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Self-diffusion of oxygen in soda-lime silicate glass

By Ryohei Terai[1]) and Yasumichi Oishi

(Communication of the Department of Nuclear Engineering, Faculty of Engineering, Kyushu University, Fukuoka (Japan))

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The self-diffusion coefficients of oxygen in $16\,Na_2O\cdot 12\,CaO\cdot 72\,SiO_2$ glass were measured in the temperature range from 500 to 1470 °C by means of an isotope exchange technique employing ^{18}O as the tracer. The results in the temperature range over 800 °C were represented by $D = 4{,}5\cdot 10^{-2}\exp(-38{,}6\cdot 10^3/RT)$. This activation energy for diffusion was in good agreement with that for viscous flow of the glass. The relationship between the oxygen self-diffusion coefficient and the viscosity was satisfactorily described by Eyring's equation rather than the Stokes-Einstein relation. The measured oxygen self-diffusion coefficients also showed agreements with the diffusion coefficients calculated from an interdiffusion kinetics and from the dissolution rate of a quartz glass in the glass melt, which indicated that these processes were governed by the diffusion of oxygen ions.

The steep temperature dependence of the oxygen self-diffusion coefficient which was determined in the transition range was explained to be due to an excess structural activation energy required for migration of oxygen ions.

Autodiffusion de l'oxygène dans un verre silico-sodo-calcique

Les coefficients d'autodiffusion de l'oxygène dans le verre $16\,Na_2O\cdot 12\,CaO\cdot 72\,SiO_2$ sont mesurés dans le domaine de températures compris entre 500 et 1470 °C par une technique d'échange d'isotopes utilisant ^{18}O comme traceur. Les résultats obtenus dans le domaine des températures supérieures à 800 °C sont représentés par $D = 4{,}5\cdot 10^{-2}\exp(-38{,}6\cdot 10^3/RT)$. Cette énergie d'activation de la diffusion est en bon accord avec celle qui correspond à l'écoulement visqueux du verre. La relation entre le coefficient d'autodiffusion de l'oxygène et la viscosité est décrite de manière plus satisfaisante par l'équation d'Eyring que par la relation de Stokes-Einstein. Les coefficients d'autodiffusion de l'oxygène mesurés concordent également avec les coefficients de diffusion calculés à partir de la cinétique d'interdiffusion et de la vitesse de dissolution d'un verre de quartz dans la fonte de verre, ce qui indique que ces processus sont contrôlés par la diffusion des ions oxygène.

On explique que la forte pente de la courbe du coefficient d'autodiffusion de l'oxygène en fonction de la température, déterminé dans le domaine de transition, est due à un excès d'énergie d'activation de la structure requise pour la migration des ions oxygène.

Selbstdiffusion von Sauerstoff in Kalk-Natronsilicatglas

Die Selbstdiffusionskoeffizienten von Sauerstoff in $16\,Na_2O\cdot 12\,CaO\cdot 72\,SiO_2$-Glas wurden im Temperaturbereich von 500 bis 1470 °C mit dem Isotopenaustauschverfahren bestimmt, wobei ^{18}O als Tracer verwendet wurde. Die Ergebnisse im Temperaturbereich über 800 °C lassen sich durch die Gleichung $D = 4{,}5\cdot 10^{-2}\exp(-38{,}6\cdot 10^3/RT)$ darstellen. Die ermittelte Aktivierungsenergie für die Diffusion stimmt gut mit der für das viskose Fließen des Glases überein. Der Zusammenhang zwischen dem Selbstdiffusionskoeffizienten des Sauerstoffs und der Viskosität wird durch die Eyringsche Beziehung besser beschrieben als mit der Stokes-Einsteinschen Gleichung. Die gemessenen Sauerstoff-Selbstdiffusionskoeffizienten stimmen auch mit den Diffusionskoeffizienten überein, die über die Interdiffusionskinetik und die Auflösungsgeschwindigkeit von Kieselglas in der Glasschmelze berechnet wurden; das deutet darauf hin, daß diese Vorgänge von der Diffusion des Sauerstoffions bestimmt werden.

Die starke Temperaturabhängigkeit des Sauerstoff-Selbstdiffusionskoeffizienten im Übergangsbereich wird darauf zurückgeführt, daß ein Überschuß an struktureller Aktivierungsenergie für die Wanderung der Sauerstoffionen erforderlich ist.

Informations on the diffusion of oxygen ions in a glass are essential in clarifying the mechanisms of kinetic processes of the glass, such as viscous flow and devitrification. The most important systems as for example commercial glass are soda-lime silicates. The present paper describes the self-diffusion of oxygen measured by means of an isotope exchange method for a $16\,Na_2O\cdot 12\,CaO\cdot 72\,SiO_2$ (wt.%) glass in a wide temperature range from 500 to 1470 °C. A portion of the data has already appeared in a previous paper [1], which discussed the relation between the self-diffusion coefficient of oxygen ion and the viscosity of the glass. For this glass, the self-diffusion coefficients of sodium ion, D^*_{Na}, in the temperature range of 300 to 1100 °C [2] and 250 to 625 °C [3] and of the calcium ion, D^*_{Ca}, in the temperature range of 650 to 850 °C [4] and 1000 to 1450 °C [5] have been already determined. The self-diffusion of oxygen, D^*_{oxy}, below the transition temperature has been already determined, too [6].

For the glasses having somewhat different compositions in the same system Na_2O-CaO-SiO_2, self-diffusion coefficients were measured by several workers. Frischat [7] measured D^*_{Na} and D^*_{Ca} in $16\,Na_2O\cdot 10\,CaO\cdot 74\,SiO_2$ and $Na_2O\cdot 2\,CaO\cdot 3\,SiO_2$ glasses below the transition ranges. Winchell [8] determined D^*_{Na} in the NBS No. 710 ($70{,}5\ SiO_2\cdot 8{,}7\ Na_2O\cdot 7{,}7\ K_2O\cdot 11{,}6\ CaO\cdot 1{,}1\ Sb_2O_3$ (wt.%)), Malkin and Mogutnov [9] determined D^*_{Na} in the molten $Na_2O\cdot CaO\cdot 4\,SiO_2$ glass. The self-diffusion coefficient of oxygen, however, has not been measured in those glasses.

1. Experimental

1.1. Sample

A $16\,Na_2O\cdot 12\,CaO\cdot 72\,SiO_2$ glass was prepared from reagent grade silica, calcium carbonate and sodium

[1]) During the time this work was done, R. Terai was a visiting researcher from Government Industrial Research Institute, Osaka, Midorigaoka 1, Ikeda City, Osaka-fu, Japan.

carbonate. The melting was carried out in a platinum crucible in an electric furnace for 15 h at 1450 to 1500 °C in air. The analytical composition of the glass is given in table 1. Some physical properties of this glass are listed in table 2. Figure 1 shows the fluidity of the glass plotted against temperature. The corresponding viscosity above 945 °C was measured by the counter balance sphere method and is represented by equation (1).

$$1/\eta = 3{,}8 \cdot 10^3 \exp(-42{,}0 \cdot 10^3/RT) \quad (\eta \text{ in P}). \qquad (1)$$

The softening point, annealing point and strain point were measured by the fiber elongation method.

1.2. Calculation of diffusion coefficient

In the isotopic exchange between the ^{16}O in the glass sample and the ^{18}O enriched gas phase, the decrease of ^{18}O content in the gas phase is controlled by the volume diffusion of oxygen ions in the glass when the isotopic equilibrium is quickly established at the glass surface. The solution of Fick's second equation is given as equation (2) by Crank [10] for the boundary condition in which a well-stirred gas phase of a limited volume is taken up from the surface of a molten glass sample in a crucible or capillary.

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{2\,\alpha\,(1+\alpha)}{1+\alpha+\alpha^2 q_n^2} \cdot e^{-Dq_n^2 t/l^2}, \qquad (2)$$

where the q_n's are the non-zero positive roots of equation (3).

$$\tan q_n = -\alpha\, q_n, \qquad (3)$$

The M_t in equation (2) is the diffusion amount of ^{18}O at time t, M_∞ the corresponding quantity after infinite time, α the ratio of the oxygen atoms in the gas phase and the glass, l the depth of the glass sample, and D the diffusion coefficient. For the cylindrical glass sample employed in measurements near the transition point, equation (4) is applied instead of equation (2).

$$\frac{M_t}{M_\infty} = \frac{1+\alpha}{1+\frac{1}{4}\alpha}\left[1 - e^{4\left(1+\frac{1}{4}\alpha\right)^2 Dt/(a^2\alpha^2)} \cdot \operatorname{erfc}\left\{2\left(1+\frac{1}{4}\alpha\right)(Dt/a^2)^{1/2}/\alpha\right\}\right], \ldots \qquad (4)$$

where a is the radius of the cylinder.

For the spherical glass sample, equation (5) is employed.

$$\frac{M_t}{M_\infty} = (1+\alpha)\left[1 - \frac{\gamma_1}{\gamma_1+\gamma_2} \cdot \operatorname{e\,erfc}\left\{\frac{3\gamma_1}{\alpha}\left(\frac{Dt}{a^2}\right)^{1/2}\right\} - \frac{\gamma_2}{\gamma_1+\gamma_2}\operatorname{e\,erfc}\left\{-\frac{3\gamma_2}{\alpha}\left(\frac{Dt}{a^2}\right)^{1/2}\right\}\right] + \text{higher terms}, \quad \ldots (5)$$

where a is the radius of the sphere, e erfc $z \equiv \exp z^2$ erfc z, and γ_1 and γ_2 are given by the following equations.

$$\gamma_1 = \frac{1}{2}\left\{\left(1+\frac{4}{3}\alpha\right)^{1/2} + 1\right\}, \quad \gamma_2 = \gamma_1 - 1.$$

The relationships between M_t/M_∞ and Dt/l or Dt/a^2 for various final uptakes previously calculated by a computer using equations (1), (3), or (4) are used in estimating D from the experimental data.

Table 1. Chemical analysis of glass sample (in wt.%)

SiO_2	CaO	Na_2O
71,1	12,1	16,1

Table 2. Some properties of glass sample used

Density	2,52 g/cm³
Linear thermal expansion coefficient (50 to 300 °C)	$111 \cdot 10^{-7}$/°C
Strain point	521 °C
Transition point	541 °C
Softening point	706 °C
Liquidus temperature	1020 °C
Temperature of maximum crystal growth rate	900 °C

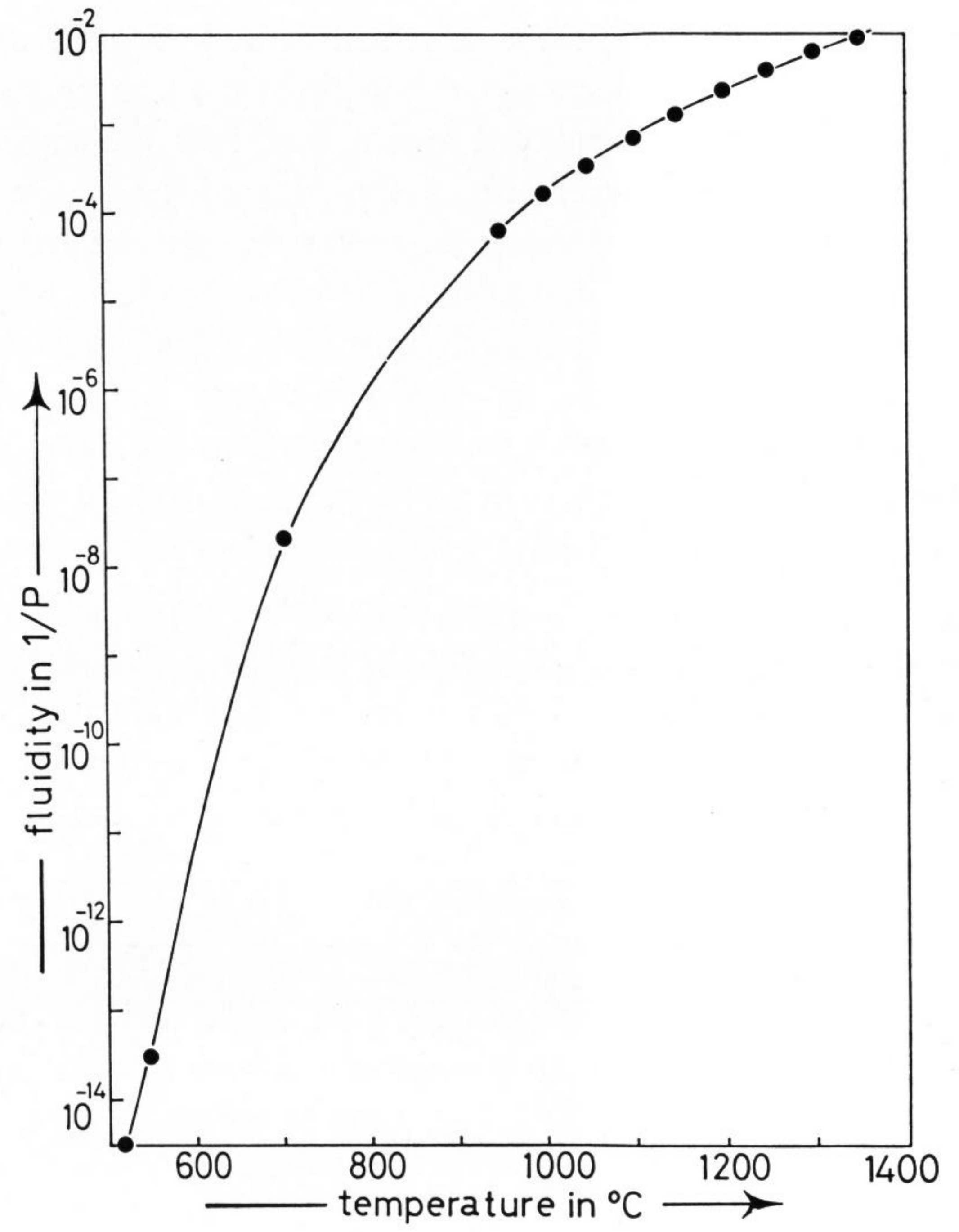

Figure 1. Fluidity of $16\,Na_2O \cdot 12\,CaO \cdot 72\,SiO_2$ glass as a function of temperature.

1.3. Diffusion experiment

The oxygen gas enriched with 5% ^{18}O was enclosed in a fused silica chamber of 195 ml after passing through a gas purifier and a moisture trap, and the pressure was adjusted to approximately 152 mmHg at room temperature. The chamber with the sample glass set in it was immersed in a water bath, then the exchange run was carried out by heating the sample inside the Pt-10Rh susceptor by means of high frequency induction. The temperature of the sample was measured by an optical pyrometer when the temperature was above 800 °C and by a Pt-PtRh thermocouple when the temperature was lower. The temperature was maintained at constant within ± 3 °C by controlling the terminal voltage.

Platinum crucibles of 3, 5, and 10 mm inner diameter were used as the sample container depending on

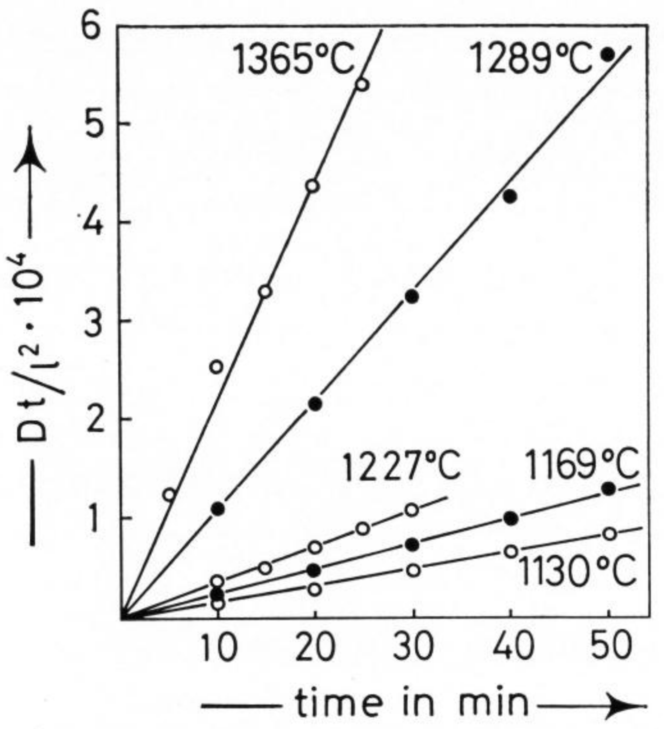

Figure 2. Plot of Dt/l^2 versus diffusion time at various temperatures for molten glass.

experimental temperatures. When a large diameter crucible was employed, the convection of the glass melt may have complicated the diffusion kinetics. This suspicion, however, was cleared when the plots of (Dt/l^2) against t produced good straight lines through the origin as shown in figures 2 and 3. For the diffusion run at 650 °C, 20 cylindrical glass samples of 1 mm in diameter and 10 mm in length were set separate from each other in a platinum crucible. For a measurement at a temperature near the transition point, T_g, glass spheres with a mean diameter of 100 μm were prepared by dropping glass particles through a carbon arc. The glass spheres of approximately 5 g were wrapped in a platinum foil and were set in a platinum crucible.

Gas samples were collected in the sample collectors of 0,6 or 1,8 ml from time to time during the diffusion annealing. The $^{18}O/^{16}O$ ratios in the gas samples were determined by a mass spectrometer, from which the diffusion amounts of ^{18}O into the glass were calculated.

2. Results

Figure 2 shows the relation between Dt/l^2 and t determined for the molten glass at high temperatures.

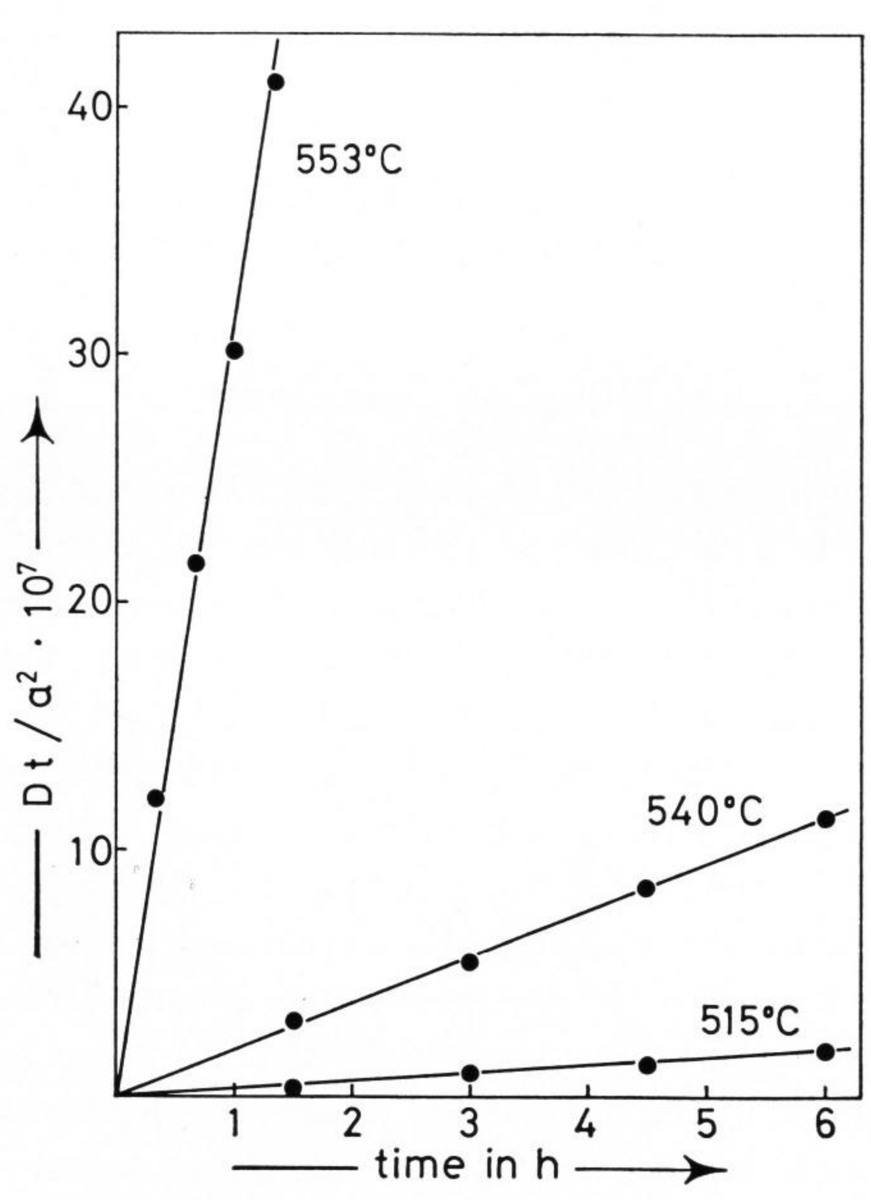

Figure 3. Plot of Dt/a^2 versus diffusion time at various temperatures for glass spheres.

The plots give straight lines passing through the origin, which indicate that the kinetics of the isotopic exchange is solely controlled by the volume diffusion. Figure 3 shows the plot of Dt/a^2 against t for the glass spheres at temperatures below T_g. These lines are also straight and pass through the origin.

The Arrhenius plotting of the determined diffusion coefficients is given in figure 4, in which the values of D^*_{Na}, D^*_{Ca}, and D^*_{oxy} determined by other investigators are also shown for comparison. The experimental results of D^*_{oxy} in the temperature range from 800 to 1470 °C can be represented by equation (6).

$$D = 4{,}5 \cdot 10^{-2} \exp(-38{,}6 \cdot 10^3/RT) \quad (D \text{ in } cm^2/s). \quad (6)$$

The diffusion coefficient below 800 °C decreases with increasing temperature dependence, thus does not give a straight line. Nonlinear temperature dependence of self-diffusion coefficient in the transition range has also been found for the sodium ion in this glass [2], and for the oxygen ion in 40 SiO_2·40 CaO·20 Al_2O_3 [11].

Furthermore, figure 4 shows the experimental results below T_g agreeing with the results of Kingery and Lecron [6] for the same glass. All the values of D^*_{oxy} obtained at various temperatures in this study are listed in table 3.

3. Discussion

3.1. Comparison of D^*_{oxy} with interdiffusion coefficients

Figure 5 compares the self-diffusion coefficient of oxygen in the present work with the interdiffusion coefficients calculated from other kinetics for the Na_2O-CaO-SiO_2 glass. D^*_{oxy} coincides closely with the interdiffusion coefficient, $\tilde{D}_{CaO}$, measured by Sucov and Gorman [12] for the concentration distribution of calcium near the interface of two glasses differing by

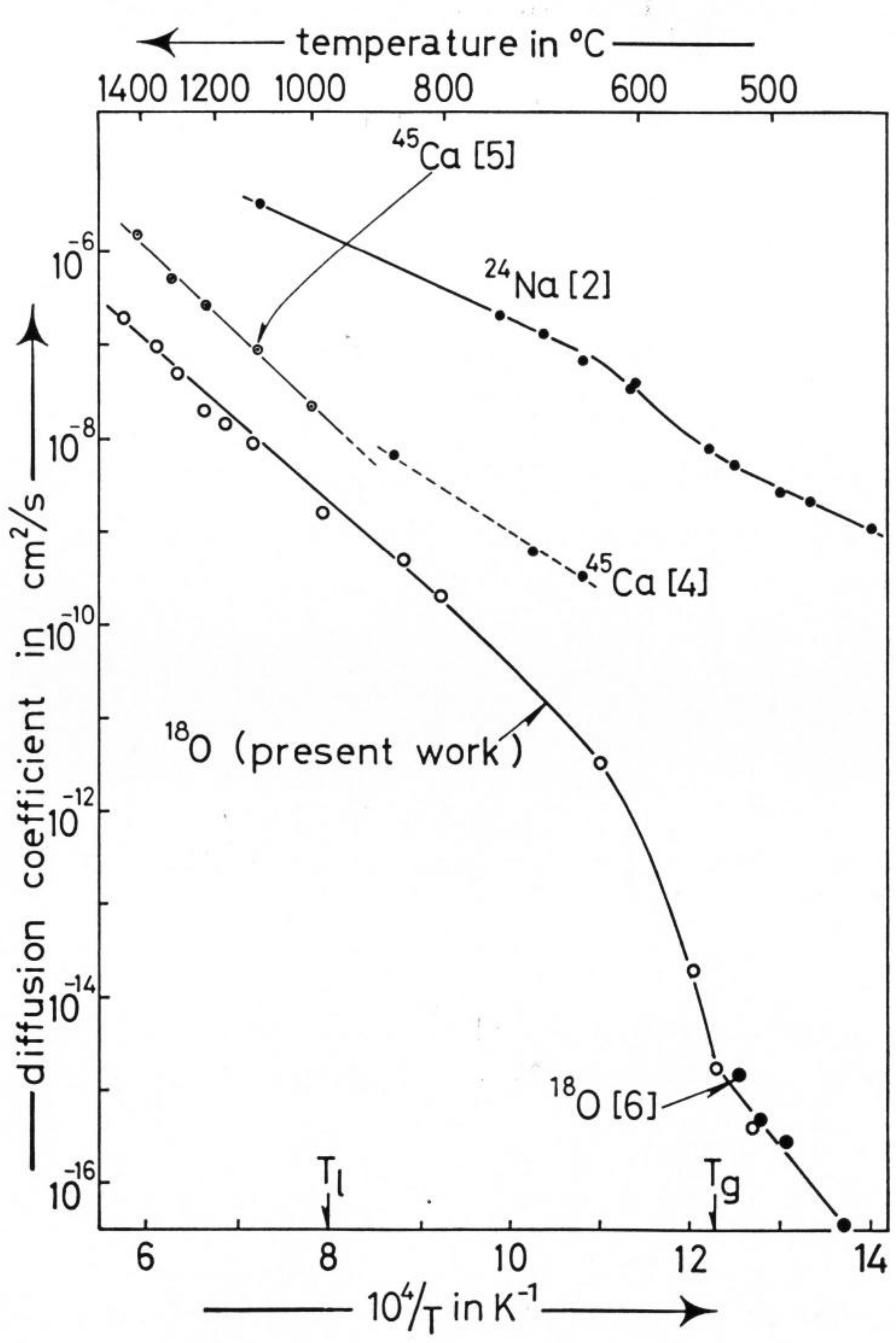

Figure 4. Self-diffusion coefficients of oxygen ion in 16 Na_2O·12 CaO·72 SiO_2 glass as a function of temperature with diffusion data of sodium, calcium respectively.

Table 3. Diffusion coefficients of oxygen ion in 16 $Na_2O \cdot 12\ CaO \cdot 72\ SiO_2$ glass

Temperature in °C	D in cm²/s
1471	$2{,}08 \cdot 10^{-7}$
1365	$1{,}04 \cdot 10^{-7}$
1289	$5{,}47 \cdot 10^{-8}$
1227	$1{,}93 \cdot 10^{-8}$
1169	$1{,}40 \cdot 10^{-8}$
1130	$9{,}04 \cdot 10^{-9}$
988	$1{,}70 \cdot 10^{-9}$
953	$4{,}90 \cdot 10^{-10}$
808	$2{,}03 \cdot 10^{-10}$
635	$3{,}41 \cdot 10^{-12}$
553	$2{,}11 \cdot 10^{-14}$
540	$1{,}77 \cdot 10^{-15}$
515	$3{,}71 \cdot 10^{-16}$

2,9 mole% in CaO content. They thought that calcium ions diffused together with oxygen ions in order to maintain the electrical neutrality in the glass. This is confirmed by the present agreement of the interdiffusion coefficient with D^*_{oxy}, i.e., the migration of CaO is controlled by the diffusion of oxygen ion which is less mobile than calcium ion. Figure 5 also shows the interdiffusion coefficient, $\tilde{D}_{SiO_2}$, calculated by Cooper and Kingery's equation [13] from the dissolution rate of a quartz glass rod into the 16 $Na_2O \cdot 10\ CaO \cdot 74\ SiO_2$ melt measured by Truhlářova and Vepřek [14]. The close agreement of $\tilde{D}_{SiO_2}$ with D^*_{oxy} indicates that the dissolution process is rate controlled by diffusion of oxygen ion.

3.2. Relation between D^*_{oxy} and viscosity

The activation energy for diffusion of oxygen ion in the temperature range from 1470 to 800 °C is 38,6 kcal/mole as shown in equation (6), while the activation energy for viscous flow in the same temperature range is 42 kcal/mole as shown in equation (11). Such agreements between $E_{D^*_{oxy}}$ and E_η are also observed in a molten slag, 40 $SiO_2 \cdot 40\ CaO \cdot 20\ Al_2O_3$ [11 and 15], a Na_2O-SiO_2 binary silicate glass [1], and a molten B_2O_3 glass [16].

The relationship between diffusion coefficient and viscosity was discussed in detail in the previous paper [1], where the relation was satisfactorily described by the equation derived by Eyring[2]) rather than by the Stokes-Einstein relation[3]). Application of the Eyring model to the present molten glass concludes that the viscous flow is rate-controlled by the diffusion of non-bridging oxygen ions, i.e., the diffusion of the faster non-bridging oxygen ions causes the migration of the slower discrete anion groups consisting of silicon and oxygen ions [17]. The diffusivity data of silicon ion for the present molten glass, which is so far lacking, is useful in confirming this interpretation.

3.3. D^*_{oxy} in the transition range

There are two problems on D^*_{oxy} in the transition range to be pointed out; the first is the steep decrease of

[2]) Eyring's relation: $D = kT/\lambda\eta$, where k is the Boltzmann constant, T is the absolute temperature, λ is the distance between two equilibrium positions, and η is the viscosity.

[3]) Stokes-Einstein relation: $D = kT/6\pi r\eta$, where r is the radius of diffusing particle.

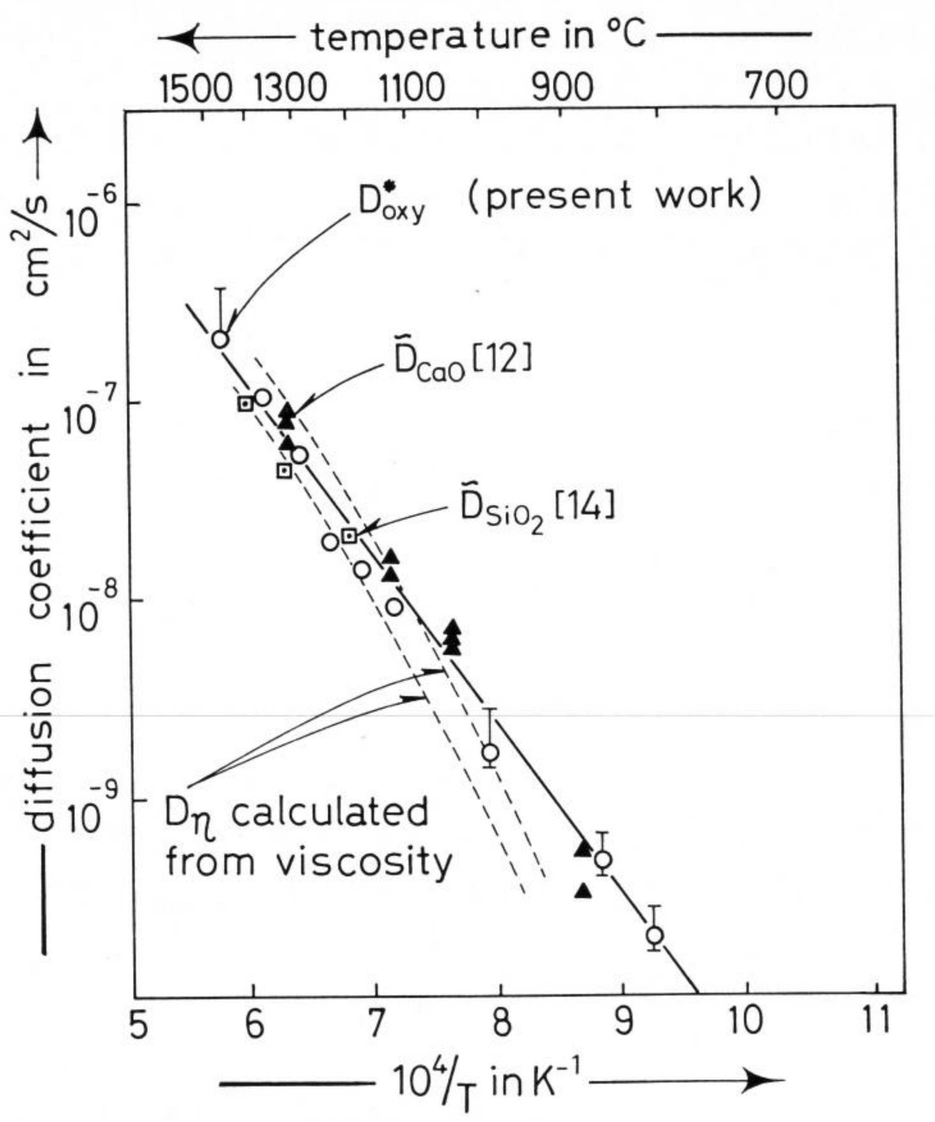

Figure 5. Self-diffusion coefficients of oxygen ion in high temperature range compared with interdiffusion coefficients, $\tilde{D}_{CaO}$ and $\tilde{D}_{SiO_2}$, and diffusion coefficients calculated from viscosity by Eyring's relation: upper dotted line for $\lambda = 1{,}4$ Å; lower dotted line for $\lambda = 2{,}8$ Å.

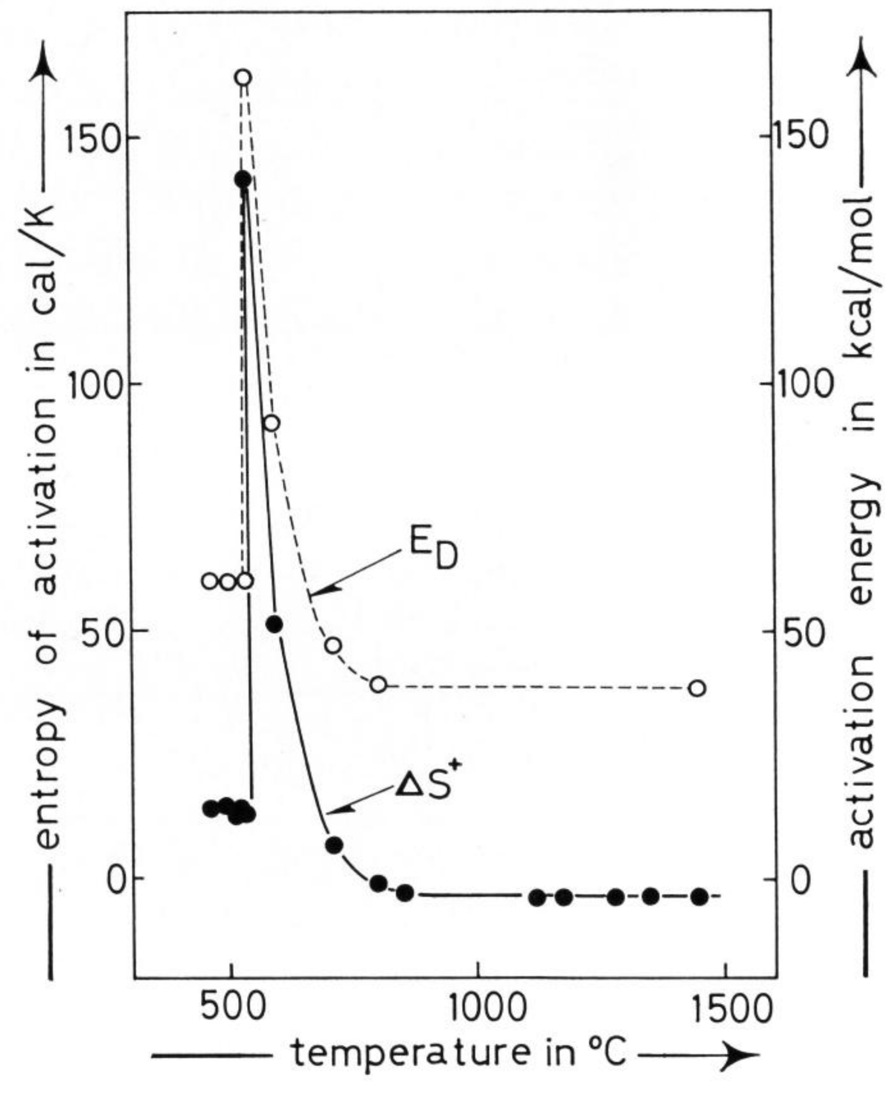

Figure 6. Activation energy and entropy of activation for diffusion of oxygen ion in 16 $Na_2O \cdot 12\ CaO \cdot 72\ SiO_2$ glass as a function of temperature.

D^*_{oxy} from 800 °C to T_g, and the second the fact that the temperature dependence of D^*_{oxy} begins to deviate from that of viscosity.

The rapid change of D^*_{oxy} in the transition range can be described in terms of the increases of the activation energy and the frequency factor. Figure 6 shows the activation energy, E_D, and the entropy of activation, ΔS^*, varying with temperature, where ΔS^* is derived with an assumption that the jump distance of oxygen ion is 3 Å. The increase of E_D and ΔS^* in this temperature range may be explained by the theory proposed by Adam and Gibbs [18]. According to their theory, the migration of oxygen ions in the transition range is accompanied by expansion of the cooperative rearranging region, which requires an excess structural activation energy. Non-linear Arrhenius relation of viscosity in the transition range has been discussed by many investigators, for example, Williams, Landel and Ferry [19], Cohen and Turnbull [20], and Macedo and Litovitz [21].

Secondly, the deviation of D_η from D^*_{oxy}, shown in figure 5, indicates that the predominant mechanism of viscous flow in the transition range is different from the mechanism above 800 °C. The viscosity of glass in the low temperature range is related to the flow of the skeleton of glass network and increases with the progress of the polymerization of flow units or with the decrease of the free volume in the glass structure as the temperature is lowered. Incidentally, crystallization of a new solid phase from a molten glass should be controlled by the oxygen diffusion rather than by the viscous flow in this temperature range. The apparent activation energy for the crystallization of devitrite ($Na_2O \cdot 3\,CaO \cdot 6\,SiO_2$) from the $16\,Na_2O \cdot 12\,CaO \cdot 72\,SiO_2$ glass [22] is approximately 40 kcal/mole, being closer to that for the oxygen diffusion, 39 kcal/mole, than to that for the viscous flow in the same temperature range, 60 kcal/mole. The relationship between the crystallization process and the oxygen diffusion will be discussed in detail elsewhere [23]. On the other hand, Burnett and Douglas [24], and Hammel [25] interpret the phase separation in the Na_2O-CaO-SiO_2 glasses, based on the coarsening mechanism theory, which says that oxygen is the rate-controlling species. However, the diffusion coefficients calculated from the growth kinetics in their phase separation do not agree with but differ from the D^*_{oxy} in present work by one order of magnitude. Thus the details of the phase separation mechanism are not obvious and require further investigation.

3.4. D^*_{oxy} below the transition range

Figure 4 shows that the present data below T_g agree with Kingery and Lecron's data [6], the activation energies being approximately 60 kcal/mole in both measurements. It is interesting to note that the activation energies for the oxygen diffusion are similar for fused silica [26 and 27], slag and glasses [6 and 28]. This agreement suggests a similar mechanism for the oxygen diffusion in these solid glasses independent of chemical compositions.

4. Conclusions

The self-diffusion coefficients of oxygen ion in $16\,Na_2O \cdot 12\,CaO \cdot 72\,SiO_2$ glass were measured by means of an isotopic exchange technique in the temperature range from 500 to 1470 °C. The Arrhenius plot of D^*_{oxy} gave a straight line at high temperatures above 800 °C. The activation energy was 38,6 kcal/mole, which agrees with that of the viscous flow. The relationship between D^*_{oxy} and viscosity was described by the Eyring equation.

The steep temperature dependence of D^*_{oxy} in the temperature range from 800 °C to T_g was consistent with the interpretation that the migration of oxygen ions required an excess structural activation energy. In this temperature range, D^*_{oxy} deviated from D_η.

Kinetic processes in the glass, such as viscous flow, crystallization, phase separation, dissolution of quartz glass, and interdiffusion were discussed in connection with the oxygen self-diffusion.

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