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Structure of Slag (VI)†

—Diffusion in Slag—

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Abstract

The diffusion behaviours of various elements inclusive of gas components such as helium, neon, nitrogen and water were summarized. It was emphasized that the structure of glass or slag such as oxygen density and the difference of coordination state of aluminium ion had remarkable effect on the diffusion of water. To discuss chemical reactions among gas-slag-molten metal, these knowledges will give considerable contribution.

Introduction

In the fields such as metal-refining, steelmaking, ceramic-spraying and surface treatment, it is necessary to make clear and to control the chemical reaction between slag/ceramic and matrix (solid or liquid phase) in the presence of gasous phase.

In the case of iron-and steel-making, the problems of deoxidation, desulphurisation, dephosphorisation, to minimize nitrogen content and the partition of alloying elements added become a subject of discussion.

In the occasion of welding a problem awaiting solution to bring the gas solubilities of hydrogen, oxygen and nitrogen in weld metal to minimum value is of important matter.

In the event of surface treatment, it is required to obtain good attachability between sprayed matter and metal matrix.

The author has considered various problems occurring when slag is used from the standpoint of structural theory, and especially in the preceding report treated about gas-absorption-behaviour in slag.

However, it can readily imagined that an ease of gas mobility in molten slag, from gas atmosphere to molten metal has to govern the problem of elemental transfer among gas, slag and molten metal ultimately. Accordingly, it becomes necessary to collectively consider the diffusion behaviours of various cation and anion in slag.

While it is frequently discussed that an intimate correlation will be arranged between diffusivity and electrical conductivity or viscosity in simple liquid, and the consideration as for these viewpoints will be treated in this report.

From the knowledge that magnitude of diffusivity of anion concerns the size, it gives important information to build up the structural theory of slag.

Experimental Procedures

1) Instantaneous plane source method

Johnston, Stark and Taylor[1] used this method to study diffusion in liquid slags. They say that this mean is by far the more convenient and also can be used to study the diffusion of short-lived isotopes. A vanishingly small amount of radioactive tracer is deposited on to the surface of slag capillary specimen. The appropriate solution of Fick's law for these conditions is given by

$$C=Q/\sqrt{D^*t}\ \exp\,(-x^2)/4D^*t \qquad (1)$$

where

C =concentration of radioactive atoms at a distance x from the deposit

Q =number of radioactive atoms deposited on the surface

D^*=diffusion coefficient of radioactive species

t =time for diffusion.

2) Capillary reservoir method

It is sometimes called immersion method. At first, the known concentration of solute is held in the capillary one side of which is closed. And then, when immersed into reservoir composed of a larger bath, it results in the occurrence of diffusion of solute element between capillary and mother bath respectively. After the desired time has passed, capillary is pulled up and the concentrational distribution of the solute is resolved with the use of boundary conditions.

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In this case, strict attentions must be paid about the experimental conditions such as temperature distribution of furnace and the cleanliness of inside of capillary.[2]

3) Sheer cell method[3]

As shown in **Fig. 1,** more than two holes are dug in the bath regions in the top as well as in the bottom. The rotation of the disk results in the connection of each holes as shown in Fig. 1(b). After the duration of experiment (fixed time), again disks are rotated to give up the diffusion.

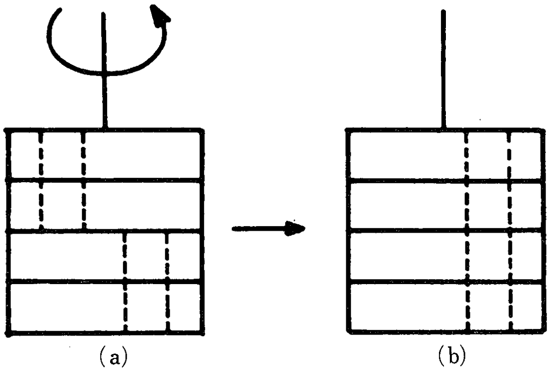


Fig. 1 Sheer cell method[3]
a) before the diffusion experiment
b) at the diffusion experiment

4) Diffusion couple method

As shown in **Fig. 2,** the upper half containing solute and the bottom one containing solvent are connected and carried into the molten state.

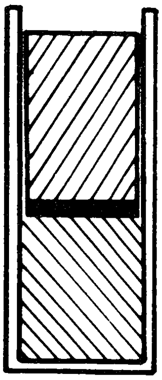


Fig. 2 Diffusion couple method

5) Electrochemical method[4]

The characteristic of ionic melt in the case of molten slag and molten salt is utilized to apply this mean.

As electrochemical cell is constructed between metal/alloy, containing diffusing component, and molten slag and the electrolysis at iso-current is carried on. If the electrode reaction is governed by diffusion, the following relation is derived:

$$i=zFD/(\delta c/\delta x)_{x=0} \qquad (2)$$

where

i =current density (Amp/cm^2)
z =number of electron related to electrode reaction
F =Faraday constant

Relationship between viscosity and diffusion coefficients[5]

1) Stokes-Einstein equation[6]

$$D=kT/6\pi\eta r \qquad (3)$$

2) Sutherland's equation[7]

$$D=kT/4\pi\eta r \qquad (4)$$

3) Eyring's equation[8]

$$D=kT/2\eta r \qquad (5)$$

4) Modified equation of Eyring's one[9]

$$D=kT/12\eta r \qquad (6)$$

5) Li-Chang's equation[10]

$$D=kT/8\eta r \qquad (7)$$

6) L. Higgins-Pople's equation[11]

$$D=3kT/10\pi\eta r \qquad (8)$$

Doremus says[12] that , for diffusion in less viscous liquids such as metals, aqueous solutions and organic materials, the relation between viscosity and diffusion coefficients is usually described quite well by Stokes-Einstein equation. Originally, Stokes-Einstein equation was derived from absolute reaction rate theory about organic liquids, and the applicability to silicate is in question.

Relationship between electrical conductivity and diffusion coefficient

Nernst-Einstein's equation

$$\sigma=z^2F^2Dc/RT \qquad (9)$$

where

σ =electrical conductivity
D =diffusion coefficient
z =ionic valence
F =Faraday constant
c =ionic concentration
R =the gas constant
T =absolute temperature.

Gosting and Harned say[13] that this relation cannot be applied to the electrolytes at finite concentration because there are interactions between ions.

Diffusion of cations in solid glasses

1) Sodium ion in glasses

Many investigators compared the electrical conductivity value and the diffusion coefficient of sodium ion in glasses such as Na_2O-SiO_2,Na_2O-Al_2O_3-SiO_2 and industrial use, and examined correction factor *f*. In **Table 1,** the correction factor presented by many investigators is compared.

Table 1 Correction factor *f*

Correction factor f	Glass used	Ref.
0.25—0.74	$Na_2O—Al_2O_3—SiO_2$	[14]
0.17—0.3	〃	[15]
0.40—0.51	〃	[16]
0.3 —0.5	〃	[17]
1.0	vitreous SiO_2	[18]
1.0	〃	[19]
1.0	〃	[20]
1.0	pyrex borosilicate	[21]

Generally speaking, correction factor *f* becomes a unity or less than unity depending on temperature and it seems valuable to estimate the diffusion coefficient from the use of Nernst-Einstein's equation. However, it still remains not clear what is the real physical mean of correction factor *f*.

As an example, diffusion coefficient of sodium ion in sodium silicate glasses are shown in **Fig. 3.**[22),23)]

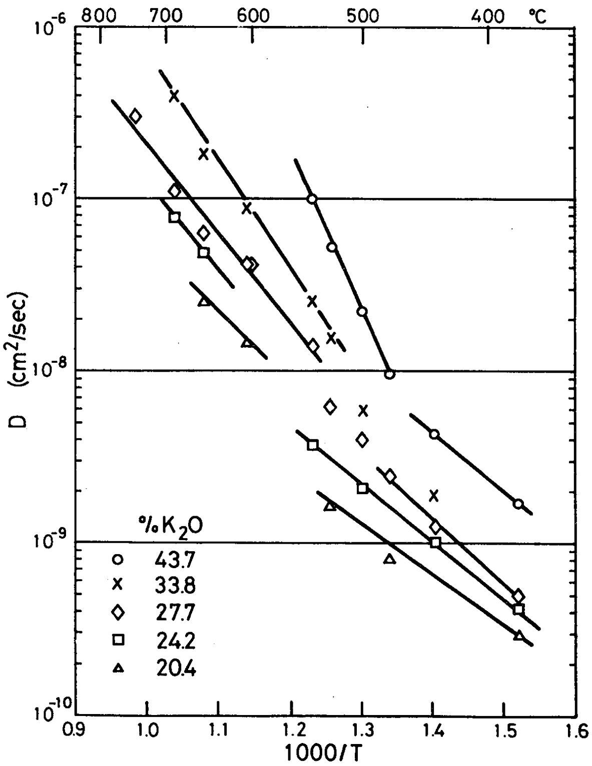


Fig. 3 Diffusion coefficients of sodium in binary sodium silicate glasses[22),23)]

It is of importance that there occurs transition break in the figure of diffusivity vs. a reciprocal expression of temperature in the case of Na_2O-SiO_2 as well as pyrex borosilicate glass, and hence activation energy changes at softening temperature. From the diagram, it is seen that the value approaches the value of SiO_2 with the decrease of Na_2O content.

2) Potassium ion in glasses

Johnson,[22)] studied the diffusion of potassium (^{42}K) tracer into various potash-silicate glasses.

The results are shown in **Fig. 4.** As in the case of sodium the diffusion coefficient was found to increase with alkali concentration, and the data fit two straight lines.

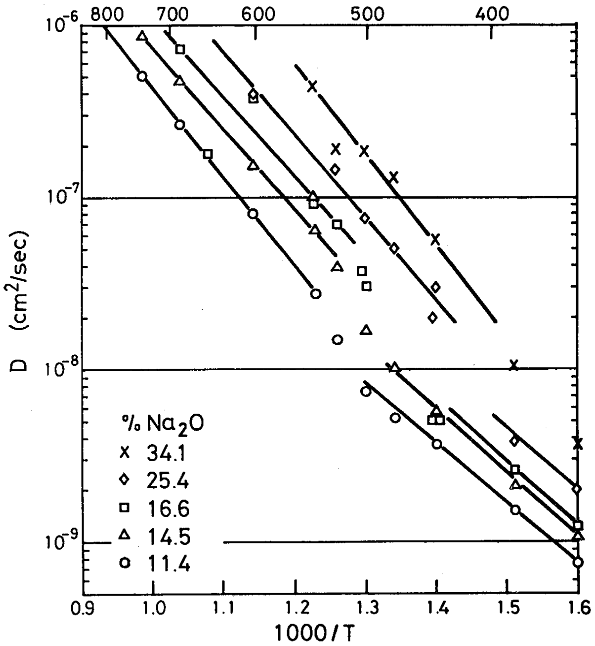


Fig. 4 Diffusion coefficients of potassium in binary potash-silicate glasses[22)]

The activation energy at the higher temperature below 525°C were in the neighbourhood of 14 kcal/mole, while at the high temperature they were around 23 kcal and seemed to increase with higher potassium content in the glass.

Evstrop'ev[24)] found that sodium diffuses faster in sodium glass than in potassium glass and that potassium diffuses faster in potassium glass than in sodium glass.

It was thought that D_{Na} in potassium glasses with the increase of K_2O content because the sodium ions may migrate partially by way of potassium-vacant sites.

3) Lithium ion in glasses

Hollabaugh and Ernsberger[25)] studied diffusion coefficient of lithium in a soda-lime-silicate glass at several different temperatures. Their results are shown in **Fig. 5.** The line in Figure 5 corresponds to an activation energy of 25.9 kcal/mole and a D_o of 1.1 cm^2/sec.

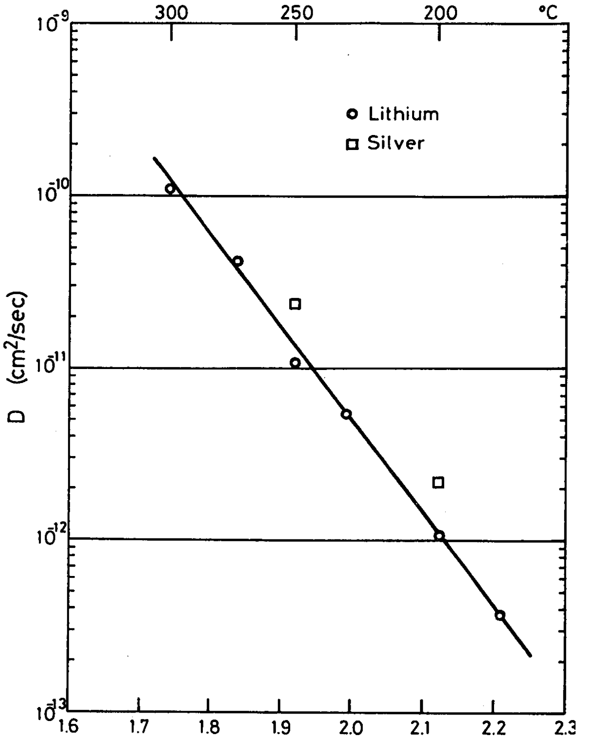


Fig. 5 Diffusion coefficients of lithium in a sodalime-silicate glass[25)]

4) Comparison of diffusion coefficient of monovalent ion

Le Clerc[26)] made a comparison of the size of the ion with the diffusion coefficient for Li, Na, K, and Ag. For the diffusion in sodium glass at 350°C, he gave the value as follows:

D_{Li} =4 by 10^{-7}(cm^2/sec)
D_{Na}=1.1 by 10^{-10} "
D_{Ag}=2.5 by 10^{-10} "
D_K =3 by 10^{-12} "

The radii of the ions being

Li$^+$ =0.60(Å)
Na$^+$ =0.95 "
Ag$^+$ =1.25 "
K$^+$ =1.33Å

The exception is that silver diffuses faster than sodium, but this discrepancy was explained from the fact that, in general, heterodiffusions are faster than autodiffusions as above described.

(5) Multivalent cations in glasses

Frischat[27)] compared the diffusion coefficients of calcium and sodium ions in glasses of the system Na_2O-CaO-SiO_2, and found that, as an example, an activation energy for calcium diffusion becomes to 53.7 kcal/mole at the temperature from 490 to 600°C. On the other hand, the value for sodium at temperature below 500°C, is 22.8 kcal/mole. At lower temperature, the diffusion coefficient of calcium in lime glass is many orders of magnitude lower than that of sodium. Frischat[28)] also measured calcium and aluminium diffusion in infrasil fused silica (Heraeus-Schott, Hanau, Germany) at 1000°C as follows:

$$D_{Na}:D_{Ca}:D_{Al}:D_O=1:2.5\times10^{-3}:1.3\times10^{-8}:1.1\times10^{-9}$$

Ghoshagore[29)] measured the diffusion coefficient of nickel in amorphous silica film, and obtained the value of about 10^{-15} cm^2/sec at 1000°C, with an activation energy of 37 kcal/mole.

Molecular diffusion in solid glasses

1) Hydrogen

Even if the atmosphere of hydrogen is raised till 850 atm., the solubility of hydrogen in glass remains constant and shows agreement with Henry's law.[30)] When hydrogen dissociates to atomic state in glass, the solution behaviour in glass must be proportional to the root of the pressure. Therefore, it is considered that hydrogen in glass diffuses as molecule.

2) Nitrogen

Although there are no direct proof that nitrogen in glass diffuses as molecule, it is thought that it is impossible to dissociate into glass network or to form a certain compound with some constituent of glass.

3) Argon

Permeability of argon is difficult when compared with nitrogen, and Reynolds[31)] gives the following values, Q=42 kcal/mole and D_{Ar}=350 cm^2/sec.

4) Oxygen

Permation velosity of oxygen is somewhat smaller when compared with that of nitrogen. Solubility data of oxygen in solid glass are unknown. As diffusion mechanism, two ways of network diffusion (lattice oxygen) and soluble oxygen must be considered. Study using gas bubbles make the molecular diffusion clear.

Schaefer, and Oel[32)] summarized the values presented by many investigators[33)-37)]. In **Table 2,** they are shown.

It is seen that remarkable difference in D_O as well as Q values exists in the case of SiO_2 glass. It is probably due to difficulty when using exchange method of ^{18}O between gas and glass.

5) Water vapor

Water entering the glass was found to be accommodated principally as hydroxyl,[38),39)] and the diffu-

Table 2 Comparison of diffusion coefficient of oxygen[32]

Composition (Mole %)	D_0(cm^2/s)	Q(kcal/mole)	T(°C)	Ref.
SiO_2 (fiber, 4 —12μm)	4.3×10^{-6}	56	900—1250	[33]
SiO_2 (crystal, 30—70μm)	3.7×10^{-9}	55	1010—1220	[33]
SiO_2 (fiber, 60, 86μm)	1.5×10^{-2}	71	925—1225	[34]
SiO_2 (fiber, 20μm)	2.0×10^{-9}	29	850—1250	[35]
45.3CaO—12.4Al_2O_3—42.3SiO_2 (sphere, 230μm)	7.5×10^{-3}	59	765— 845	[36]
12.8CaO—15.5Na_2O—71.5SiO_2 (sphere, 230μm)	$2.0\times10^{+3}$	66.5	460— 525	[36]
45.0CaO—13.3Al_2O_3—41.7SiO_2 (fiber, 18μm)	2.8×10^{-3}	57.7	625— 830	[37]
42.2CaO—15.7Al_2O_3—42.1B_2O_3 (fiber, 30μm)	9.5×10^{-7}	35.4	475— 600	[37]
25.9CaO—12.7Al_2O_3—61.4B_2O_3 (fiber, 17μm)	5.2×10^{-5}	46.6	500— 600	[37]
33.0PbO—53.4SiO_2—8.7K_2O (compact)	1.0×10^{-10}	12	275— 425	[32]
69.0PbO—31.0B_2O_3 (thin plate, 10—30μm)	6.0×10^{-10}	11	275— 425	[32]

Table 3 Molecular diffusion in fused silica[42]

Molecule	Diameter (Å)	Diffusion coefficient (cm^2/sec)		Activation energy Q (kcal/mole)	Ref.
		25°C	1000°C		
Helium	2.0	2.4×10^{-8}	5.5×10^{-5}	4.8	[44]
Neon	2.4	5.0×10^{-12}	2.5×10^{-6}	8.8	[45] [47]
Hydrogen(Deuterium)	2.5	2.2×10^{-11}	7.3×10^{-6}	8.5	[46] [47]
Argon	3.2	—	1.4×10^{-9}	26.6	[47]
Oxygen	3.2	—	6.6×10^{-9}	25	[48]
Water	3.3	—	$=3\times10^{-9}$	17	[38] [49]
Nitrogen	3.4	—	26 ?	26 ?	[43] [50]
Krypton	4.2	—	46	46	[47]
Xenon	4.9	—		72	[51]

sion coefficient was found to vary with concentration.[40],[41] Following chemical reaction is given, but it is said that diffusing quantity is lesser than reaction product.

$$H_2O + -Si-O-Si- = 2(-Si-OH) \qquad (10)$$

6) Comparison of diffusion coefficient for molecular diffusion in fused silica

Doremus compared diffusion coefficients of various molecular species in fused silica[42]. It is summarized in **Table 3.**

Doremus says[42] that the size of the diffusing ion affects molecular diffusion in fused silica quite strongly, in contrast to the small dependence of solubility on size.

Also, Doremus[12],[42],[52] says that diffusion coefficients of various molecular gases in glass can be derived from the value of the solubility C_i/C_g (C_i: the concentration of the gas in the glass, C_g: its concentration in the gas phase).

Doremus summarized the values and they are given in **Table 4.**

Table 4 Solubilities, C_i/C_g, of gases in fused silica[52]

Molecular diameter (Å)	Gas	Temp. (°C)			Ref.
		25	600	1000	
2.0	He		0.030		[53]
		0.025	0.030	0.034	[44]
2.4	Ne		0.021	0.020	[45]
2.5	H_2		0.028		[53]
			0.026	0.049 (at 850 atm)	[30]
			0.025	0.028	[46]
3.2	O_2			0.010	[48]

It will be seen that molecular solubilities in fused silica is their relative insensitivity to temperature, molecular size, and pressure.

Diffusion of cation in glass melt and molten slag

1) Calcium ion

At first, Tower, Paris and Chipman[53] measured self-diffusion coefficient of ^{45}Ca by using diffusion couple method.

As a specimen, a silicate slag containing about 40%SiO_2, 40%CaO, and 20%Al_2O_3 was used. The diffusion coefficients given by various investigators were arranged by Kawai[4], and the following equation was presented.

$$D_{Ca}=6.26\times 10^2 \exp(-68,600/RT) \qquad (11)$$

Moreover, Kawai says[4], that inverse proportion between viscosity and diffusion coefficient is recognizable as follows:

$$D\eta=\text{const.} \qquad (12)$$

2) Silicon ion

Towers and Chipman[55] measured diffusion coefficient of silicon in a slag containing about 38.5%CaO, 20.9%Al_2O_3, and 40.5%SiO_2. They say that the value of D_{Si} is about one tenth of that of D_{Ca}, and the activation energy for silicon is roughly the same magnitude as found for calcium.

$$D_{Si}=10^2,\ Q=70$$

3) Iron ion

Johnston, Stark and Taylor[1] studied diffusion coefficient of iron ion in a slag containing 38%CaO, 42%SiO_2, and 20%Al_2O_3. According to their measurement, the following values are given.

$$D_{Fe^{2+}}(\text{at } 1450\,^\circ\text{C})=9.55\times 10^{-6}\ \text{cm}^2/\text{sec}$$

$$Q=29.6\ \text{kcal/mole}$$

4) Aluminium ion

Henderson, Yang and Derge[56] measured diffusion coefficient of aluminium ion in slag containing 43.75% CaO, 42%SiO_2, and 20%Al_2O_3. Kawai[4] corrected the value as follows:

$$D_{Al}=5.4 \exp(-56,000/RT) \qquad (13)$$

Diffusion of anion in various glass melts and molten slags

1) Phosphorus ion

Voronstsov and Esin[57] measured diffusion coeffisent of phosphorus ion in a slag containing 40%CaO, 40%SiO_2, and 20%Al_2O_3. The value obtained is as follows:

$$D_P=4.5\times 10^{-6}\ \text{cm}^2/\text{sec (at } 1450\,^\circ\text{C)}$$

Perron and Bell[58] studied diffusion of phosphorous and sodium in the Na_2O-P_2O_5-SiO_2 melts. In **Table 5**, the diffusion coefficients and the activation energies of sodium and phosphorus are given.

It is seen that the diffusivity coefficient for sodium is about three times that of phorphorus at the lower

Table 5 Diffusion coefficients and activation energies for the system $Na_2O\cdot 2SiO_2$-$3Na_2O\cdot P_2O_5$[58]

Mole fraction $Na_2O\cdot 2SiO_2$	Diffusion coefficient (cm²/sec)		Activation energy (cal/mole)	
	Na	P	Na	P
1.00	5.76×10^{-4}		7,050±350	
0.95	2.77×10^{-3}	4.27×10^{-3}	11,500±500	15,850±750
0.90	1.56×10^{-3}	5.20×10^{-2}	9,600±550	22,400±200
0.85	1.34×10^{-3}	3.76×10^{-4}	9,050±300	8,400±400
0.80	2.19×10^{-3}	9.27×10^{-3}	11,300±350	18,550±200

temperature (1300 °K) but the difference tends to decrease with temperature and at 1650 °K there is only a factor of two.

2) Sulphur ion

Saito and Kawai[59] measured diffusion coefficient of sulphur ion in a slag containing 50 %CaO, 40 %SiO_2, and 10 %Al_2O_3 with diffusion couple method. The values obtained are sa follows:

$D_S=8.9\times10^{-7}$ cm²/sec (at 1445 °C)

$Q\pm=49$ kcal/mole

3) Fluorine ion

Johnston, Stark and Taylor[1] measured diffusion coefficient of fluorine ion in slag and their influence on other species' diffusion. In **Fig. 6(a)**, the additive effects are shown.

From the diagram, we can see that the diffusion coefficient and the activation energy of fluorine ion in slag are remarkably large, and fluorine ion accerelates the diffusion of calcium ion by a factor of two or more when compared with **Fig. 6(b)**.

$D_F=2.5\times10^{-5}$ cm²/sec (at 1450 °C)

4) Oxygen ion

Koros and King[60] reported that diffusion coefficient of oxygen ion in slag is too large, and thereafter Oishi, Ueda and Terai[61] measured the value from the exchange velocity of oxygen between gas, enriched with ^{18}O, and slag. They gave the values as follows:

($40CaO\cdot20Al_2O_3\cdot40SiO_2$, 1330~1570 °C)

$$D_O=18\exp(-54{,}300/RT) \tag{14}$$

$Q=54$ kcal/mole(c.f., $Q_{O(\mathrm{solid})}$

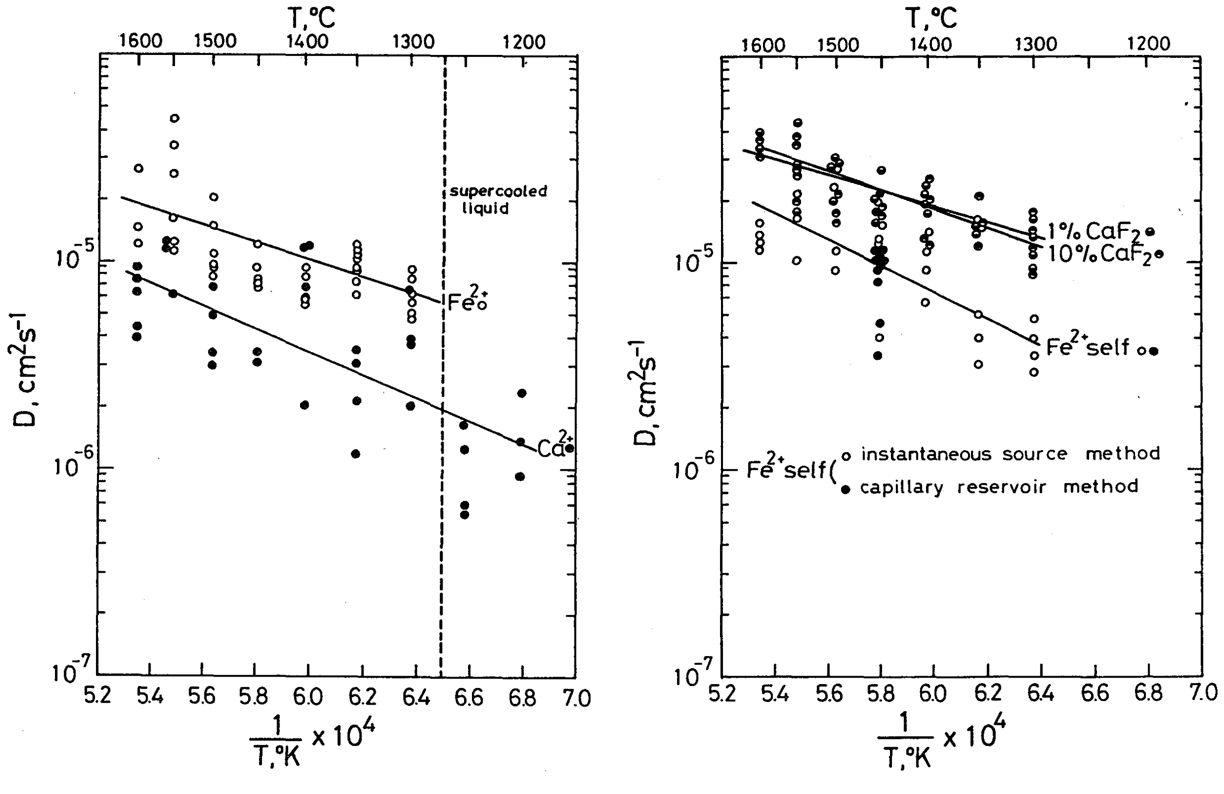


Fig. 6 The additive effct of CaF_2 on the chemical diffusion[1]
a) without CaF_2
b) when CaF_2 was added

Table 6 Diffusion coefficients and activation energies of oxygen ion in the glass melts and molten slags[61],[65],[66]

Composition (wt%)	D_0(cm²/sec)	Q(kcal/mole)	T(°C)	Ref.
$16Na_2O-12CaO-72SiO_2$	4.5×10^{-2}	38.6	800−1400	[65]
$20Na_2O-80SiO_2$	7.9×10^{-2}	44.5	1061−1395	[61]
$40CaO-20Al_2O_3-40SiO_2$	4.0×10^{-6}	95±20	1370−1530	[55]
$39.84CaO-19.72Al_2O_3-41.09SiO_2$	$(9.2\pm2.2)\times10$	59.6±2.7	1320−1540	[66]

$=58^{62)}-59^{62),63)}$, $Q_\eta=60^{64)}$)

For other data, the following values are given in **Table 6.**

In **Fig. 7**[67], the summarized results concerning oxygen, calcium, aluminium, and silicon ions in slag are shown. From the diagram, it is said that clacium ion in slag diffuses as single ion or as ionic pair with vacancy such as $Ca^{2+}O^{2-}$, and aluminium ion on slag diffuses as the form of Al^{3+} ion or as AlO_4^{5-} ion. On the other hand, it says that silicon ion in slag diffuses as SiO_4^{4-} ion. However it remains not clear to move so faster in the case of oxygen ion in slag.

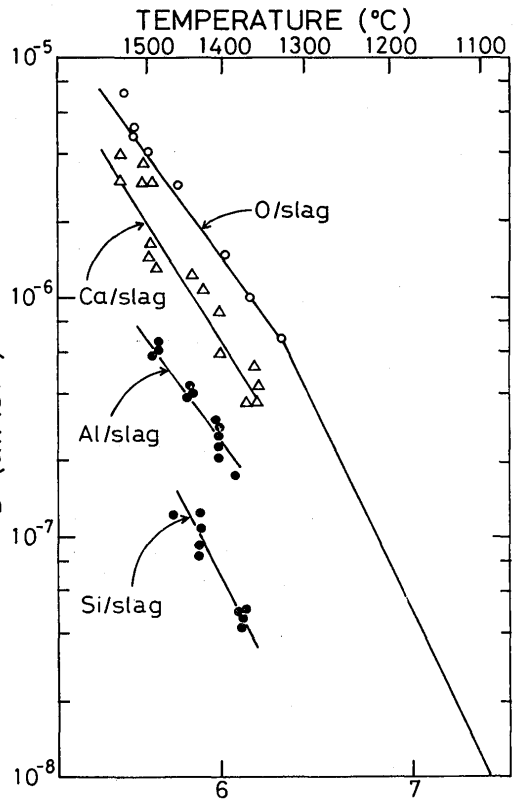


Fig. 7 Comparison of diffusion coefficients[67]

Molecular diffusion in various glass melts and molten slags

1) Helium

Mulfinger and Scholtz[68),69)] studied in detail about the relation between solubility and diffusion coefficient of helium in glass melts. The results obtained are as follows:

1-1) With the increase of the content of modifier oxide in glass, the diffusion coefficient of helium in glass becomes larger.

1-2) With the order, Li_2O,Na_2O and K_2O, the solubility of helium in glass increases. **(Fig. 8)**[68].

1-3) In the case of glass of the system Na_2O-CaO-SiO_2, the diffusion coefficient of helium in glass does not show increase as straight line with the increase of the content of modifier oxide. Below the softening temperature, the diffusion of helium is hindered because the increase of modifier oxide fills up the voids. At the liquidus state, diffusivity of molecule depends on the viscosity

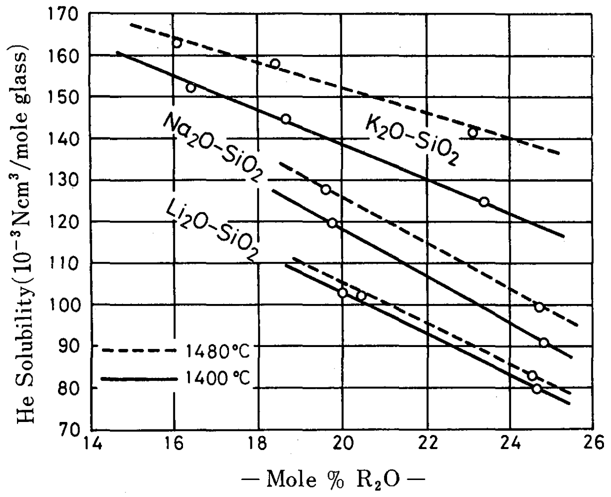


Fig. 8 Solubility change of helium in a glass melt with the increase of alkali oxide addition[68]

Table 7 Relationship between viscosity of glass and solubility of helium[69]

Glass	Temp. (°C)	He solubility (Ncm³/mole glass)	Viscosity (logη)	D_{He} ($\times 10^4$ cm³/sec)
$25Na_2O-75SiO_2$	1480	99.2	1.7	3.01
$20Li_2O-80SiO_2$	〃	102.46	2.0	1.43
$20Na_2O-80SiO_2$	〃	119.14×10^{-3}	2.2	2.05
$20K_2O-80SiO_2$	〃	157.55	2.2	3.33

because it acts to open or close of voids to existing molecule.

However, number of voids influences diffusivity of molecule in the same way. **(Table 7)**69)

2) Neon and nitrogen

Mulfinger, Dietzel, Rhön and Navarro70) studied the physical solubility of neon and nitrogen inclusive of helium in the glass melt. In **Table 8**, the results obtained are given.

Table 8 Solubility of helium, neon and nitrogen70)
* represents gasNcm^3/2 mole O^{2-} glass

Glass	Temp. (°C)	He*	Ne*	N_2*
$74SiO_2-16Na_2O-10CaO$	1300 1400 1480	0.094 0.097 0.102	0.045 0.046 0.047	0.010 0.011 0.016
$75SiO_2-25Li_2O$	1480	0.093	0.050	0.033
$16.5K_2O-83.5SiO_2$	1480	0.178	0.103	0.039

* represents gasNcm^3/2mole O^{2-}glass

The results obtained are summerized as follows:

2–1) With the increase of the content of modifier oxide in glass, the solubility of helium becomes smaller. On the contrary, the solubility of neon becomes larger when modifier oxide is K_2O. On the other hand, the solubility of nitrogen is independent on the content of modifier oxide. **(Fig. 9)**

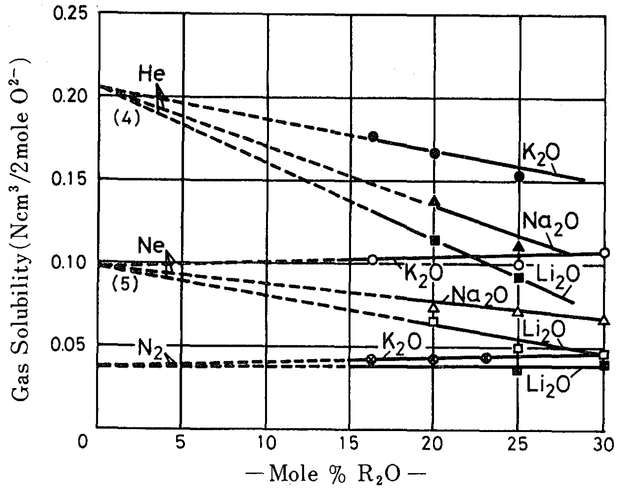


Fig. 9 Solubility change of gases in a glass melt with the increase of alkali oxide addition70)

2–2) In the case of Na_2O-K_2O-SiO_2 glass melt, the solubility of nitrogen becomes larger with the increase of temperature. However the solubility of helium and neon does not show remarkable change. **(Fig. 10)**

Mulfinger71) studied the physical or chemical solubility of nitrogen in the Na_2O-CaO-SiO_2 glass melt under the experimental conditions given in **Table 9.** The results obtained are shown in **Fig. 11.**

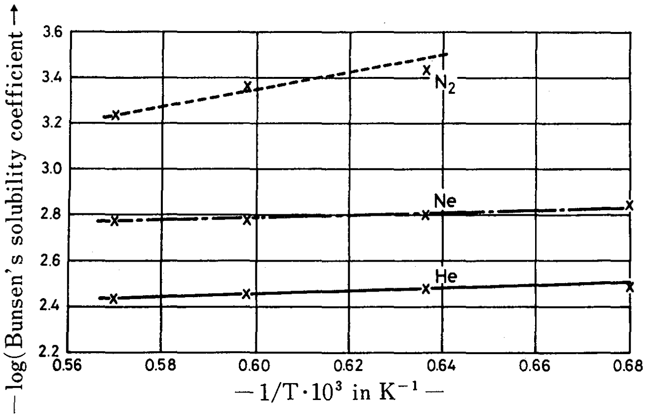


Fig. 10 Solubility change of gases in a glass melt of the system Na_2O-K_2O-SiO_2 with changing temperature70)

Table 9 Experimental conditions for nitrogen contents shown in Fig. 11$^{71)}$

Symbol	Solubility	Pretreatment
A	Physical (equilibrium value)	N_2 bubbled through melt; 16hr, 1400°C
B	〃	Glass melted in gas furnace with oxidizing flame; 2hr, 1400°C
C	Chemical	Powdered glass(75—150μ) passed through A-N plasma
D	〃	Glass melted in gas furnace with reducing flame; 2hr, 1400°C
E	〃	Melt bubbled with H_2/N_2(80/20) mixture; 5hr, 1400°C
F	〃	Glass with 3wt% carbon added; melt bubbled with N_2; 2hr, 1400°C
G	〃	Ammonia bubbled through melt; 5hr, 1400°C

From these results, it is seen that the solubility of nitrogen in glass melt or molten slag is very low except special conditions such as reduced state, the coexistence with carbon, and generation of atomic nitrogen. Mulfinger71) indicate the reaction of nitrogen with glass melt as follows:

$$\text{glass-O-} + \text{nitrogen (molecule)} + \text{reducing agent} \begin{cases} \text{e.g. carbon} \rightleftharpoons \text{glass-N=} + CO \\ \text{e.g. hydrogen} \rightleftharpoons \text{glass-NH-} + H_2O \\ \quad\text{or} \quad \rightleftharpoons \text{glass-}NH_2 + H_2O \end{cases} \qquad (15)$$

$$\text{glass-O-} + \text{nitrogen (atomic)} \rightleftharpoons \text{glass-N=} + O_2 \qquad (16)$$

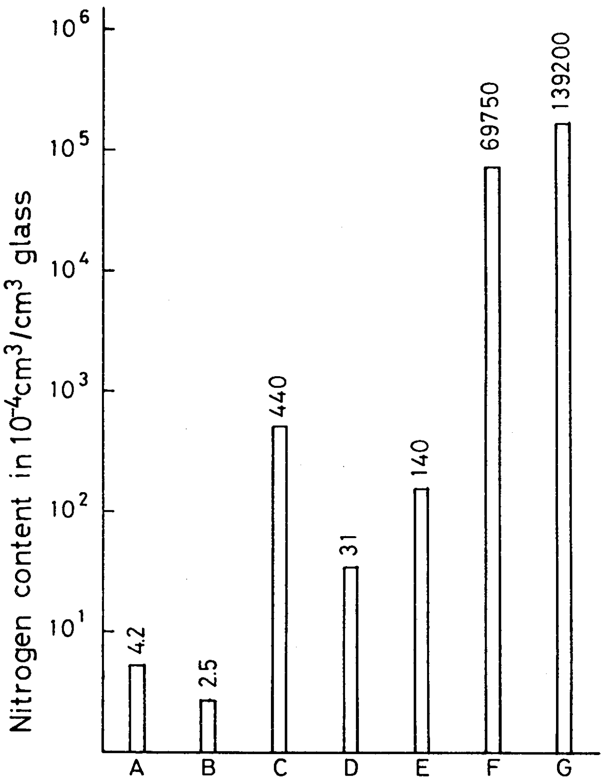


Fig. 11 Nitrogen content of Na_2O-CaO-SiO_2 glass under various experimental conditions[71]

Mulfinger also says[71] that these are equilibrium reactions, therefore they depend on the partial pressure of the gases in the furnace atmosphere according to the law of mass action.

Furthermore he says[71] that the nitrogen can present as dissolved nitrides, and NH= or NH_2-groups can be formed by hydrolysis with small amounts of water vapor. It is an important matter that these nitrogen-hydrogen compounds are formed directly in the presence of nitrogen and hydrogen with release of water. In the nitrogen-plasma torch, atomic nitrogen is introduced and the nitrogen is incorporated as dissolved nitrides and oxygen is released.

Naturally, the diffusion velocity of nitrogen depends on the existing form in glass melt or molten slag. It must be emphasized that the experimental conditions in steelmaking, welding and plasma spraying plays essential role on subsequent behaviour of nitrogen.

3) Water vapour

As the author summarized in the preceding report[72], water vapour can be dissolved as OH^-.

$$H_2O_{(gas)} + O^{2-}{}_{(melt)} = 2OH^-{}_{(melt)} \tag{15}$$

Accordingly, it is thought that the most simple representation of the diffusion of water in the oxide melt is jumping mean of proton(H^+) from OH^- group to a neighboring half-bonded oxygen(O^-). The more the number of half-bonded oxygen is, the greater diffusion velocity of water in the oxide melt becomes. Scholtz and Mulfinger[73] studied in detail about the diffusion behaviour of water in the molten glass. In **Fig. 12**[73], relationship between the content of modifier oxide and the diffusion coefficient of water at 1400°C in the alkalisilicate glass is shown. With the increase of the content of modifier oxide, the diffusion coefficient of water becomes larger. Meanwhile, the strongest correlation was observed between the diffusion coefficient of water in binary silicate glass and a sort of alkali metal oxide added. That is, the greater cation-oxygen interaction parameter (z/a^2: z, cation valency. a, internuclear distance.), the larger the diffusion coefficient of water becomes.

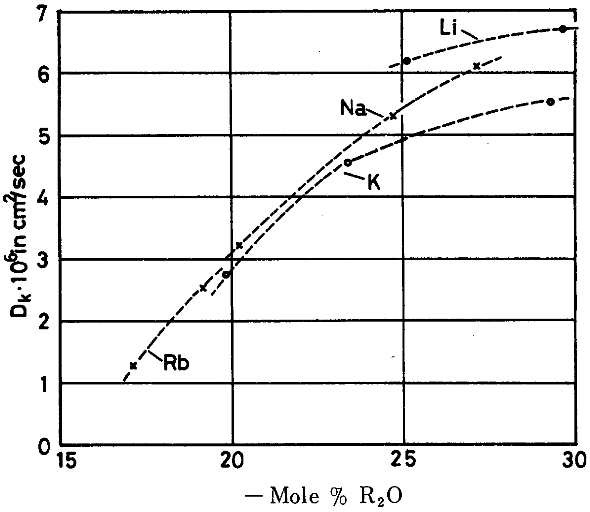


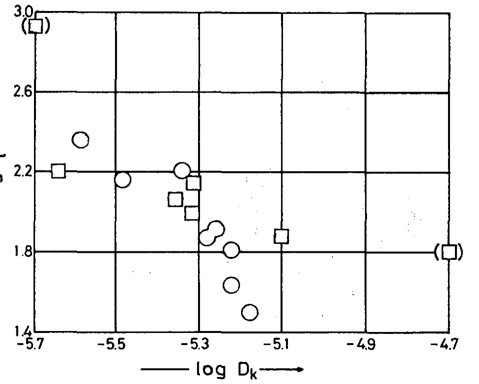
Fig. 12 Relationship between the diffusion coefficient of water in a glass melt and alkali oxide content[73]

Furthermore Scholtz and Mulfinger[73] considered the relation between the viscosity and the diffusion coefficient of water in the silicate melt at 1400°C. These relations are shown in **Fig. 13**[73].

Williams[74] summarized the value concerning diffusion coefficient of water in the oxide melt. In **Table 10**, the values are given.

Discussion

Terai[75] studied self-diffusion of sodium ions in sodium aluminosilicate glasses and the influence of Al/Na ratio in glasses on self-diffusion of sodium ions. Further, Haider and Roberts[76] studied the diffusion of water in aluminosilicate glasses and disscussed relation between the diffusion coefficient of water and the ratio of Al/Na. As an example, diffusion



○ = binary alkali-silicate melt
□ = silicate melt containing other component
( ) = questionable value

Fig. 13 Relationship between the diffusion coefficient of water in the oxide melt and the viscosity[78]

coefficient of water and the Al_2O_3 content in glass is compared in **Fig. 14**[76].

As like as electrical conductivity, mechanical property and so on, the variation of diffusion coefficient occurs at the content of Al/Na=1. Clearly an diffusion behaviour is related to the structure of glass. In the case of the diffusion of water, it depends on the combined state of oxygen, that is to say, the number of half-bonded oxygen. On the other hand, the diffusion of cation depends on the oxygen density in glass.

As for the physical meaning of correlation factor *f* between Nernst-Einstein's equation and diffusion coefficient, Shewman[77] and Goto, Sasabe and Kawakami[78],[79] discussed in detail.

Table 10 Diffusion coefficient of water in glass[74]

Glass composition(m/o)	Temp.(°C)	D(cm^2/sec)	Ref.
$74.9SiO_2-25.1Li_2O$	1300−1400	0.0025exp(−20,000/RT)	[73]
$70.3SiO_2-29.7Li_2O$	1100−1400	0.002 exp(−18,900/RT)	〃
$79.8SiO_2-20.2Na_2O$	1200−1400	0.0033exp(−22,700/RT)	〃
$75.1SiO_2-24.9Na_2O$	1000−1400	0.003 exp(−20,800/RT)	〃
$72.8SiO_2-27.2Na_2O$	1000−1400	0.0028exp(−20,300/RT)	〃
$80.1SiO_2-19.9K_2O$	1000−1400	0.026 exp(−30,300/RT)	〃
$76.8SiO_2-23.2K_2O$	1000−1400	0.028 exp(−29,800/RT)	〃
$70.9SiO_2-29.1K_2O$	1000−1400	0.005 exp(−22,700/RT)	〃
$82.9SiO_2-17.1Rb_2O$	1000−1400	0.014 exp(−30,900/RT)	〃
$80.9SiO_2-19.1Rb_2O$	1000−1400	0.014 exp(−28,700/RT)	〃
$74.1SiO_2-16.5Na_2O-9.4(MgO+CaO)$	1000−1400	0.023 exp(−28,000/RT)	〃
$74.8SiO_2-20.9Na_2O-0.1(MgO+CaO)$ $+4.2(Fe_2O_3+Al_2O_3)$	1100−1400	0.001 exp(−20,500/RT)	〃
$67.9SiO_2-19.4Na_2O-0.2(MgO+CaO)$ $+12B_2O_3+0.5(Fe_2O_3+Al_2O_3)$	1100−1400	0.15 exp(−30,000/RT)	〃
$53.0SiO_2-23.1BaO-19.7B_2O_3-4.2$ $(Fe_2O_3+Al_2O_3)$	1000−1400	0.4 exp(−35,000/RT)	〃
$84.5SiO_2-8.6Na_2O-5.9K_2O-1.0PbO$	1200−1400	0.011 exp(−31,000/RT)	〃
$70.3SiO_2-13.2Na_2O-7.7(MgO+CaO)$ $-5.2ZnO-1.6B_2O_3-2.0(Fe_2O_3+Al_2O_3)$	1000−1400	0.0087exp(−25,200/RT)	〃
$71.3SiO_2-8.6Na_2O-5.7K_2O-12.4$ $(MgO+CaO)-0.7BaO-1.2(Fe_2O_3+Al_2O_3)$	1100−1400	0.0049exp(−23,000/RT)	〃

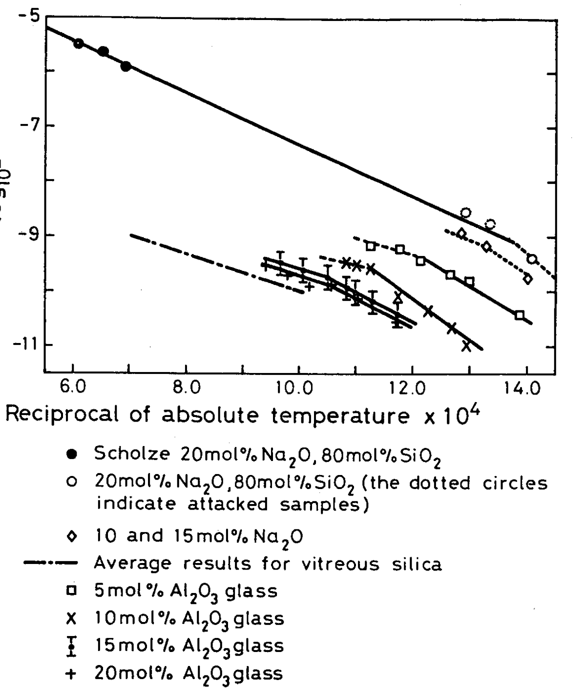


Fig. 14 Relationship between the diffusion coefficient of water and Al_2O_3/Na_2O content of $Na_2O-Al_2O_3-SiO_2$ glass

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