l)}} = 14.39 a_{MnO_{(R.S.)}} \qquad [14]$$

Figure 13 shows that the activity of MnO calculated with the help of the conversion equations coincides relatively well with the measured one, although with considerable scatter.

IV. CONCLUSIONS

The thermodynamic equilibrium between the metal and the slag system of CaO-MgO-SiO_2-Al_2O_3-P_2O_5-MnO-Fe_tO has been investigated in a MgO or Al_2O_3 crucible at 1873 K. The reoxidation phenomena were discussed by virtue of the activities and activity coefficients of Fe_tO and MnO according to variations in slag compositions. By using a regular solution model, the oxygen potential in the slag was also estimated quantitatively.

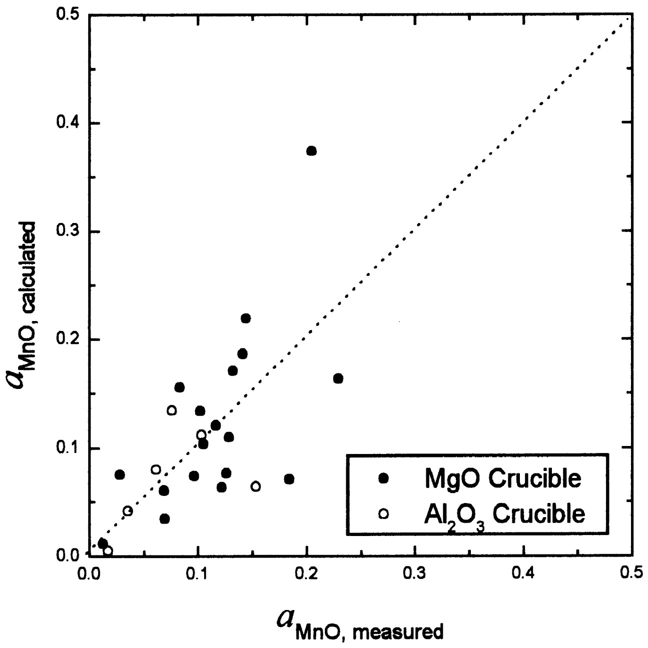

Fig. 13—Linear correlation of a_{MnO} between the measured values and calculated ones by the regular solution model using the new conversion equation.

1. The activity coefficient of Fe_tO has a maximum value at $B((X_{CaO} + X_{MgO} + X_{MnO})/(X_{SiO_2} + X_{Al_2O_3} + X_{P_2O_5})) \cong$ 2.5 at a given mole fraction range of Fe_tO, while that of MnO shows an increase with increasing basicity, with significant scatter.
2. For the CaO-$MgO_{sat.}$-SiO_2-Al_2O_3-P_2O_5-MnO-Fe_tO slag, the values of $\gamma_{Fe_tO_{(l)}}$ and $\gamma_{MnO_{(l)}}$ decreased with an increase of P_2O_5 content up to a critical P_2O_5 content, and thereafter increased. It is, thus, suggested that as the effect of P_2O_5 on the activity coefficients of Fe_tO and MnO seems to be very significant in the narrow concentration range of P_2O_5 considered in this work, P_2O_5 content in the ladle slag should be controlled cautiously within 0.5 to 0.8 pct for the minimization of aluminum reoxidation by slag.
3. The activity coefficients of Fe_tO and MnO increase with the increasing (pct CaO)/(pct Al_2O_3) ratio of slags. However, it is suggested that a moderate (pct CaO)/(pct Al_2O_3) ratio in the given ladle slag should be selected within the ratio of 1.8.
4. From the correlation between the measured values of Fe_tO and MnO activities and the calculated ones by the regular solution model, the general conversion equations for the estimation of activities of Fe_tO and MnO were reasonably deduced at 1873 K as follows.

For the CaO-$MgO_{sat.}$-SiO_2-Al_2O_3-P_2O_5-MnO(<13 pct)-Fe_tO(<30 pct) slags,

$$a_{Fe_tO_{(l)}} = 0.864 a_{FeO_{(R.S)}},\ a_{MnO_{(l)}} = 6.38 a_{MnO_{(R.S.)}}$$

For the CaO-MgO-SiO_2-$Al_2O_{3sat.}$-P_2O_5-MnO(<9 pct)-Fe_tO(<12.5 pct) slags,

$$a_{Fe_tO_{(l)}} = 2.086 a_{FeO_{(R.S)}},\ a_{MnO_{(l)}} = 14.39 a_{MnO_{(R.S.)}}$$

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