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Structure of Slag (VII)[†]

— Indicators to Difine Basicity of Slag —

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Abstract

Various indicators to define basicity of oxide melt such as (1) solution behavior of various gases (CO_2, SO_3 and water vapor), (2) coloring behavior of 3d transition elements, and (3) addition of element which is capable the transition of 6s-6p were summarized.

1. Introduction

It is an important matter to standardize the property of slag with a concept such as basicity or acidity because it helps our expectation concerning the ability of chemical reaction. Therefore, many researchers paid their attention deeply on this subject[1].

With our knowledge until today, the concept will be recognized as follows: According to the mechanism on the desulphorization reaction by Fincham and Richardson[2], it is generally accepted for that there exists three sorts of oxygen in molten slag under the following equilibrium

$$O^0 + O^{2-} = 2O^-. \tag{1}$$

In connection with the measurement of physical properties of slag, it has become clear that O^0 and O^-, respectively, gave and important effect on the solution of water vapor in molten slag.[3]-[5]

Furthermore, it was proved that the amount of O^- had correlation on the diffusibility of water through slag[6].

From these facts, it will be seen that the reactivity of molten slag could be judged from the amount of each oxygen species.

In 1940, Lux[7], Dietzel[8],[9], Flood and Förland[10], and Förland and Tashiro[11] developed the trial to determine the amount of free oxygen ion (O^{2-}) in molten glass. The study is now proceeding by Frohberg et al.[12].

To express the basicity of slag with the following index,

$$pO = -\log a_{O^{2-}}, \tag{2}$$

has been intended until now. However, there were many troublesome problems for the dynamical measurement of molten slag. Following these experimental difficulties, the original means, to apply various physical measurements on specimen which rapidly solidified from the molten state and to estimate the structure of molten slag should be jointly used.

In this report, the author exclude the electrochemical[7]-[12] as well as other physical means using chemical shift study with electron spectroscopy for the chemical analysis (ESCA)[13], molar refractivity[14] and Raman scattering[15]. Accordingly, the following subjects,

   1) solution behavior of various gases (CO_2, SO_3 and water vapor)

   2) coloring behavior of 3d transition elements

and 3) addition of element which is capable the transition of 6s - 6p, are in order, treated.

2. Solution Behavior of Various Gases (CO_2, SO_3 and Water Vapor)

2.1.1 CO_2 Solubility

In "Physical Chemistry of Melts", Tomlinson described that basicity or acidity of slag can be determined from the following property that the solubility of CO_2 increases with the increase of the basicity of slag[16].

The question "how much can gas be solved in glass?" has been continually presented since olden times. Eitel and Weyl studied the solubility of CO_2 in glass under high pressure of CO_2 and recognized that it increases with the increase of alkali-oxide content in glass as well as the

increase of CO_2 pressure[17]. Kröger and Goldmann[18] and Mahiux[19] studied the solubility of CO_2 with using radioactive tracer labelled with ^{14}C in B_2O_3-SiO_2, Na_2O-B_2O_3-SiO_2, Na_2O-CaO-SiO_2 and Na_2O-SiO_2 glasses. Under the conditions of P_{CO_2}=7.6mmHg, Mahiux admitted that glass of the system 28.5Na_2O-15CaO-56.5SiO_2 solved 0.05cc/g CO_2 at 1200°C and the solubility of CO_2 decreased to 0.02cc/g when glass of the 9.7CaO-74.85SiO_2 system was used. Kröger and Goldmann studied the CO_2 solubility by cutting the glass specimen to be three layers. The results obtained from this study are summarized as follows:

1) Absorption velocity of CO_2 in glass depended on the viscosity of melt.

2) Even if glass composition was changed from binary to three components, no particular change as to CO_2 solubility was recognized.

3) The glass containing carbonate former such as CaO showed less CO_2 solubility than B_2O_3-SiO_2 system. Besides CO_2 solubility decreased with the rising temperature of melt.

4) When compared CO_2 solubility between the glasses of Na_2O-SiO_2 and Na_2O-CaO-SiO_2 system, it was considered that CaO component showed no effect on CO_2 solubility. That is to say, it can be thought that CaO does not play an important role on CO_2 solubility in glass.

Accordingly, it can be interpreted that the equilibrium could shift on the left with the increase of CO_2 pressure as shown in equation 3.

$$(X\ SiO_2 \cdot Y\ Na_2CO_3)_{glass}$$
$$= (X\ SiO_2 \cdot Y\ Na_2O)_{glass} + Y\ CO_2 \qquad (3)$$
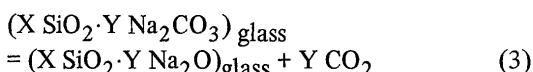
On the other hand, it will be understood that the equilibrium would shift on the right in the case of equation 4.

$$(X\ SiO_2 \cdot Z\ CaCO_3)_{glass}$$
$$= (X\ SiO_2 \cdot Z\ CaO)_{glass} + Z\ CO_2 \qquad (4)$$
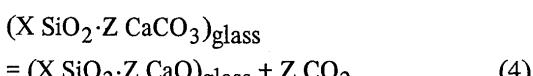
Pearce introduced the activity of free oxygen ion in glass with the following equations[20].

$$CO_2 + O_2 \overset{K}{=} CO_3^{2-} \qquad (5)$$

$$K = (a_{CO_3^{2-}}) / (P_{CO_2})(a_{O^{2-}}) \qquad (6)$$
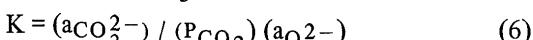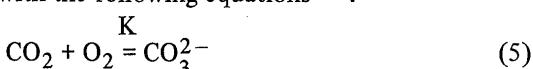
Under the conditions such as P_{CO_2}= 1 atm. and with the addition of smaller quantities of carbonate, the equation can be modified as follows:

$$K = (\%CO_3^{2-}) / (a_{O^{2-}}) = K'/(a_{O^{2-}}). \qquad (7)$$
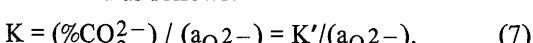
Further, the following relations can be introduced.

$$\log K = -\Delta H/4.575T + \Delta S/4.575 \qquad (8)$$
$$\log K' = A/T + C + \log a_{O^{2-}} \qquad (9)$$
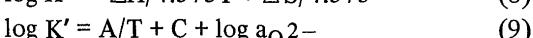
These relations were only applied on the system having comparatively higher activity of free oxygen ion
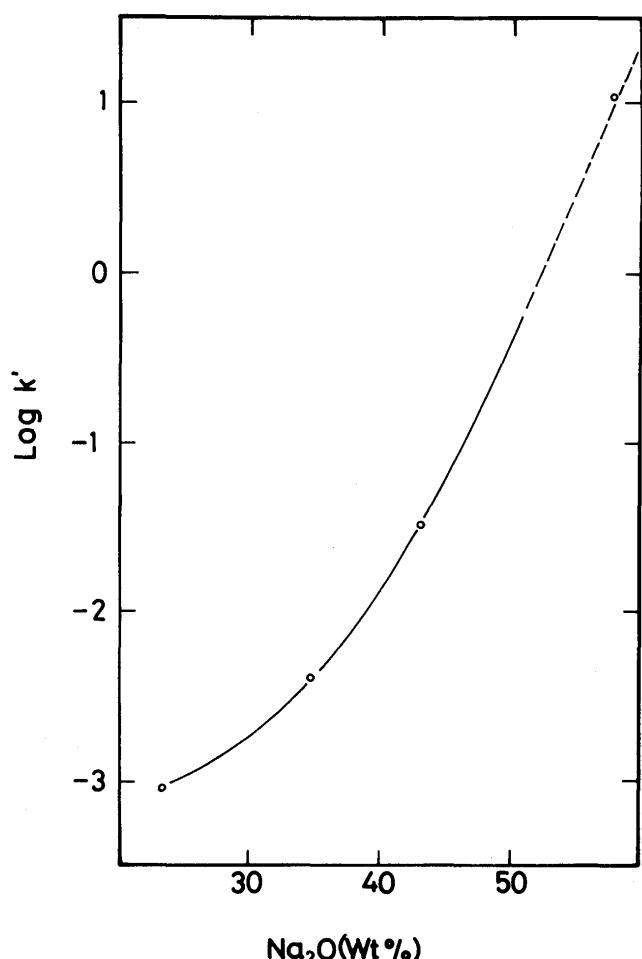

Fig. 1 Variation of oxygen ion activity with composition[20]

and lower melting temperature. K' value at certain temperature is in proportion to an activity of free oxygen ion and has dependency on a composition of glass. Figure 1 shows the change of log K' as for four kinds of composition. It is obvious that Na_2O content with only smaller addition gives remarkable effect on an activity of free oxygen ion in glass and the effect becomes considerable when the Na_2O content in glass is too much.

Franz and Scholze[21] gave the following index with using the data concerning CO_2 solubility in glass of Na_2O-SiO_2 system presented by Weyl[22]. The results are given in Table 1.

$$\Delta O = \log X_1\ (CO_2)/X_2\ (CO_2), \qquad (10)$$

where $X_1\ (CO_2)$ represents the CO_2 solubility in standard glass and $X_2\ (CO_2)$ is the one in probe glass.

Pearce compared the value of free oxygen ion activity calculated about glass of Na_2O-SiO_2 system with the one as for Na_2O-B_2O_3 system[24]. He used the following equations,

$$Na_2O\ (s, l) + CO_2\ (g) \overset{K_1}{=} Na_2CO_3\ (s, l), \qquad (11)$$

$$Na_2O\ (s, l) \overset{K_2}{=} 2Na\ (g) + 1/2\ O_2\ (g), \qquad (12)$$
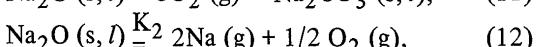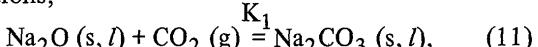
Table 1 ΔpO value from CO2 solubility[21]

Glass 1 (X_1) (mol ratio)		Glass 2 (X_2) (mol ratio)		ΔpO	X_1 (CO_2) / X_2 (CO_2)
Na_2O	SiO_2	Na_2O	SiO_2		
50	50	44.2	55.8	0.16	1.44
		38.2	61.8	0.34	2.16
		35.2	64.8	0.37	2.32
		33.3	66.7	0.41	2.60
		28.2	71.8	0.58	3.82
		26.5	7.35	0.73	5.40

$$CO_2 \text{ (g)} \underset{=}{\overset{K3}{}} C \text{ (s)} + O_2 \text{ (g)} \qquad , \qquad (13)$$

and $\quad 2Na \text{ (g)} + C \text{ (s)} + 3/3 \, O_2 \text{ (g)} \underset{=}{\overset{K4}{}} Na_2CO_3 \text{ (s, } l\text{)}. \quad (14)$
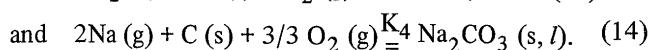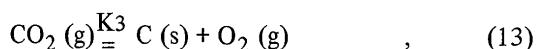
From the mutual relations, with combining next equation,

$$CO_2 + O^{2-} \underset{=}{\overset{K5}{}} CO_3^{2-} , \qquad (15)$$
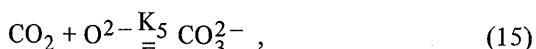
the conclusive equation is introduced.

$$a_{O^{2-}} = a_{CO_3^{2-}} / p_{CO_2} \cdot K_5 \qquad (16)$$
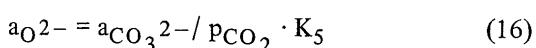
When infinitesimal dilution was taken as standard state, the equality, $a_{CO_3^{2-}} = N_{CO_3^{2-}}$, can be accepted and the equality, $K_5 = K$, can be realized when pure Na_2O was

Fig. 2 Variation of log a_O^{2-} with composition for sodium borate and sodium silicate melts[24]

taken as standard state for free oxygen ion. **Figure 2** shows these results.

2.1.2 SO$_3$ solubility

Turkdogan and Darken studied about an equiliblium between SO_2 gas and molten slag[25]. They obtained K_{SO_4} of calcium ferrite at various temperatures with the following equations.

$$SO_2 + 1/2 \, O_2 + O^{2-} \underset{=}{\overset{K_{SO_4}}{}} SO_4^{2-} \qquad (17)$$

$$K_{SO_4} = (\%S) / (p_{SO_2}) (p_{O_2})^{1/2} \qquad (18)$$
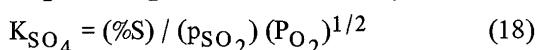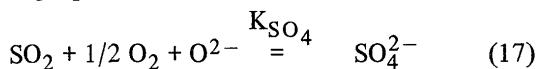
Hence, the following relation can be derived.

$$k_{SO_4} = (a_{SO_4}{}^{2-}) / (P_{SO_2}) (P_{O_2})^{1/2} \cdot (a_{O^{2-}})$$

$$= B (K_{SO_4}) / (a_{O^{2-}}) \qquad (19)$$

When the conversion coefficient between (S%) and ($\%SO_4^{2-}$), B, is introduced, $a_O{}^{2-}$ can be obtained. Good coincidence was found when these treatments were applied on glass of $CaO\text{-}SiO_2$ system[2, 26].

As for the reaction when $SO_2 + 1/2 \, O_2$ gases were blown into molten glass, Holmquist induced equation(21) through equation(20)on the supposition that no pyrosulphate could be formed.

$$SO_2 + 1/2 \, O_2 + O^{2-} = SO_4^{2-} \qquad (20)$$

$$[SO_4^{2-}] = k_{SO_4} [O^{2-}] P_{SO_2} \cdot P_{O_2}{}^{1/2} \qquad (21)$$
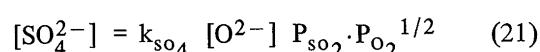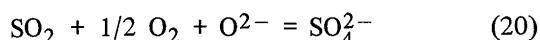
In **Table 2**, free oxygen ion activity obtained from the saturation curve of SO_3 (dotted line) at $1200°C$ in **Figure 3** is given with the simplified treatment that sulfate activity becomes nearly unity and therefrom the following equation can be used.

$$[O^{2-}] = 1/k_{SO_4} \cdot 1/(P_{SO_2} \cdot P_{O_2}{}^{1/2}) \qquad (22)$$
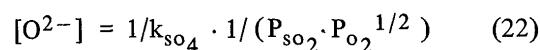
It becomes clear that the results obtained experimentally showed good agreement with the one calculated from means by Toop and Samis[28].

Table 2 Comparison of free oxygen ion activity from experiment and theory[26]

SiO_2/Na_2O	N_{SiO_2}	$10^4 \times P_{SO_2} \cdot P_{O_2}^{1/2}$	$10^{-4} \times P_{SO_2} \cdot P_{O_2}^{1/2}$	$\%O^{2-}$ K=0.001
1.50	0.60	1.9	0.52	0.050
1.75	0.64	3.0	0.33	0.039
2.00	0.67	4.5	0.22	0.028
2.50	0.71	9	0.11	0.019
3.00	0.75	15	0.07	0.013
4.00	0.80	33	0.03	0.006
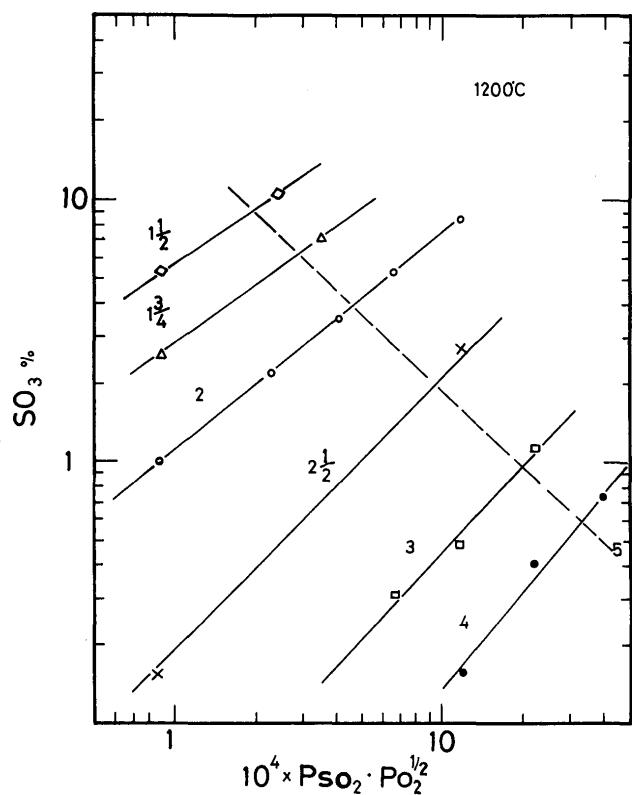
Fig. 3 Log-log plot of wt% SO_3 in melt vs. $10^4 \times P_{SO_2} \cdot P_{O_2}^{1/2}$ at 1200°C for silica to soda ratios of 1.50, 1.75, 2.00, 2.50, 3.00, and 4.00. The dashed line represents saturation[26]

From a practical point of view the most important question is to know the difference of role on basicity between Na_2O composition in glass and CaO in slag. In connection with this problem, Papadopoulos studied both effect on SO_3 solubility in glass and slag in detail[29]. At higher SiO_2 composition (67.5 - 77.5mol%), the following relation can be admitted.

$$[O^0] + [O^-] = [O_{total}] \qquad (23)$$

Using equation(24)induced from simple calculation, last term in the right hand, $[Na^+]^2[O^-]2/[O^0]$ = J, was compared with the solubility of SO_3.

$$[SO_3] = P_{SO_3}\left\{K\ (\gamma_{Na^+})^2\ (\gamma_{o^-})^2\ /\gamma_{o^0}\cdot\gamma_{Na_2SO_4}\right\}$$
$$\left\{[Na^+]^2\ [O^-]^2/[O^0]\right\} \qquad (24)$$

It will be seen that good correlation between the solubility of SO_3 and J value is not materialized as shown in Table 3, but good linear relation between them was

Table 3 Comparison of SO_3 solubility in glasses and J value calculated (P_{SO_3}=0.01atm., 1370°C)

| Glass	SiO_2	CaO	Na_2O	SO_3	J
1	0.721	0.136	0.127	0.00745	0.0154
2	0.741	0.089	0.159	0.00664	0.0205
3	0.707	0.200	0.083	0.00280	0.0080
4	0.653	0.195	0.133	0.01216	0.0315
5	0.685	0.145	0.154	0.01066	0.0317
6	0.778	0.090	0.123	0.00360	0.0084
7	0.778	0.144	0.071	0.00133	0.0029

recognized when diagrammatized in Figure 4.

In Figure 5, an effect on the solubility of SO_3 when
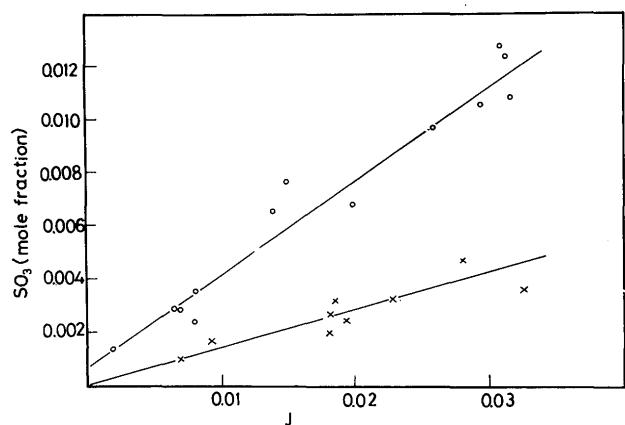
Fig. 4 Dependence of SO_3 solubility in soda-lime-silica melts at 1370°C on the composition parameter J [29]
P_{SO_3} = 0.01atm.
x SO_2 alone, nominal P_{SO_2} = 10^{-4} atm

$$f_{H_2O} (g) = K_2 \cdot P_{H_2}{}^0 \qquad (27)$$

Activity of OH^- ion in oxide melt is proportional to the square root of water vapor, so the following equation can be derived.

$$a_{OH^-} = L\sqrt{P_{H_2O}} \text{ or } a_{OH^-}{}^2 = L^2 \cdot P_{H_2O}, (28)$$

where L denotes the solubility of water vapor in oxide melt. When summarized the equations above-described, the following equation can be obtained.

$$a_{O^2-} = K_3 \cdot L^2 \qquad (29)$$

At $P_{H_2O} = 1$, the equation

$$a_{O^2-} = K_3 \cdot X_{H_2O}{}^2 \qquad (30)$$

is given.

To remove K_3 with the use of equation (24)

$$a_{O_1^2}{}^- / a_{O_2^2}{}^- = \{(X_1(H_2O)/X(H_2O)\}^2 \qquad (31)$$

can be derived.

Accordingly, the following equation is obtained.

$$pO_2 - pO_1 = \Delta pO = 2 \log X_1/X_2 \qquad (32)$$

Fig. 5 Composition parameter J in soda-line-silica glasses[29]

Na_2O was substituted with CaO are shown. The more Na_2O to CaO was substituted, the less the solubility of SO_3 becomes. In analogy with the equation (10) given by Franz and Scholze[21], we can determine ΔpO from the following equation.

$$\Delta pO = \log X_1 (SO_3)/X_2(SO_3), \qquad (24)$$

where $X_1(SO_3)$ and $X_2(SO_3)$ denoting the solubility of SO_3 in standard and probe specimens respectively.

2.1.3 H_2O Solubility

In previous report[1], the author summarized problems about the solubility of water vapor in glass and slag melts. Therefore, the problem to determine the basicity of them is only treated in this report.

As obvious from the following equation, it was proved that the more an activity of free oxygen ion in glass or slag is, the more solubility of water vapor becomes.

$$H_2O(g) + O^{2-}(\text{glass, slag}) = 2OH^-(\text{glass, slag}) \qquad (25)$$
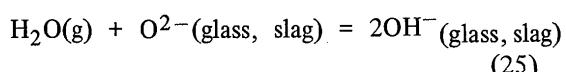
Using this equation, equilibrium constant K_1 can be derived.

$$K_1 = (a_{OH^-})^2/a_{O^2-} \cdot f_{H_2O}(g), \qquad (26)$$

where, f_{H_2O} represents fugacity of water vapor in gas. Accordingly, the following relation is given.

Fig. 6 Basicity of binary alkali-silicate melt [21]

In **Figure 6**, an example which treated the solubility data of water vapor at $1700°C$ in glass of $M_2O\text{-}SiO_2$ system with eq. (32) is shown.

The comparison between cation-oxygen attraction parameter and the content of M_2O used is shown in **Figure 7**.

ΔpO value obtained from the solubility of water vapor in glass is given in **Table 4**. An interesting contrast between Tables (1) and (4) should be discussed.
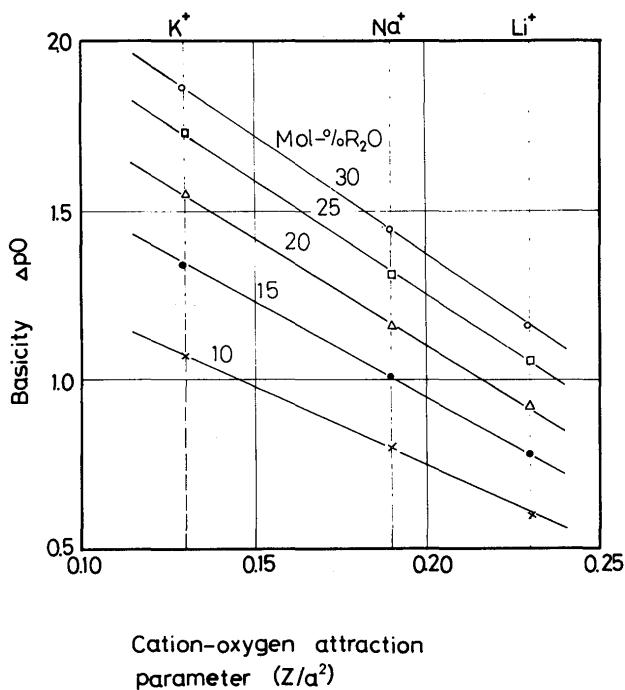
Fig. 7   Relationship between basicity and field strength of cation[21]

Fig. 8   Free-oxygen factor vs. MOA factor when Na_2O and CaO were substituted for SiO_2 in amber glasses[30]

Table 4 Λ pO value from water vapor solubility[21]

Glass 1 (X_1)		Glass 2 (X_2)		pO	X_1 (H_2O) / X_2 (H_2O)
(mol ratio)					(at 1250°C)
Na_2O	SiO_2	Na_2O	SiO_2		
50	50	44.2	55.8	0.09	1.11
		38.2	61.8	0.20	1.25
		35.2	64.8	0.24	1.33
		33.3	66.7	0.29	1.38
		28.2	71.8	0.40	1.58
		26.5	73.5	0.44	1.65

Harding[30] studied the interrelation between the solubility of water vapor and the alkali- or alkaline earth oxide content, and compared his result with the one by Uys and King[31] and Franz and Scholze[32]. Principal conclusions obtained are as follows:

1) Acidic oxide melt can solve much water vapor than basic one. This fact can be interpretted from that bridging oxygen could only contribute to the solution of water vapor with following equation.

$$- Si - O - Si - + H_2O = [-Si - OH]   (33)$$

2) Accordingly, the solubility of water vapor increases when Na_2O or K_2O substituted to Li_2O having greater cation-oxygen attraction parameter.

3) The substitution to MgO, CaO or SrO from Na_2O does not give an effect on the solubility of water vapor but BaO showed a meager action on the

solubility of water vapor. Only this fact can not accept the solution mechanism given as equation (33).

4) It seems difficult to extend the data obtained as for binary system onto ternary system. (In ref. (32), an example is shown.)

In **Figure 8**, comparison between (Fe^{3+}/Fe^{2+}) and $(O^-)^2/(O^0) \propto (O^{2-})$ is shown. In summary, it can be said that the quantity of (Fe^{3+}/Fe^{2+}) shows increase with increasing of (O^{2-}) quantity.

Furthermore in **Figure 9**, the quantity of (Fe^{3+}/Fe^{2+}), which is called as metallic oxygen activity, is compared with field strength index = Σ (mol fraction x field strength x number of cations/molecule).

As might be expected, the strongest dependence between these factors and the solubility of water vapor was observed.

3.1   Judgement by Various Coloring Agents

3.1.1   Preface

We can obtain many fruitful informations as following by adding various coloring agents in oxide melt,[33]
1) oxidation state of glass or slag,

agent has been considered many times over the past years, it has disadvantage that it is impossible to know continuous variation of inner oxygen potential in oxide melt in the same manner as indicators added for the determination of pH in aqueous solution. However equivalent quantity of alkali or alkaline earth oxide necessitated for a color change in oxide melt by adding coloring agent can be determined and hence we can obtain the information as for basicity or acidity of oxide melt.

In **Table 5**, classification of color change when used various coloring agents by Weyl[33] is given.

From a practical point of view the two most important questions are to know color change with the variation of partial oxygen pressure equilibrated as well as the variation of chemical composition. As is seen in the other papers, this has not been reported in the literature.

Furthermore the notices should be paid for its application and correct method of usage[34].

1) Under violent oxidizing or reducing conditions, it does not necessarily follow that a redox ion, which can take various valence states, takes only one state.

2) When solution means with chemical reagent is used to determine valence state, we should pay attention on the following Cannizaro reaction.

$$2Cu^+ = Cu^0 + Cu^{2+} \qquad (34)$$

$$V^{3+} + V^{5+} = 2V^{4+} \qquad (35)$$

Fig. 9 Field-strength factor vs. MOA factor for amber glasses with substitutions noted.[30]

2) basicity or acidity

3) coordination number of ion and to know the change with temperature or composition,

4) disorder of electric field in the neighborhood of an ion.

Table 5 Color induced from coloring ion in glass[33]

Ion	Network former	Modifier
Cr^{3+}	—	green
Cr^{6+}	yellow	—
Cu^{2+}	yellowish-brown	blue
Cu^+	—	colorless, brown fluorescence
Co^{2+}	purple	pink
Ni^{2+}	purple	yellow
Mn^{2+}	nearly colorless, green fluorescence	weak orange, with red fluorescence
Mn^{3+}	purple	—
Fe^{2+}	—	absorption in the infrared
Fe^{3+}	deep brown	weak yellow to pink
U^{6+}	yellowish-orange	weak yellow, strong green fluorescence
V^{3+}	—	green
V^{4+}	—	blue
V^{5+}	colorless to yellow	—

An effective extent of a coloring agent can be determined from the necessary inner oxygen potential for the color change. Although the application of coloring

Moreover, it should be noticed that a redox ion can take different coordination number though same valency state depending on the melting temperature and the

solidifying velocity. As an example, there appears MO_4 or MO_6 (M---Fe, Co, Ni).

As described above, it is necessary to use only one or multiple agents depending on the characteristic of indicator used as occasion calls, the choice of the judgement such as physical or chemical means.

3.1.2 $Cr^{6+} - Cr^{3+}$

The application of this agent in glass was done in 19 century. At first, Irmann[35] studied the relation between partial oxygen pressure and the ratio of Cr^{6+}/Cr^{3+} and found that the ratio changed with $P_{O_2}^{1/4}$.

$$(Cr^{3+})_{glass} + 3/4\ O_2\ (g) \rightarrow (Cr^{6+})_{glass} \qquad (36)$$
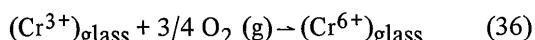
Nath and Douglas studied the variation of the ratio, Cr^{6+}/Cr^{3+}, with the change of alkali oxide content such as Li_2O, Na_2O and K_2O, and the results are shown in **Figure 10.**[37]
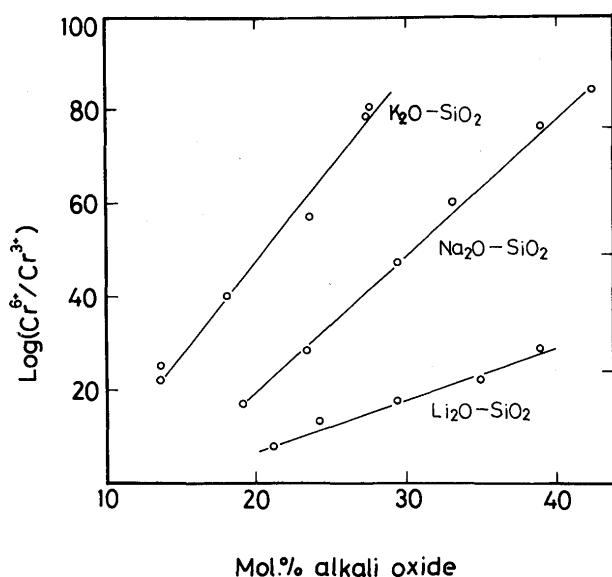

Fig. 10   Equilibrium (Cr^{6+}/Cr^{3+}) ratio in different alkali silicate glasses at 1400°C [37]

3.1.3 $Fe^{3+} - Fe^{2+}$

Michel and Schumann[38] found that the ratio of Fe^{3+}/Fe^{2+} changed with $P_{O_2}^{1/4}$ in silicate slag. From olden times, the utilization of the ratio, Fe^{3+}/Fe^{2+}, to decide basicity of oxide melt has been recommended. However, there are many troublesome problems and reexamination is necessary.

1) One has to point out that the relation of the coordination site of Fe^{3+} and slag composition is uncertain as often pointed out that Fe^{3+} takes tetrahedral site in case of silicate but it takes octahedral site on the occasion of phosphate[39].

2) Though assignment of each optical absorption sites has

became clear[40], it occurs frequently broad band and hence it is difficult to treat quantitatively.

3) It is thought that at higher temperature (molten state) it is apt to occupy $Fe^{3+}O_4$ (tetrahedral site) but at lower temperature (solidified) to occupy octahedral site as $Fe^{3+}O_6$ is easier. Accordingly, the occupied ratio of both sites are determined from various factors such as melting temperature, cooling velocity, and viscosity of melt. Further we should pay our attention that the occupation of tetrahedral site increases with the increase of CaO/SiO_2 ratio or P_{O_2}.

As above described, more detailed experimental research is required to determine the ratio of total Fe^{3+}/Fe^{2+}.

Here, the author should like to show our result as for total Fe^{3+}/Fe^{2+} with the change of CaO/SiO_2 ratio ro P_{O_2} with Mössbauer means[40]. In **Figure 11**, the result of
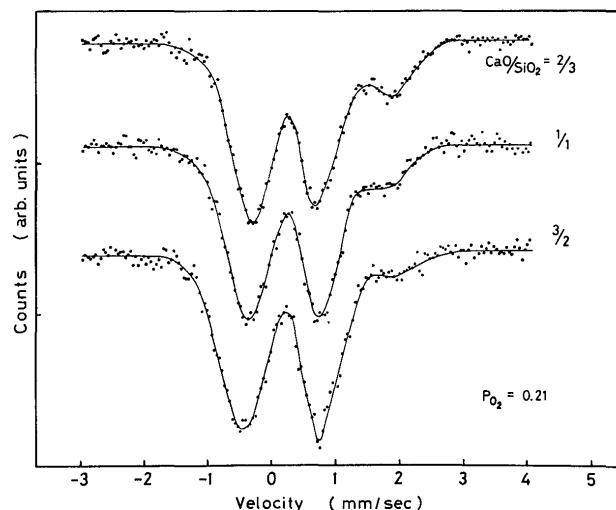

Fig. 11   Mössbauer spectra of glasses with various compositions produced in air [40]
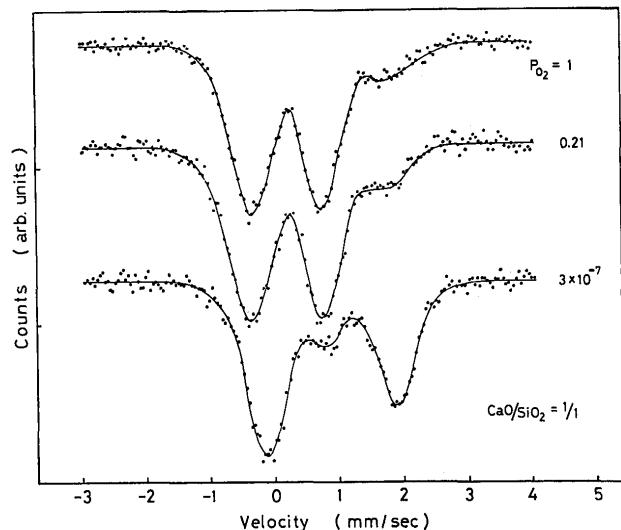
Fig. 12   Mössbauer spectra of glasses with constant composition (CaO/SiO2 = 1/1) produced under various oxygen pressures (P_{O_2})[40]

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CaO–SiO$_2$ slag containing 0.2mol% Fe$_2$O$_3$ with the change of CaO/SiO$_2$ ratio is shown. In **Figure 12**, the result with the change of P$_{O_2}$ is shown. In **Figure 13**, the

obvious at a glance the contribution of each alkali metal oxide (Li, Na and K) on basicity of glass. It can be read off the gradient that to add small quantity of K$_2$O has
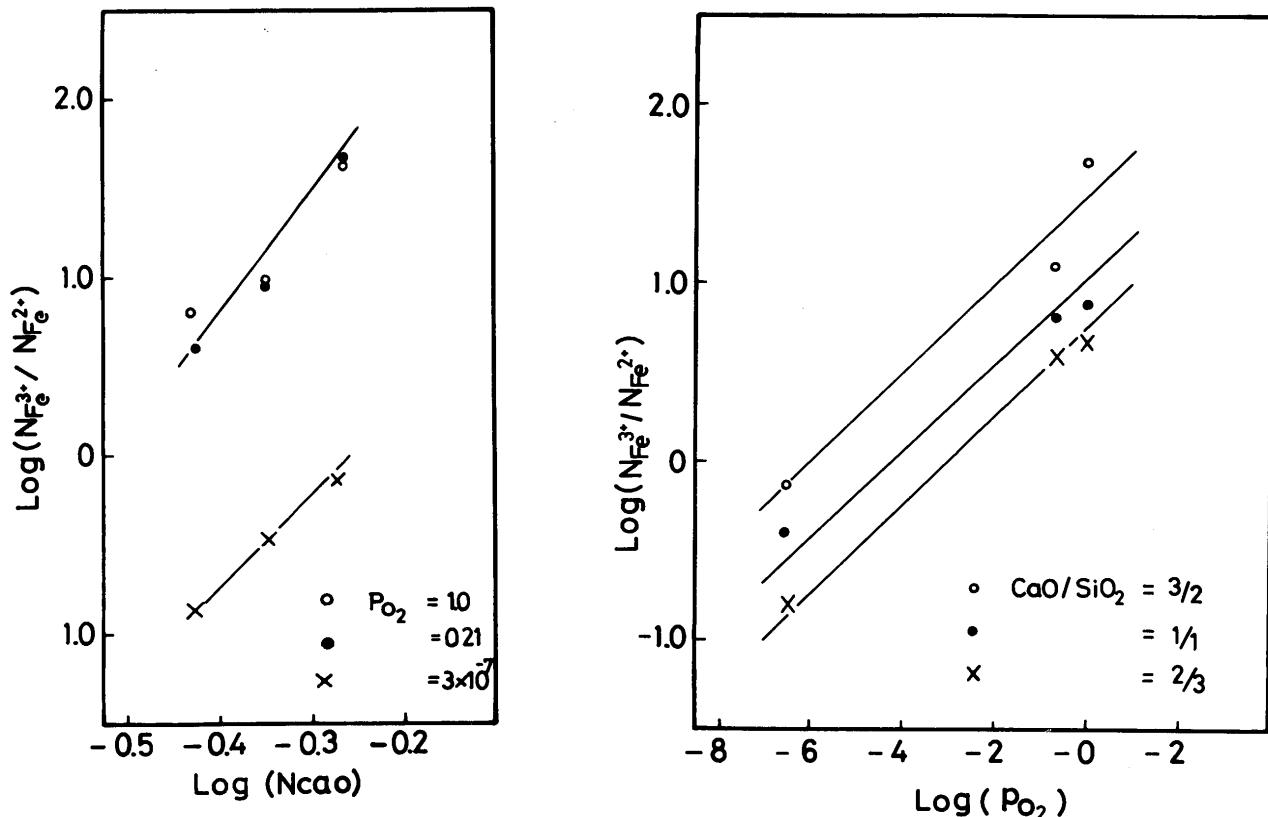

Fig. 13 The effects of N$_{cao}$ and P$_{o2}$ on N$_{Fe3+}$/N$_{Fe2+}$[40]

relation between the ratio of total Fe^{2+}/Fe^{3+} and N$_{CaO}$ or P$_{O_2}$ is shown. In each cases, it will be seen the 1/4 grade.

Let us pick up some points which are problems.

1) In case of P$_{O_2}$ = 0.21 or 1 atm., the ratio, Fe$^{3+}_{tet}$/(Fe$^{3+}_{tet}$ + Fe$^{3+}_{oct}$), remains in the neighborhood of 0.5 even if the ratio, CaO/SiO$_2$, was changed.

2) On the occasion of P$_{O_2}$ = 3 X 10^{-7}atm., the ratio of Fe^{3+}/(Fe$^{3+}_{tet}$ + Fe$^{3+}_{oct}$) changes from 0.3 to 0.5 with the increase of CaO content.

3) With the decrease of Fe$_2$O$_3$ content, coordination state of Fe^{3+} becomes unclear. As seen in **Figure 14**, it seems to be quite all right to consider the possibility of both occupations, tetrahedral and octahedral sites, as for Fe^{2+} ion.

3.1.4   Other transition metal ions

Paul and Lahili expressed the relation between $\triangle$G = RTlnP$_{O_2}$ and redox reaction of various transition metal ions (Cr, Mn, Ce, As, Sb and Fe)[41]. Especially, he treated the reaction of Mn^{3+} –Mn^{2+} in detail and the result is shown in **Figure 15**. From this diagram, it is

more effect on the increase of oxygen ion activity than Na$_2$O and Li$_2$O.

However, it should be solved contradiction to interpret the following equations.

$$Mn^{2+} + 1/4 \, O_2 = Mn^{3+} + 1/2 \, O^{2-} \qquad (37)$$

$$K = [Mn^{3+}] \, [O^{2-}]^{1/2} / [Mn^{2+}] \, P_{O_2}{}^{1/4} \quad (38)$$
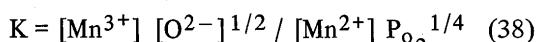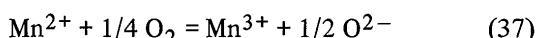
Accordingly, it has been taken various countermeasures introducing activity coefficient[42] or to consider the formation of complex negative ion[43], [44].

We have studied the behavior of Mn indicator in glass of Na$_2$O-SiO$_2$ system when Na$_2$O content was changed, and considered the following possibility that, depending on partial pressure of oxygen, either Mn^{2+} can be changed to octahedral Mn^{3+}, or tetrahedral Mn^{2+} can be transfered to octahedral Mn^{2+} [45]. In **Figure 16**, the relation between O^{2-} content measured with molar refractivity and Mn^{3+} is shown. In **Figure 17**, O^{2-} content which was given by Kapoor and Frohberg[46] and by Masson, Smith and Whiteway[47] is compared with Mn^{3+}. These results can explain well the experimental evidence that a large change as for Mn^{3+}/Mn^{2+} can not be
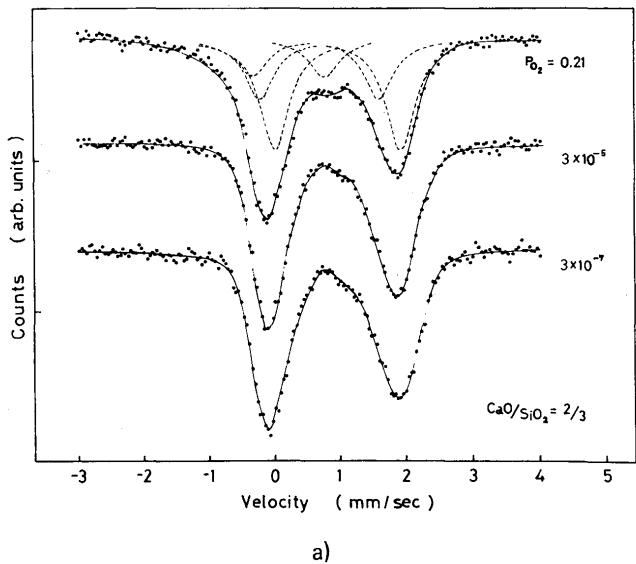
a)
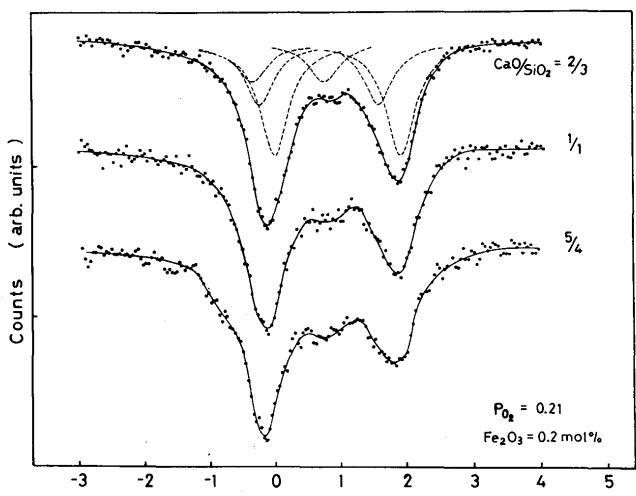
b)

**Fig. 14** Mössbauer spectra of glasses with various compositions
a)   produced in air
b)   Mössbauer spectra of glasses with constant composition (CaO/SiO_2 = 2/3) produced under various oxygen pressures

expected with a inconsiderable change of partial oxygen pressure.

Johnston added various indicators (Ti, Sn, Fe, Sb, Ce, Mn, Co, or Ni) in $Na_2O \cdot 2SiO_2$ glass and obtained the
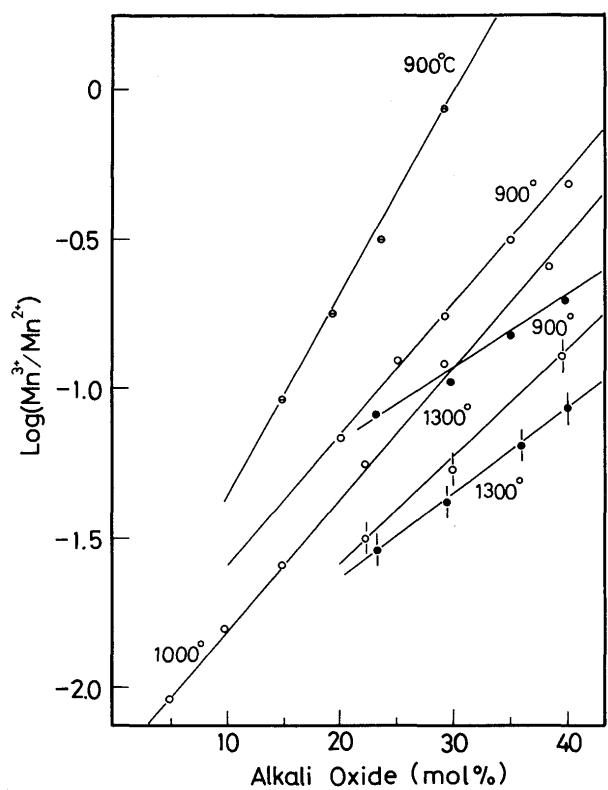
Fig. 15 Variation of Mn^{3+} — Mn^{2+} equilibrium with basicity in binary alkali borate glasses[41]
$\ominus$ = $K_2O\ B_2O_3$, o = $Na_2O\ B_2O_3$, ● = $Li_2O\ B_2O_3$
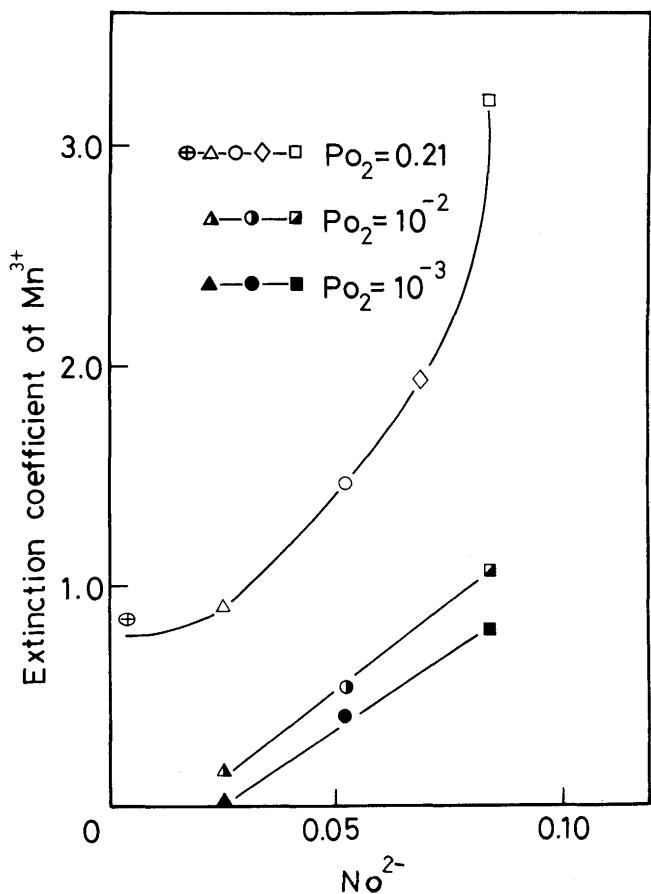
Fig. 16 Dependency of $E_{Mn^{3+}}$ upon the content of the free oxygen, $N_O{}^{2-}$, decided from molar refractivity[45]
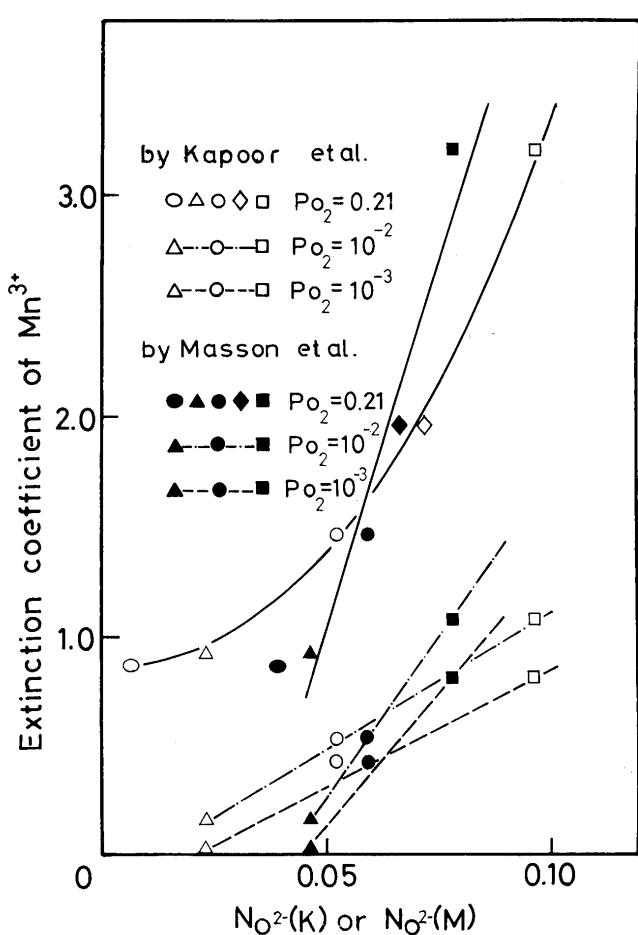
Fig. 17 Dependency of $E_{Mn^{3+}}$ upon $N_{O^{2-}}$ decided from theoretical approaches[45]
(N_{O^2}–(K); after Kapoor and Frohberg, N_{O^2}–(M); after Masson, Smith and Whiteway)

results as shown in **Figure 18**. He indicated that the
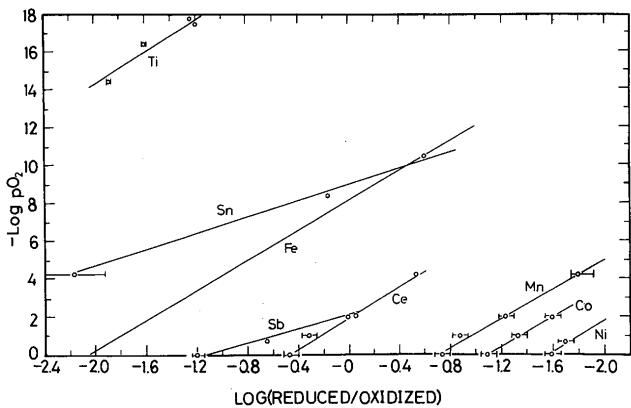
Fig. 18 Equilibrium dependence of log $(M^{x+}/M^{(x+n)+})$ on log $-P_{O_2}$

gradient can be changed by own impurity, but did not study the effect of compositional change. The experiment as for Cr^{6+}—Cr^{3+} was unsuccessful because

chromium did not sufficiently dissolve in glass. Likewise the experiment used vanadin showed problem as given in equation (35) because there can exist three species such as V^{5+}, V^{4+} and V^{3+} depending on partial oxygen pressure. It was only certified 1/4 gradient law between V^{5+}/V^{4+} and between V^{4+}/V^{3+}.

Douglas, Nath and Paul[51] obtained experimental equation for the change of $N_{oxidized}/N_{reduced}$ with compositional change by using indicator such as Cr[36], Ce[49] and Fe[50].

Though a problem when two species of redox ion were inserted is treated[52], it will be neglect because the author think that the extension from binary to ternary composition is important.

4.1 Means Using Tl^+, Pb^{2+} or Bi^{3+}

As above mentioned, there exists difficult problem in using transition metal ion as indicator to determine basicity of oxide melt. Therefore, we can say that the mean is second-hand information depending on partial pressure at the time of melting.

Duffy and Ingram noticed that gradual change in basicity of oxide melt would follow with the use of $d^{10}s^2$ metal ion such as Tl^+, Pb^{2+} or Bi^{3+} directly from s - p transition occuring in ultraviolet region, that is to say, an ability giving negative charge from oxygens constituted glass or slag.[53]

As shown in **Figure 19**, it will be understood that the
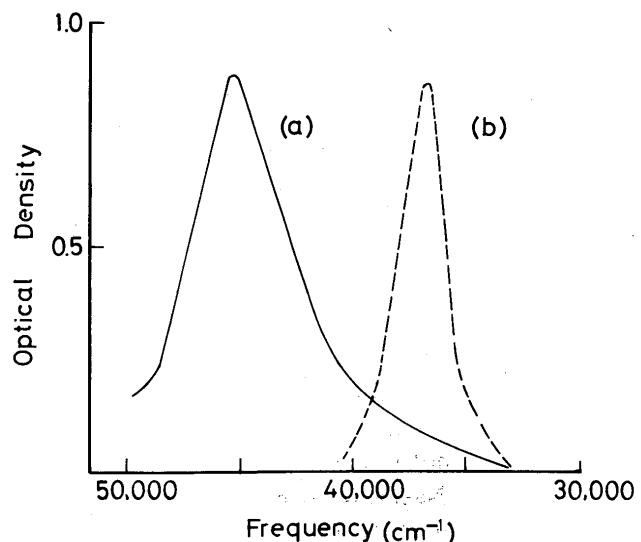
Fig. 19 Absorption spectrum of Pb^{2+} in sodium borate (20% Na_2O) glass (a) and in 11MHC (b).[53]

optical shift is notable. It was found that the optical shift became smaller with the increase of basicity of oxide

melt[54].

As principle, we can obtain optical basicity Λ from the following equation.

$$\Lambda_{Pb\,(II)} = (\nu_{free\ ion} - \nu_{glass}) / (\nu_{free\ ion} - \nu_{o^2-})$$

$$= \Delta\nu_{glass}/\Delta\nu_{o^2-} = \Delta\nu_{glass}/31{,}000 \quad (40)$$

, where, $\nu_{free\ ion}$ is an imaginary value and it can be obtained from interpolation of various frequencies which was determined with indicators. The value is thought as frequency when the indicator is existing as gaseous state. As for Pb (II), it becomes 60,700 cm^{-1} [55]. ν_{o^2-} gives the frequency of Pb (II) in "ionic" oxide (for an example, CaO). The difference between 60,700 and ν_{o^2-} gives the situation which Pb (II) ion can be given an electron density from free oxide. The ratio of the difference, 31,000 cm^{-1}, and the electron donor power of oxides in glass has been termed as optical density.

When there exist oxides more than two species, the basicity moderating power, γ, introduced with the use of Pauling's electronegativity values is used for the correction because the poralization or attractive force for an electron differs in each cations.

$$\gamma = 1.36\,(x - 0.26) \quad (41)$$

, where x is denoting the Pauling's electronegativity values.

Accordingly, the equation is transformed as follows:

$$(\nu_{glass} - \nu_{o^2-}) = (\nu_{free\ ion} - \nu_{o^2-}) \cdot$$

$$\{(Z_A r_A/2)(1 - 1/\gamma_A) + (Z_B r_B/2) \cdot$$

$$(1 - 1/\gamma_B) + \cdots \cdots \} \quad (42)$$

, where Z_A and Z_B denote oxidation number of cation A and B, and r_A and r_B represent oxygen ion ratio in total oxygen number of cation A and B.

The good correspondence between optical basicity and molar refractivity has been given[53], and many interesting results were obtained with the thought[54].

The results obtained can be summerized as follows:

1) In $B_2O_3 \cdot M_2O$ glass, $\Lambda_{Pb(II)}$ takes an order, $Li^+ < Na^+ < K^+$, and the result supports an usual concept.

2) When boron or potassium was substituted with aluminium ion in $K_2O\ B_2O_3$ glass, Λ decreases in the latter case but it increases in the former. Form this evidence, it was shown that Al (III) has a lesser effect to decrease basicity than B (III).

3) There seems no difference of Λ between Na_2O-SiO_2 (30:70) and Na_2O-SiO_2-CaO (20:70:10) glasses. It is considered that Ca(II) ion behaves similar action with alkali metal ion.

In addition to these results, many interesting articles such that, for an example, the good correspondence between the change of transition temperature of Na_2O-B_2O_3 glass with the change of Na_2O content and

the value was observed.[55]

5. Summary

The author have introduced various trials to define basicity of oxide melt. In spite of the presentation of various means which seem powerful to determine the nation of basicity, it gives the possibility to give information only in binary system, especially, about alkali metal ions such as Li, Na and K. As a drawback is pointed out in the interpretation of redox reaction as well as electrochemical means[56], [57] the solution of investigator in these field are wished.

It has become clear that there exists difficulty to extend our knowledge from binary to multiple system.

It should be performed to use jointly with various means of state analysis such as NMR and ESR.

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