Redox Equilibria of Fe and Mn in the Na₂O–B₂O₃ Melts

Bong-Hoon PARK and Hideaki SUITO

Research Institute of Mineral Dressing and Metallurgy, Tohoku University, Katahira, Aoba-ku, Sendai, Miyagi-ken, 980 Japan.

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The Fe²⁺/Fe³⁺ and Mn²⁺/Mn³⁺ redox equilibria in the Na₂O–B₂O₃ melts have been individually measured as a function of the melt compositions, temperatures, oxygen partial pressures, and dopant element concentrations. The mutual interaction of these two redox couples has been studied by electron spin resonance (ESR) in the Na₂O·2B₂O₃ melts.

The redox ratios of Fe and Mn in the Na₂O–B₂O₃ melts tend to decrease with increasing the dopant concentration. A plot of log [(M²⁺)/(M³⁺)] vs. –log P_{O₂} indicated a straight line of the slope of 8 and 4 for Fe and Mn, respectively. The values for the reduction enthalpy of Fe and Mn in Na₂O–B₂O₃ melts were found to be 80–120 kJ/mol and 40–60 kJ/mol, respectively. The redox ratio of Fe and Mn decreased with increasing the X_{Na₂O}/X_{B₂O₃} ratio. It was shown by ESR spectroscopy that the electron exchange reaction: Fe²⁺+Mn³⁺=Fe³⁺+Mn²⁺ proceeded to the right.

KEY WORDS: redox; dopant; Fe²⁺/Fe³⁺; Mn²⁺/Mn³⁺; Na₂O–B₂O₃; ESR; mutual interaction.

1. Introduction

The redox equilibria in the glass-forming melts have been extensively studied in the fields of glass chemistry, geochemistry, and metallurgy. Discrepancies, however, exist in the interpretation concerning the previous experimental results on the dependence of dopant concentration^{1–5)} upon redox ratios as well as the mutual interaction of redox couples.^{4,6,7)}

The manganese partitioning between α-Fe₂O₃ crystal and Na₂O–B₂O₃ fluxes have been previously studied by the present authors⁸⁾ in the series of the works for the purpose of purifying α-Fe₂O₃ crystal using the Na₂O–B₂O₃ flux.^{9,10)} As a result, the fundamental study on the redox equilibria of Fe and Mn in the melts was found to be necessary for the determination of the chemical components in the partition between solid and liquid phases.

The present investigation has been carried out for studying the redox ratios of Fe and Mn in the Na₂O–B₂O₃ melts as a function of dopant concentrations, oxygen partial pressures, temperatures, and melt compositions. The mutual interaction of redox couples has also been studied by electron spin resonance (ESR) spectroscopy.

2. Experimental

2.1. Preparation of Sample

Samples were prepared from guaranteed grade reagents, Na₂B₄O₇ (Fe<0.002 wt%, Mn<0.001 wt%) and B₂O₃ (Fe<0.0008 wt%, heavy metals <0.0015 wt%), which were mixed homogeneously for the melt compositions of X_{Na₂O}/X_{B₂O₃}=1/2, 1/3 and 1/4. The Fe (0.15–15.9 wt%) and Mn (0.20–12.4 wt%) contents were adjusted by adding Fe₃O₄ or Fe₂O₃ and MnO or MnO₂, respectively. The 5–10 g of the sample in a Pt crucible was melted at 800–1100°C

for 2–72 h using the vertical resistance furnace (SiC heating element) and after a given time, it was then quenched by various cooling rates; a sandwich type of water cooled Cu plate, water or air. The furnace atmosphere was controlled by air or Ar–O₂, CO–CO₂ gas mixtures, which was injected from 3 cm above the melt surface. The melt was occasionally stirred with a Pt stirrer in some experiments except those for the attainment of equilibrium. The oxygen partial pressure was measured at 800°C using a ZrO₂–11 mol% CaO solid electrolyte having air as reference electrode. The oxygen partial pressure in Ar–O₂ mixture was determined by use of the relationship between emf and reciprocal flow rate, since the value of emf was found to be dependent on the flow rate.¹¹⁾ In the case of CO–CO₂ mixture, on the other hand, the value of emf was found to be independent on the flow rate in the studied range of 200–400 ml/min.

2.2. Analysis

The wet analyses were employed for the determination of the Fe²⁺ and Mn³⁺ contents. The finely powdered samples (0.1–1.0 g) were dissolved with H₂SO₄ (1+25) under CO₂ or N₂ atmosphere. The Fe²⁺ content in the sample was determined by colorimetry with o-phenanthroline.¹²⁾ The Mn³⁺ content was determined by the same method with dissolving the sample together with iron (II) ammonium sulfate solution. Potassium dichromate titration method (JIS-M-8213) was also employed in this experiment. The former method which is superior in the low concentration range was mainly used, despite the fact that the both methods indicated the fairly good agreement. The Fe²⁺ and Mn³⁺ contents were subtracted from those of T.Fe¹²⁾ and T.Mn (JIS-M-8215) to obtain the Fe³⁺ and Mn²⁺ contents, respectively.

In the system where Fe and Mn coexist, the ESR spectroscopy was employed to analyze the Fe³⁺ and

Mn²⁺ contents. The finely powdered samples (100 mg) in quartz sample tubes were analyzed at the liquid nitrogen temperature of 77.4 K by means of spectrometer (JEOL-JES2XG). Representative X-band spectrum of the sample doped with Fe and Mn is shown in Fig. 1, where the ESR peak at $g^*=4.25$ is attributed to the presence of Fe³⁺ and that at $g=2.0$ is to the Mn²⁺ ion. These values of g are well agreed with those of $g=4.27$ for Fe³⁺ and $g=2.00$ for Mn²⁺.¹³⁾ The peak intensities are related to the concentrations of specific redox ions, while the peak shapes and positions are related to the structural incorporation of that ion in the glass. Since the curve is the absorption first derivative line, the integrated absorption intensity, I is expressed by the following approximate equation.¹⁴⁾

$$I = A_{pp} \cdot H_{pp}^2 / W \quad \dots\dots\dots(1)$$

where, A_{pp} : the peak-to-peak distance

H_{pp} : the width of peak

W : the weight of sample.

The calibration lines were obtained from the relation between the integrated intensity and the concentrations of Fe³⁺ and Mn²⁺ ions determined by chemical analysis for the individual redox ions. The results are shown in Fig. 2, in which the good linearity expressed by the equation of (wt% Mn²⁺) = 0.143 · I was established with respect to Mn. The curved relationship was established with respect to Fe, since the peak shape was changed with increasing T.Fe contents. It cannot be considered, however, that the curved relationship was attributed to the experimental errors, judging from the fact that the linearity was obtained by integrating twice the absorption spectra.

3. Results and Discussion

3.1. Time for Attainment of Equilibrium

The time for attainment of equilibria of the Fe and Mn redox ratios was studied in the Na₂O·2B₂O₃ melts at 1 000°C under air. These results are illustrated in Figs. 3 and 4, indicating that the equilibrium is

Fig. 1. Representative X-band ESR spectrum at 9.16 GHz of Na₂O·2B₂O₃ glass containing Fe and Mn simultaneously.

Fig. 2. Calibration of the Fe³⁺ and Mn²⁺ ESR peak intensities to the concentrations of each ion determined by chemical analysis.

Fig. 3. Attainment of the Fe redox equilibrium with time of melting at 1 000°C for the Na₂O·2B₂O₃ melt containing 0.3 wt% T.Fe under air.

Fig. 4. Attainment of the Mn redox equilibrium with time of melting at 1 000°C for the Na₂O·2B₂O₃ melt containing 0.2 wt% T.Mn under air.

* $g = h\nu / \mu_B B$: h : Planck's constant, ν : Spectrometer frequency, μ_B : Bohr magneton, B : Magnetic field.

Table 1. Equilibrium compositions. (wt%)

$\log P_{O_2}$ (atm)	Temp. (°C)	Na ₂ O	B ₂ O ₃	Fe ²⁺	T. Fe
-0.68	800	27.5	64.6	0.038	5.53
		26.2	59.7	0.072	9.87
		17.2	75.9	0.055	4.88
	1 000	24.3	55.8	0.16	13.9
		30.0	64.7	0.055	3.48
		30.8	67.4	0.019	1.21
		31.2	67.4	0.013	0.99
		31.7	69.7	0.0093	0.35
		31.2	69.1	0.0092	0.35
		31.4	67.5	0.0085	0.35
		24.2	56.1	0.17	13.8
		31.7	68.1	0.0069	0.16
		31.2	68.3	0.0082	0.37
		30.8	68.7	0.0066	0.36
		30.5	68.4	0.011	0.74
		31.1	68.7	0.0031	0.15
		16.7	72.0	0.14	7.91
		18.7	79.5	0.015	0.71
		18.3	77.5	0.061	3.46
		16.2	69.3	0.18	9.80
		18.5	81.0	0.0064	0.37
		18.5	81.0	0.0069	0.37
-4.0	1 000	31.2	68.3	0.020	0.36
		30.6	68.3	0.039	0.72
		29.9	65.1	0.17	3.50
		30.8	68.7	0.019	0.35
		24.6	54.4	0.66	14.5
-8.1	1 000	30.9	68.0	0.077	0.74
		29.4	65.5	0.25	3.59
		30.7	68.7	0.053	0.37
		24.9	55.3	0.86	13.8
-0.68	1 100	23.1	52.8	0.41	15.9
		15.9	69.7	0.35	10.4

(continued. . .)

attained within 10 h for Fe and 5 h for Mn. The equilibrium was approached from both reduced and oxidized directions with addition of Fe₃O₄, Fe₂O₃ for Fe and MnO, MnO₂ for Mn, respectively. It was found in the case of the Fe₃O₄ addition that the redox ratio within 10 h was below the equilibrium value. This may be explained by the oxidation of Fe₃O₄ particles before melting.

The values of the redox ion in the present equilibrium experiments are summarized in Table 1.

3.2. Influence of Dopant Concentration

The dependence of dopant concentration upon the redox ratios of Fe and Mn was investigated in the Na₂O·2B₂O₃ and Na₂O·4B₂O₃ melts at 1 000°C. These results at various oxygen partial pressure are illustrated in Figs. 5 and 6. The Fe²⁺/Fe³⁺ ratios increase with decreasing T.Fe content in the Na₂O·2B₂O₃ melt. However, the dependence of dopant concentration was not observed in the Na₂O·4B₂O₃ melt under air atmosphere. The Mn²⁺/Mn³⁺ ratios in the low concentration range tend to increase with decreasing T.Mn by a smaller extent than those in

Table 1. Continued.

$\log P_{O_2}$ (atm)	Temp. (°C)	Na ₂ O	B ₂ O ₃	Mn ³⁺	T. Mn
-0.68	800	30.3	68.0	0.56	1.23
		22.2	76.0	0.33	1.29
	900	30.7	65.9	0.52	1.84
		23.4	75.1	0.25	1.18
		18.3	80.1	0.18	1.27
	1 000	31.7	68.0	0.040	0.21
		31.6	68.1	0.041	0.24
		31.6	68.2	0.043	0.24
		30.9	68.8	0.040	0.20
		29.8	66.9	0.66	2.97
		31.0	68.2	0.12	0.58
		30.4	65.6	0.73	3.04
		26.3	57.0	2.83	12.4
		31.2	68.6	0.037	0.20
		30.1	68.0	0.16	0.75
		30.6	68.9	0.086	0.41
		30.9	68.4	0.11	0.51
		29.9	66.8	0.57	2.48
		26.1	57.6	2.82	12.3
-4.0	1 000	22.1	76.3	0.15	1.16
		18.6	80.9	0.039	0.39
		18.7	80.8	0.023	0.34
		17.9	78.3	0.32	2.91
		18.6	81.0	0.030	0.34
		16.2	68.4	1.22	11.8
		25.6	57.7	0.81	12.4
		30.1	66.1	0.16	2.98
		30.5	68.8	0.024	0.55
		31.2	68.0	0.024	0.59
-8.1	1 000	30.8	68.8	0.012	0.28
		18.5	80.8	0.0016	0.31
		30.6	68.7	0.0065	0.56
		30.2	68.3	0.028	1.16
		30.0	66.2	0.037	2.97
		25.6	58.4	0.82	12.3
		25.8	58.3	0.66	12.3
		30.4	65.8	0.23	1.82
-0.68	1 100	30.4	65.7	0.27	1.82
		22.4	75.3	0.18	1.78
		17.8	79.7	0.14	1.85

the Fe²⁺/Fe³⁺ equilibrium.

In the case of $\log P_{O_2} = -8.1$, however, the experimental points are considerably scattered and besides the Mn²⁺/Mn³⁺ ratios decrease to a great degree over the high concentration range of T.Mn. The reason for this is not due to the change of melt composition by addition of Mn, but due to the following experimental procedure; that is, the CO-CO₂ gas mixture was used for the oxygen partial pressure of 10^{-8.1} atm in the present work. Therefore after equilibration, Ar gas was introduced for purging for a few minutes and then the sample was rapidly cooled. This shift of oxygen partial pressure may be the cause of the scatter of the experimental points as well as the marked decrease of the redox ratio with the increase of T.Mn content in comparison with the results obtained at $\log P_{O_2} = -4.0$ atm. The results obtained by Paul and Lahiri¹⁵⁾ under air are also included in

Fig. 5. Effect of T.Fe content on the Fe²⁺/Fe³⁺ ratio for the Na₂O-B₂O₃ melts at 1 000°C.

Fig. 6. Effect of T.Mn content on the Mn²⁺/Mn³⁺ ratio for the Na₂O-B₂O₃ melts at 1 000°C.

Fig. 6 for comparison, indicating that their values are higher than those of the present work.

As shown in Fig. 5, the Fe²⁺/Fe³⁺ ratio obtained at log P_{O₂} = -8.1 atm increases more with decrease of the T.Fe content, compared with that obtained at log P_{O₂} = -4.0 atm. This may be also explained by the above reason; however the experimental confirmation could not be made due to the difficulty of controlling oxygen partial pressure such as log P_{O₂} = -8.1 atm by the Ar-O₂ gas mixture.

It has been pointed out that redox ratios change on account of the change of temperature during cooling.^{4,16)} To confirm this, the sample was cooled under the various cooling rates—a sandwich type of water cooled Cu plate, water or air. As indicated in

Figs. 5 and 6, the change of the redox ratios due to the different cooling rates was not recognized. Accordingly, it can be concluded that the cooling rate used in this experiment was rapidly enough to preserve the equilibrium redox ratio that existed in the melt. Namely, the redox ratio in the melt was considered to be frozen without interaction with oxygen in the gas and/or the bulk. Goldman⁵⁾ confirmed experimentally that the redox ratio was not affected by the cooling rate as well as the oxygen partial pressure during cooling. On the other hand, Brückner¹⁶⁾ pointed out that the redox ratio might be changed during cooling by the reaction of O₂ not in the atmosphere, but in the bulk melt.

A number of the previous investigators¹⁻⁵⁾ have reported the dopant concentration dependence of redox ratio, particularly with the Fe redox. Although Goldman⁵⁾ explained the cause for the dopant concentration dependence by non-equilibrium state between gas and melt, this is discarded from the present results on the dependence of the cooling rate as shown in Figs. 5 and 6. The reason for the dopant concentration dependence may be understood thermodynamically from the change in the activity coefficient of Fe³⁺ ion with increase of its concentration, since the concentration of Fe²⁺ is always low. On the other hand, the effect of Fe³⁺ ion as a network modifier may be regarded as the reason for the dopant concentration dependence in the high concentration range. The more detailed on this subject are supposed to be necessary in future.

3.3. Factors Affecting Redox Equilibria

The redox ions such as Fe³⁺ and Mn³⁺ are considered to exist as complex anions in the melt. However, identification of such complex anions is not straightforward in general. In this paper, therefore, the redox ions are assumed to exist as single ions for the sake of simplicity. The treatment for the complex anions will be described in Sec. 3.3.3.

The reaction between redox ions in the melt is given by the following ionic equation:

where, M^{m+}, M^{(m-n)+}: the oxidation and reduction states of M ion, respectively

n: the number of electron transferred between redox ions.

The equilibrium constant K_M for Eq. (2) is represented as follows:

$$K_M = (a_M^{(m-n)+} \cdot P_{O_2}^n) / (a_M^{m+} \cdot a_{O^{2-}}^n) \quad \text{.....(3)}$$

where, a_i: the activity of i species

P_{O₂}: the oxygen partial pressure.

By taking logarithm in both sides of Eq. (3), we obtain,

$$\log [(M^{(m-n)+}) / (M^{m+})] = -(n/4) \log (P_{O_2}) + (1/4) \log K_M + (2n/4) \log (a_{O^{2-}}) + \beta_M \quad \text{.....(4)}$$

where, (M^{(m-n)+}) / (M^{m+}): the redox ratio

β_M: the constant related to the activity coefficient of redox ion.

Provided that β_M is constant, the redox ratio is determined by the oxygen partial pressure, the equilibrium constant which is a function of temperature, and the activity of O^{2-} ion in the melt.

3.3.1. Oxygen Partial Pressure

Under the constant temperature and melt composition, Eq. (4) may be rewritten as follows:

$$-\log P_{O_2} = (4/n) \cdot \log [(M^{(m-n)+})/(M^{m+})] + A_M \quad (5)$$

where, $A_M = -\log (K_M^{1/n} \cdot a_{O^{2-}}^{2/n}) - \frac{4}{n} \beta_M$.

Thus, a plot of $-\log$ (imposed oxygen partial pressure) against $\log$ (ratio of $Fe^{2+}(Mn^{2+})$ to $Fe^{3+}(Mn^{3+})$ concentrations) should be linear with a slope of 4 at the constant temperature, melt composition, and total dopant content, since $n=1$. Such a plot is displayed in Fig. 7 for the $Na_2O \cdot 2B_2O_3$ melts at 1 000°C. The result for the Mn^{2+}/Mn^{3+} ratio at the oxygen partial pressure of $10^{-8.1}$ atm is slightly deviated from the line with the slope of 4. For the Fe^{2+}/Fe^{3+} equilibrium, the slope was found to be 8, which is different from the predicted value. The oxygen partial pressure dependence of the Fe^{2+}/Fe^{3+} redox ratio in silicate melts obtained by the other workers is also included in Fig. 7, showing that the slopes of the lines vary with the melt compositions^{3,5,17}) and particularly the slope of 6.9 was reported at the composition of the high T.Fe content.¹⁸) The reason for this deviation may be explained by the term A_M in Eq. (5) which varies with the melt composition due to the change of the Fe^{2+}/Fe^{3+} ratio. Moreover it was found that in the present work, the Fe^{2+}/Fe^{3+} ratio varied even at the composition of the low T.Fe content as shown in

Fig. 7. Dependence of $\log (\%M^{red}/\%M^{ox})$ on $-\log P_{O_2}$ for the $Na_2O \cdot 2B_2O_3$ melts at 1 000°C compared with the previous works.

Fig. 5, although the reason for this is not clear. This may be related to the reason for the considerable deviation from the theoretical value. For the Mn^{2+}/Mn^{3+} equilibrium, the linearity with a slope of 4 was reported in the range of $-\log P_{O_2}=0-4$.^{3,19})

3.3.2. Temperature

Under the condition of the constant oxygen partial pressure and melt composition, the following relation given by Eq. (7) is obtained by substituting Eq. (4) to the van't Hoff isochore given by Eq. (6):

$$\partial(\Delta G^\circ/T)/\partial(1/T) = \partial(-R \ln K)/\partial(1/T) = \Delta H^\circ \quad (6)$$

$$\log [(M^{(m-n)+})/(M^{m+})] = -\Delta H^\circ/2.303R \cdot (1/T) + B_M \quad (7)$$

where, $B_M = (\Delta S^\circ/2.303R) + \log (a_{O^{2-}}^{2n/4} P_{O_2}^{n/4}) + \beta_M$: the constant term related to the oxygen partial pressure and melt composition

ΔH° : the enthalpy change of reduction given by Eq. (2)

R : the gas constant

ΔS° : the entropy change of reduction given by Eq. (2).

If the activity coefficients of redox ions, $a_{O^{2-}}$, and ΔH° remain constant over the temperature range, then the logarithm of redox ratio will be linearly related to the reciprocal absolute temperature. Since the reduction of a multivalent element given by Eq. (2) is always endothermic, the $(M^{(m-n)+})/(M^{m+})$ ratio increases with temperature. The temperature dependence of redox ratio is illustrated in Figs. 8 and 9. For the Fe^{2+}/Fe^{3+} equilibrium in the $Na_2O \cdot 2B_2O_3$ melts, the linear relation was not observed in the range of the low temperature, since the T.Fe content at the saturated composition (5.5–15.9 wt%) was chosen for these temperatures. The values of the enthalpy change of reduction ΔH° calculated from Eq. (7) are listed in Table 2 as a function of melt composition. The value of ΔH° for various melts obtained by the previous workers are summarized in Table 3 for comparison. The value of the reduction enthalpy is dependent on the melt composition as well as the properties of dopant element and the extent of which is correlated to the ease of reduction of the redox couple as monitored by the reduction potential.

3.3.3. Melt Composition

It is apparent from Figs. 8 and 9 that the Fe^{2+}/Fe^{3+} and Mn^{2+}/Mn^{3+} ratios decrease with increasing the Na_2O content, i.e., $a_{O^{2-}}$ in the melt at the constant temperature. According to Eq. (2), these experimental results indicate that the activity coefficients of redox ions change to a greater degree with melt composition than does $a_{O^{2-}}$ in the melt. Alternatively, the relation between the redox ratio and $a_{O^{2-}}$ may be explained by the following reaction given by Eq. (8) in which complex anion is assumed.^{20,21})

It may be noted that the slope of $-(n/4)$ in the

- 1: $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ -1.75wt% T.Fe¹⁷⁾
 2: $\text{Na}_2\text{O} \cdot \text{P}_2\text{O}_5$ -1.0wt% T.Fe²⁸⁾
 3: Lime-silicate-0.5wt% T.Fe⁵⁾

Fig. 8. Temperature dependence of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ equilibrium in the $\text{Na}_2\text{O}-\text{B}_2\text{O}_3$ melts under air compared with the previous works.

- 1: $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ -1.4wt% T.Mn¹⁹⁾
 2: $\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3$ -0.3wt% T.Mn¹⁵⁾
 2': $\text{Na}_2\text{O} \cdot 4\text{B}_2\text{O}_3$ -0.3wt% T.Mn¹⁵⁾

Fig. 9. Temperature dependence of the $\text{Mn}^{2+}/\text{Mn}^{3+}$ equilibrium in the $\text{Na}_2\text{O}-\text{B}_2\text{O}_3$ melts under air compared with the previous works.

plot of $-\log P_{\text{O}_2}$ vs. $\log$ (redox ratio) calculated from Eqs. (4) and (5) will not be changed in the use of Eq. (8) instead of Eq. (2). The enthalpy change in Eq. (8) may be calculated by the method similar to Eq. (7).

Table 2. The value of the enthalpy change of reduction.

Dopant element	$X_{\text{Na}_2\text{O}}/X_{\text{B}_2\text{O}_3}$	ΔH° (kJ/mol)
Fe	1/2	120
	1/4	80
Mn	1/2	60
	1/3	50
	1/4	40

Table 3. The value of ΔH° for the various melts.

Dopant element	Melt	Dopant conc. (wt%)	ΔH° (kJ/mol)	Ref.
Fe	$\text{Na}_2\text{O} \cdot \text{P}_2\text{O}_5$	1	47.0-53.3	2)
	Boro-silicate	1.03	126±42	3)
	Boro-silicate	<0.5	115.5	5)
	Lime-silicate	0.2-1.4	97±42	14)
	$\text{Na}_2\text{O} \cdot 2\text{SiO}_2$	1.75	115	17)
	Boro-silicate	1	307	18)
		5	281	
		10	172	
Mn	$\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3$	0.3	45-60	15)
	$\text{Na}_2\text{O} \cdot 2\text{SiO}_2$	1.4	57.75	19)

3.4. Mutual Interactions of Fe and Mn Redox Couples

The $\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3$ melt containing Fe (0.72-1.0 wt% T.Fe) and Mn (0.075-0.48 wt% T.Mn) simultaneously at 1 000°C under air was rapidly cooled in a sandwich type of water cooled Cu plate. The $\text{Fe}^{2+}/\text{Fe}^{3+}$ and $\text{Mn}^{2+}/\text{Mn}^{3+}$ ratios in the glass sample were determined by ESR spectroscopy. These results are given in Table 4. It can be predicted from the comparison of the results for a single multivalent redox ratio with those for the above two multivalent elements system, that the following electron exchange reaction would proceed to the right,

However, when the more than one multivalent element is present in the melt, discrepancy exists in the interpretation concerning the electron exchange reaction between redox ions. In the case where two multivalent elements are introduced into the melt, the redox ratios are fixed only by the reaction given by Eq. (2), that is, by a given oxygen partial pressure and melt composition, not by the mutual interactions of the redox couples. Paul and Douglas⁶⁾ consider that the reaction between redox ions in the melt is analogous to the oxidation-reduction titration in aqueous solutions and no evidence of complex formation was found. In addition, Schreiber and his co-workers⁷⁾ confirmed experimentally the existence of the mutual interaction in the melt, whose driving forces are i) the difference in relative reduction potential, and ii) the effect of interaction potentials (which are measures of the direct interaction by complexing *etc.*) of the two redox couples. This mutual interaction is proportional to the difference in the A_{M} term in Eq. (5), which corresponds to the relative value of the reduction enthalpy in the individual redox equilib-

Table 4. The value of wt% Fe³⁺ and wt% Mn²⁺ by ESR measurements for the two elements system compared with the single multivalent ratio determined by chemical analysis. (wt%)

Dopant concentration		Single system		Two elements system	
T. Fe	T. Mn	Fe ³⁺	Mn ²⁺	Fe ³⁺	Mn ²⁺
1.0	0.46	0.98	0.33	1.0	0.43
1.0	0.48	0.98	0.33	1.0	0.42
0.72	0.075	0.71	—	0.81	0.091

rium.

At this time, the mutual redox interaction at the melting temperature is not universally accepted. An alternative theory is that each individual redox equilibrium in the melt is established independently without any effects from mutual interaction. The interaction then takes place during quenching, depending on the enthalpy change ΔH° in Eq. (9) as well as the temperature dependence of the activity coefficient of redox ions.⁴⁾

Rüssel²²⁾ discussed theoretically the occurrence of electron exchange reaction during cooling and pointed out that the redox ratio varied with the cooling rate in the Na₂O(10mol%)-CaO(10mol%)-SiO₂(74mol%) melt. It was found impossible to check his theoretical approach with respect to the electron exchange reaction occurring during cooling, since physical properties such as diffusion coefficient of redox ion in the present Na₂O-B₂O₃ melts are not available. It cannot be concluded thus from the present results for the quenched glass samples whether the cause of the mutual interaction is attributed to the change of the activity coefficients of the respective ions due to mixing at a given temperature or to that due to the change of temperature during cooling.

4. Summary

Redox equilibria of Fe and Mn in the Na₂O-B₂O₃ melts have been determined as a function of dopant concentrations, oxygen partial pressures, temperatures and melt compositions. The results obtained are summarized as follows:

(1) The redox ratios (M²⁺/M³⁺) of Fe and Mn in the Na₂O·2B₂O₃ melt tend to decrease with increasing dopant concentration.

(2) A plot of $\log [(M^{2+})/(M^{3+})]$ vs. $-\log P_{O_2}$

shows a straight line of the slope of 8 and 4 for Fe and Mn, respectively.

(3) The values for the reduction enthalpy calculated from the temperature dependence of the redox ratios of Fe and Mn were found to be 80–120 and 40–60 kJ/mol, respectively. The M²⁺/M³⁺ ratios decreased with increasing the $X_{Na_2O}/X_{B_2O_3}$ ratio.

(4) It was shown by ESR spectroscopy that the electron exchange reaction: $Fe^{2+} + Mn^{3+} = Fe^{3+} + Mn^{2+}$ proceeded to the right; however the exchange reaction occurring during cooling could not be defined.

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