

# Interaction of ions in molten slag, salts and oxide compounds on diffusion

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**Abstract:** The diffusion of a ion in slag, salts and oxide compounds is influenced from other ions in the surroundings. The linear relations between the fluxes and the forces of ions are defined as the phenomenological equations. The proportional coefficients named as the transport coefficients represent the interaction of ions on diffusion. The transport coefficients between  $i$  ion and  $j$  ion are reciprocal and the relation is called as the Onsager's reciprocal theorem. The fluxes of ions are defined on a coordinate and one flux is not independent. The transport coefficients should be satisfied the entropy production on diffusion. The transport coefficients can be calculated from some of the transport properties such as electrical conductivity, transference numbers, tracer diffusivities, interdiffusivities. Others can be determined from the transport coefficients. The diagonal terms in the transport coefficients are positive and the other terms are positive or negative. The values of transport coefficients in some slag, salts and oxide compounds are examined from the non-equilibrium thermodynamics.

**Key words:** irreversible thermodynamics, transport coefficients, diffusion, electric conductivity, transference number

## 1. Introduction

Diffusion phenomena take place in multicomponent metallic solutions and in complex slag melts in many metallurgical processes under both isothermal and nonisothermal conditions. There are two types of coupling effects on the interaction among ion fluxes and that between heat flow and ion fluxes. The phenomena of "up-hill diffusion" under isothermal condition and "thermal diffusion" and thermo-electromotive force under nonisothermal condition have been observed at high temperature. In the present lecture, the coupling phenomena under isothermal condition will be discussed.

When an ionic species is migrating in a multicomponent compound under electrochemical potential gradients, coupling phenomena take place among diffusion jumps of different ions. That is, the fluxes of ions interfere each other.

The flux of a kind of  $i$  ion,  $j_i$ , is phenomenologically described to be proportional to the electrochemical potentials of all kind of ions,  $k$ ,  $X_k$  as forces;

$$j_i = \sum_{k=1}^n L_{ik} X_k \cdot \cdot \cdot \cdot \cdot \cdot \cdot (1)$$

$$X_k = -(\nabla\mu_k + Z_k F \nabla\varphi) \cdot \cdot \cdot \cdot \cdot \cdot \cdot (2)$$

where  $n$  is the number of kinds of ions.  $\nabla$  is gradient.  $\mu_k$  and  $Z_k$  are the chemical potential and the valence of ion  $k$ , respectively.  $F$  is Faraday constant and  $\varphi$  is the electrical potential. The proportional coefficient,  $L_{ik}$ , represents the coupling effect between the fluxes of ion  $i$  and  $k$  and is called as the transport coefficient [1].

## 2. Relation between transport coefficients and physical properties [2]

These coupling phenomena are theoretically related to physical properties such as tracer diffusivities,  $D_i^{\text{tr}}$ , interdiffusivities,  $D_{ik}$ , electrical conductivity,  $\sigma$ , and transference numbers of ions,  $t_i$ .

The total electric current density,  $I$ , is the summation of the fluxes of ions;

$$I = \sum_{i=1}^n Z_i F j_i \cdot \dots \cdot \dots \cdot \dots \cdot \dots \cdot (3)$$

without chemical potential gradients of ions, as  $\sigma = I/\varphi$ ,

$$\sigma = F^2 \sum_{i=1}^n \sum_{k=1}^n Z_i Z_k L_{ik} \dots \dots \dots (4)$$

The transference number of  $i$  ion can be defined as the ratio of the partial electric current by  $i$  ion to the total current,

$$t_i = Z_i F j_i / I.$$

$$t_i = \frac{Z_i \sum_{k=1}^n Z_k L_{ik}}{\sum_{i=1}^n \sum_{k=1}^n Z_i Z_k L_{ik}} \dots \dots \dots (5)$$

The Hittorf transference number relative to  $r$  ion is described using the relative flux of  $C_i(v_i - v_r) = j_i -$

$$j_r (C_i/C_r);$$

$$t_{ir}^H = \frac{Z_i \sum_{k=1}^n Z_k (L_{ik} - L_{rk} C_i/C_r)}{\sum_{i=1}^n \sum_{k=1}^n Z_i Z_k L_{ik}} \dots \dots (6)$$

The flux of  $i$  ion tracer,  $j_{i^*}$ , oppositely diffuses to that of  $i$  ion,  $j_i$  under the uniform concentration of other ions. Thus,  $j_{i^*} + j_i = 0$ . If the isotope effect is negligible small, the fluxes could be expressed as  $j_{i^*} = -L_{i^*i^*} \nabla \mu_{i^*}$  and  $j_i = -L_{ii} \nabla \mu_i$ . Using the Gibbs-Duhem's relation,  $C_{i^*} \nabla \mu_{i^*} + C_i \nabla \mu_i = 0$ , the relation of  $L_{i^*i^*} = L_{ii} (C_{i^*}/C_i)$  is obtained. As

the concentration of  $i$  ion tracer is dilute,  $\nabla \mu_{i^*} = (RT/C_{i^*}) \nabla C_{i^*}$ . The relation of  $j_{i^*} = -RT(L_{ii}/C_i) \nabla C_{i^*}$  is

obtained. Comparing the previous equation with the Fick's law,  $j_{i^*} = -D_i^{\text{tr}} \nabla C_{i^*}$ , one obtained the following equation.

$$D_i^{\text{tr}} = RT \frac{L_{ii}}{C_i} \dots \dots \dots (7)$$

When ions mutually diffuse in a multicomponent system, there is not net current,  $I = 0$ . The electric potential gradient is calculated as

$$\nabla\varphi = -\frac{\sum_{i=1}^n \sum_{k=1}^n Z_k L_{ik} \nabla\mu_k}{F \sum_{i=1}^n \sum_{k=1}^n Z_i Z_k L_{ik}} \dots\dots(8)$$

Substituting the equation (8) into (1) and (2), one obtains

$$j_i = -\sum_{k=1}^n T_{ik} \nabla\mu_k \dots\dots\dots(9)$$

$$T_{ik} = L_{ik} - \frac{\sum_{i'=1}^n Z_{i'} L_{i'k} \sum_{k'=1}^n Z_{k'} L_{ik'}}{\sum_{i'=1}^n \sum_{k'=1}^n Z_{i'} Z_{k'} L_{i'k'}} \dots(10)$$

Assuming the local equilibrium in material system,

$$\frac{\mu_\alpha}{Z_\alpha} + \frac{\mu_\beta}{|Z_\beta|} = \frac{\mu_{\alpha\beta}}{Z_\alpha} \dots\dots\dots(11)$$

$$\frac{\mu_\alpha}{Z_\alpha} + \mu_e = \frac{\mu_{[\alpha]}}{Z_\alpha} \dots\dots\dots(12)$$

$$\frac{\mu_\beta}{|Z_\beta|} + \mu_p = \frac{\mu_{[\beta]}}{|Z_\beta|} \dots\dots\dots(13)$$

where  $\alpha$  is cation including positive hole, p, and  $\beta$  is anion including electron, e.  $\alpha\beta$ ,  $[\alpha]$  and  $[\beta]$  are neutral compound, metal and gas, respectively. Using the equations (11) to (13) with the master cation, A, and the master anion, B,  $\nabla\mu_k$  can be replaced to the chemical potential gradients of neutral components. The equation (9) can be rewritten as

$$j_i = -\sum_{\alpha=1}^n T_{i\alpha} \nabla\mu_{\alpha B} + \sum_{\alpha=1}^n \left(\frac{Z_\alpha}{Z_A}\right) T_{i\alpha} \nabla\mu_{AB} - \sum_{\beta=1}^n \left(\frac{|Z_\beta|}{Z_A}\right) T_{i\beta} \nabla\mu_{A\beta} \dots\dots(14)$$

When the flux of ions,  $J_i$ , are defined relative to the center of gravity,

$$J_i = j_i - C_i v_0 \dots\dots\dots(15)$$

where  $v_0$  is the velocity of the external coordinate relative to the center of gravity. The summation of  $J_i$  with the unit of  $\text{kg/m}^2\text{s}$  is zero. Using  $v_0 = \sum_{i=1}^n j_i / C$  ( $C = \sum_{i=1}^n C_i$ ) and the equation (14), the equation (15) can be compared with the Fick's law on the interdiffusion of multicomponent system,

$$J_i = -\sum_{k \neq A, B}^n \widetilde{D}_{ik}^{AB} \nabla C_k \quad (i \neq A, B) \dots\dots\dots(16)$$

Rewriting the concentration gradient of ions to that of electrical neutral components,  $\alpha\beta$ , such as

$$\nabla C_\alpha = \sum_{\beta}^n \nabla C_{\alpha\beta} \quad \text{and} \quad \nabla C_\beta = \sum_{\alpha}^n \left(\frac{Z_\alpha}{Z_\beta}\right) \nabla C_{\alpha\beta}$$

one obtains the relation of the interdiffusion coefficients,  $\widetilde{D}_{ik}^{AB}$  to  $L_{ik}$ .

### 3. Independent number of transport coefficients

When the mean velocity of ions is employed as the external coordination, the summation of  $j_i$  with the unit of mole/m<sup>2</sup>s is zero. Then, the summation of coefficients of each force in the equation (1) is always zero.

$$\sum_{i=1}^n L_{ik} = 0 \quad (k = 1 \text{ to } n) \dots \dots \dots (17)$$

There are the Onsager reciprocal relations,

$$L_{ik} = L_{ki} \quad (i \neq k) \dots \dots \dots (18)$$

The number of transference coefficients is  $n^2$ . From the number of  $n$  of the equation (17) and  $n(n-1)/2$  of (18), the independent number of transference coefficients is  $n(n-1)/2$ .

The number of electrical conductivity is one, that of Hittorf transference number is  $n-1$ , that of tracer diffusivity is  $n$  and that of interdiffusivity is  $(n-2)^2$ . The total number of these physical properties is  $2n+(n-2)^2$  and is larger than that of transference coefficients because  $n \geq 2$ . Thus, all of transference coefficients can be calculated from the physical properties of the  $n(n-1)/2$  number.

According to the second law of thermodynamics, the entropy production,  $S_i$ , is positive,  $TdS_i = \sum_i^n j_i X_i \geq 0$ . Substituting the equations of (1) and (2), the following restrictions are obtained.

$$L_{ii} \geq 0 \text{ and } L_{ii} L_{kk} \geq L_{ik}^2 \dots \dots \dots (19)$$

### 4. Calculation of transport coefficients

#### 4.1 Simple salt AB (A cation, B anion) : $n=2$

The number of independent transport coefficient is one.

$$L_{AA} = L_{BB} = -L_{AB}$$

$$\sigma = F^2 (Z_A - Z_B)^2 L_{AA}$$

$$D_A^{tr} = RT \frac{L_{AA}}{C_A}, \quad D_B^{tr} = RT \frac{L_{BB}}{C_B}$$

1) The case of NaCl at 1111K [3]

The electric conductivity of NaCl is  $3.695 \times 10^2 \Omega^{-1} m^{-1}$  and the self diffusivity of  $Na^+$  is  $6.73 \times 10^{-9} m^2 s^{-1}$ . the density is  $1,536 \text{ kg} \cdot m^{-3}$ .  $L_{NaNa}$  calculated from the electrical conductivity is  $0.992 \times 10^{-8} \text{ mol}^2 J^{-1} m^{-1} s^{-1}$  and that from the self diffusivity is  $1.91 \times 10^{-8} \text{ mol}^2 J^{-1} m^{-1} s^{-1}$ . These two values coincide each other. Using the equations (4), (5) and (7), the transference number is calculated from the electrical conductivity and the self diffusivity.

$$t_A = \frac{F^2}{\sigma} Z_A (Z_A - Z_B) \frac{C_A}{RT} D_A$$

The calculated transference number is 0.965 and the measured ones are  $0.87 \pm 0.06$  at 1123K and  $0.62 \pm 0.06$  at 1133K.

2) The case of  $\text{PbCl}_2$  at 783K [3]

The electrical conductivity is  $5.891 \times 10^2 \Omega^{-1} \text{m}^{-1}$  and the self diffusivity of  $\text{Pb}^{2+}$  is  $0.99 \times 10^{-9} \text{m}^2 \text{s}^{-1}$  and that of  $\text{Cl}^{-1}$  is  $1.78 \times 10^{-9} \text{m}^2 \text{s}^{-1}$ .  $L_{\text{PbPb}}$  calculated from the electrical conductivity is  $1.757 \times 10^{-9} \text{mol}^2 \text{J}^{-1} \text{m}^{-1} \text{s}^{-1}$  and that from the self diffusivity is  $3.34 \times 10^{-9} \text{mol}^2 \text{J}^{-1} \text{m}^{-1} \text{s}^{-1}$ . These values are in good agreement. The calculated transference number is 0.317 and the measured one is  $0.24 \pm 0.01$  at 798K. The ratio of the self diffusivity of Pb to that of Cl is equal to that of the concentration of Cl to that of Pb and is 0.5. From the measured values of self diffusivities, the ratio is 0.556.

#### 4.2 Binary salt of AO-BO (A, B cation, O anion) : n=3

The number of independent transport coefficients is 3.

$$L_{AA} + L_{AB} + L_{AO} = 0, L_{BA} + L_{BB} + L_{BO} = 0, L_{OA} + L_{OB} + L_{OO} = 0$$

$$L_{AB} = L_{BA}, L_{AO} = L_{OA}, L_{BO} = L_{OB}$$

$$\sigma = F^2 (Z_A^2 L_{AA} + Z_B^2 L_{BB} + Z_O^2 L_{OO} + 2Z_A Z_B L_{AB} + 2Z_A Z_O L_{AO} + 2Z_B Z_O L_{BO})$$

$$D_A^{\text{tr}} = RT \frac{L_{AA}}{C_A}, D_B^{\text{tr}} = RT \frac{L_{BB}}{C_B}, D_O^{\text{tr}} = RT \frac{L_{OO}}{C_O}$$

$${}^r t_A = \frac{Z_A \left\{ (Z_A L_{AA} + Z_B L_{AB} + Z_O L_{AO}) - (Z_A L_{OA} + Z_B L_{OB} + Z_O L_{OO}) C_A / C_O \right\}}{(Z_A^2 L_{AA} + Z_B^2 L_{BB} + Z_O^2 L_{OO} + 2Z_A Z_B L_{AB} + 2Z_A Z_O L_{AO} + 2Z_B Z_O L_{BO})}$$

$${}^o t_A + {}^o t_B = 1$$

$$\widetilde{D}_{AB} = \left\{ \left( \frac{N_{BO}}{N_{AO}} \right) T_{AA} - 2T_{AB} + \left( \frac{N_{AO}}{N_{BO}} \right) T_{BB} \right\} V_m RT \left( 1 + \frac{\partial \ln \gamma_{AO}}{\partial \ln N_{AO}} \right) \dots (20)$$

where  $N_{i0}$  is mole fraction and  $\gamma_{AO}$  is activity coefficient.

3) The case of  $\text{NaNO}_3$ - $\text{AgNO}_3$  melt at 613K

The electric conductivity and the density of  $\text{NaNO}_3$ - $\text{AgNO}_3$  melt were measured by J. Byrne et al. [4] in 1952. The self diffusivities of  $\text{Ag}^+$  and  $\text{Na}^+$  in  $\text{NaNO}_3$ - $\text{AgNO}_3$  melt were measured as the functions of concentration and temperature by S. Zuca et al. [5] in 1974. The transport coefficients are calculated from these physical properties. The calculated values are shown in Figure 1.

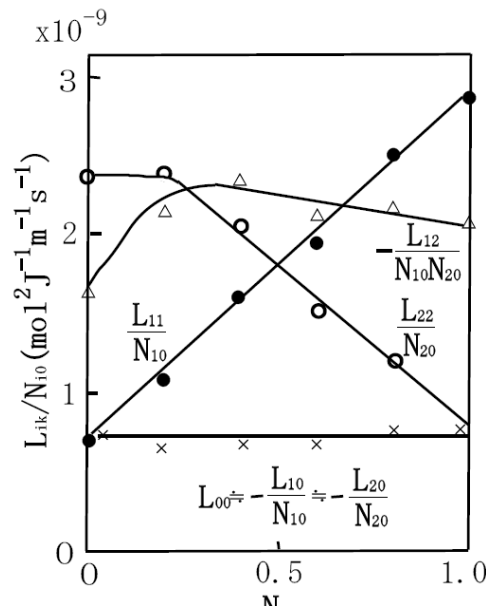


Figure 1 Lik of NaNO<sub>3</sub>-AgNO<sub>3</sub> system at 613K (1:Na, 2:Ag, 0: NO<sub>3</sub>)

4) The case of PbO-SiO<sub>2</sub> system at 1123K

The electric conductivity, the tracer diffusivities of Pb and Si in molten PbO-SiO<sub>2</sub> system were measured by B. Langanke et al. [6] in 1979. The density was summarized in handbook of glass data [7]. The calculated transport coefficients were shown in Figure 2.

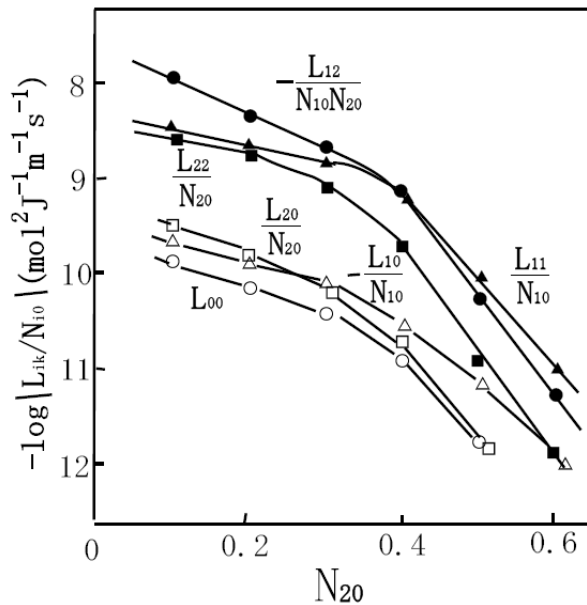


Figure 2 Lik of PbO-SiO<sub>2</sub> system at 1123K (1:Pb, 2:Si, 0: O)

From the transport coefficients, the interdiffusivity and the Hittorf transference number can be calculated. The electric conductivity of PbO-0.4SiO<sub>2</sub> is 11.22Ω<sup>-1</sup>m<sup>-1</sup> at 1123K. The tracer diffusivities of Pb and Si are 7.94x10<sup>-11</sup> m<sup>2</sup>s<sup>-1</sup> and 3.98x10<sup>-11</sup> m<sup>2</sup>s<sup>-1</sup>, respectively. The density is 6,450 kg·m<sup>-3</sup> and the molar volume is 2.45x10<sup>-5</sup> m<sup>3</sup>mol<sup>-1</sup>.

The transport coefficients of  $L_{PbPb}$  and  $L_{SiSi}$  are calculated to be  $20.84 \times 10^{-11}$  and  $6.96 \times 10^{-11} \text{ mol}^2 \text{J}^{-1} \text{m}^{-1} \text{s}^{-1}$ .  $L_{PbSi}$ ,  $L_{PbO}$ ,  $L_{SiO}$  and  $L_{OO}$  are  $-9.66 \times 10^{-11}$ ,  $-11.18 \times 10^{-11}$ ,  $2.70 \times 10^{-11}$  and  $8.48 \times 10^{-11} \text{ mol}^2 \text{J}^{-1} \text{m}^{-1} \text{s}^{-1}$ , respectively.

The calculated Hittorf transference number of  $Pb^{2+}$  is 0.63, while the measured value is 0.79.

Using the equation (10),  $T_{PbPb}$ ,  $T_{SiSi}$  and  $T_{PbSi}$  are calculated to be  $1.55 \times 10^{-10}$ ,  $6.88 \times 10^{-11}$  and  $-1.03 \times 10^{-10} \text{ mol}^2 \text{J}^{-1} \text{m}^{-1} \text{s}^{-1}$ . As  $\left(1 + \frac{\partial \ln \gamma_{AO}}{\partial \ln N_{AO}}\right) = 0.36$ ,  $\widetilde{D}_{PbSi}^{CO}$  is calculated to be  $3.4 \times 10^{-11} \text{ m}^2 \text{s}^{-1}$ , while the measured value is  $1.6 \times 10^{-11} \text{ m}^2 \text{s}^{-1}$ . The calculated values coincide with the measured ones [6].

### 4.3 Ternary oxide melt of AO-BO-CO : n=4

The number of independent transport coefficients is 6.

The interdiffusivities in ternary oxide melt are defined as

$$J_A = -\widetilde{D}_{AA}^{CO} \nabla C_{AO} - \widetilde{D}_{AB}^{CO} \nabla C_{BO}$$

$$J_B = -\widetilde{D}_{BA}^{CO} \nabla C_{AO} - \widetilde{D}_{BB}^{CO} \nabla C_{BO}$$

where A, B and C are cations and O is oxygen anion.

The interdiffusivities are restricted by a real solution of Fick's second law as the following relations.

$$\widetilde{D}_{AA}^{CO} + \widetilde{D}_{BB}^{CO} \geq 0$$

$$\widetilde{D}_{AA}^{CO} \widetilde{D}_{BB}^{CO} - \widetilde{D}_{AB}^{CO} \widetilde{D}_{BA}^{CO} \geq 0$$

$$\left(\widetilde{D}_{AA}^{CO} - \widetilde{D}_{BB}^{CO}\right)^2 + 4 \widetilde{D}_{AB}^{CO} \widetilde{D}_{BA}^{CO} \geq 0$$

The interdiffusivities can be related to the transport coefficients.

$$\widetilde{D}_{AA}^{CO} = \frac{RT}{C} \left[ \frac{C_B + C_C}{C_A} T_{AA} - T_{BA} - T_{CA} - \frac{C_A}{C_C} \left( \frac{C_B + C_C}{C_A} T_{AC} - T_{BC} - T_{CC} \right) \right] \left( 1 + \frac{\partial \ln \gamma_{AO}}{\partial \ln N_{AO}} \right) \frac{C_{BO}}{C_{CO}}$$

$$\widetilde{D}_{AB}^{CO} = \frac{RT}{C} \left[ \frac{C_A}{C_B} \left( \frac{C_B + C_C}{C_A} T_{AB} - T_{BB} - T_{CB} \right) - \frac{C_A}{C_C} \left( \frac{C_B + C_C}{C_A} T_{AC} - T_{BC} - T_{CC} \right) \right] \left( 1 + \frac{\partial \ln \gamma_{BO}}{\partial \ln N_{BO}} \right) \frac{C_{AO}}{C_{CO}}$$

$$\widetilde{D}_{BA}^{CO} = \frac{RT}{C} \left[ \frac{C_B}{C_A} \left( \frac{C_A + C_C}{C_B} T_{BA} - T_{AA} - T_{CA} \right) - \frac{C_B}{C_C} \left( \frac{C_A + C_C}{C_B} T_{BC} - T_{AC} - T_{CC} \right) \right] \left( 1 + \frac{\partial \ln \gamma_{AO}}{\partial \ln N_{AO}} \right) \frac{C_{BO}}{C_{CO}}$$

$$\widetilde{D}_{BB}^{CO} = \frac{RT}{C} \left[ \frac{C_A + C_C}{C_B} T_{BB} - T_{AB} - T_{CB} - \frac{C_B}{C_C} \left( \frac{C_A + C_C}{C_B} T_{BC} - T_{AC} - T_{CC} \right) \right] \left( 1 + \frac{\partial \ln \gamma_{BO}}{\partial \ln N_{BO}} \right) \frac{C_{AO}}{C_{CO}}$$

where  $C^{-1} = V_m$ .

5) The case of 40CaO-40SiO<sub>2</sub>-20Al<sub>2</sub>O<sub>3</sub> (mass%) system at 1773K [2]

The tracer diffusivity of calcium was measured to be  $2.1 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$  by H. Towers et al. in 1957. The tracer diffusivity of aluminum can be estimated to be  $6.3 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$  from the measured value by J. Henderson et al. in 1961. The tracer diffusivity of silicon can be estimated to be  $2.3 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$  from the measured value by H. Towers et al. in 1957. The electric conductivity was measured to be  $12.7 \Omega^{-1} \text{ m}^{-1}$  by R. Kammel et al. in 1965. The Hittorf transference numbers of calcium and aluminum can be estimated to be 0.95 and 0.04, respectively from the measured values by O. A. Esin et al. in 1955, V. I. Markin et al. in 1958 and A. Adachi et al. in 1962.

The transport coefficients are calculated.  $L_{\text{CaCa}} = 2.63 \times 10^{-10} \text{ mol}^2 \text{ J}^{-1} \text{ m}^{-1} \text{ s}^{-1}$ ,  $L_{\text{SiSi}} = 4.30 \times 10^{-11}$ ,  $L_{\text{AlAl}} = 2.63 \times 10^{-11}$ ,  $L_{\text{Oo}} = 1.22 \times 10^{-11}$ ,  $L_{\text{CaSi}} = -4.54 \times 10^{-11}$ ,  $L_{\text{CaAl}} = -4.78 \times 10^{-11}$ ,  $L_{\text{SiAl}} = -1.31 \times 10^{-10}$ ,  $L_{\text{CaO}} = -1.70 \times 10^{-10}$ ,  $L_{\text{SiO}} = 1.46 \times 10^{-11}$  and  $L_{\text{AlO}} = 1.22 \times 10^{-10}$ .

The interdiffusivities are calculated to be  $\widetilde{D}_{\text{CaCa}}^{\text{AlO}} = 3.20 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ ,  $\widetilde{D}_{\text{CaSi}}^{\text{AlO}} = -1.08 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ ,  $\widetilde{D}_{\text{SiCa}}^{\text{AlO}} = -1.06 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$  and  $\widetilde{D}_{\text{SiSi}}^{\text{AlO}} = 2.04 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ . Figure 3 shows the concentration profiles of CaO, SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> under interdiffusion. The up-hill diffusion of Al<sub>2</sub>O<sub>3</sub> [8] is well represented.

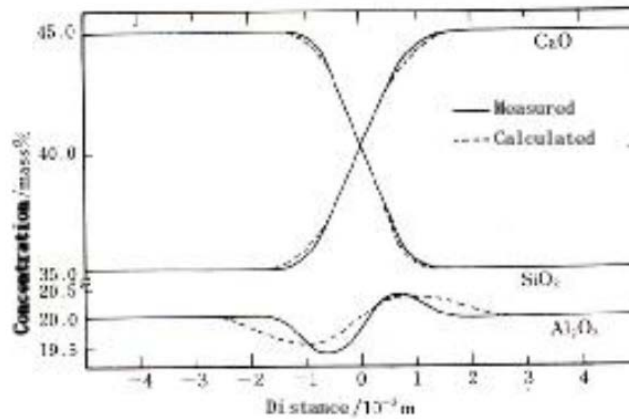


Figure 3 Calculated profiles of CaO, SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> in molten slag at 1773K in comparison with the measured profiles.

## 5. Discussion on the transport coefficients

The transport coefficients in ionic melts have the order of  $10^{-10}$  to  $10^{-11} \text{ mol}^2 \text{ J}^{-1} \text{ m}^{-1} \text{ s}^{-1}$ . The diagonal terms of transport coefficients,  $L_{ii}$ , are positive but the cross terms,  $L_{ik}$  ( $i \neq k$ ), are positive or negative.

When the cross term of  $L_{AB}$  in the binary salt is assumed to be zero, the equation (20) can be expressed as the function of tracer diffusivities and electric conductivity and transference numbers.

$$\widetilde{D}_{AB} = \left[ (C_B D_A + C_A D_B) - \left( C_B \frac{h_A}{Z_A} - C_A \frac{h_B}{Z_B} \right) \frac{RT\sigma}{C_A C_B F^2} \right] \left( 1 + \frac{\partial \ln \gamma_{AO}}{\partial \ln N_{AO}} \right) \dots (21)$$



This is the same equation expressed by W.Muller et al. [9]

In the case that  $L_{AA}$  and  $L_{BB}$  are larger than  $L_{OO}$ , the equation (20) can be expressed as

$$\widetilde{D}_{AB} = \frac{D_A D_B (Z_A N_{AO} + Z_B N_{BO})^2}{Z_A^2 N_{AO} D_A + Z_B^2 N_{BO} D_B} \dots\dots\dots (22)$$

In the case that  $L_{AA}$  and  $L_{BB}$  are smaller than  $L_{OO}$ , from the equation (20), one obtain the Darken's equation.

$$\widetilde{D}_{AB} = N_{BO} D_A + N_{AO} D_B \dots\dots\dots (23)$$

where  $\left(1 + \frac{\partial \ln \gamma_{AO}}{\partial \ln N_{AO}}\right) = 1$ . The equation (23) can be applied to alloy systems.

## 6. Conclusions

The transport coefficients of elementary components in molten salts and slags can be calculated from their physical properties such as tracer diffusivities, electrical conductivity, transference numbers and interdiffusivities. In ionic salts and oxide melts, the transport coefficients are almost same order. As the independent number of transport coefficients are smaller than that of their physical properties, one can calculate the unknown parameters. If the cross terms is assumed to be zero, the simple relation between their physical properties.

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