Relation between Tracer Diffusivity and Electrical Conductivity on Multi-component Oxide Slags at 900° to 1600°C*

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I. Object of the Present Communication

When the micro-mechanism on the transport of ionic species is the same for the electrical conduction and for the tracer diffusion in the ionic solutions, one can derive¹⁾ a simple relation between the conductivity and the diffusivity, called Nernst-Einstein relation:

$$\sigma = \frac{n_i(z_i e)^2}{kTf t_i} D_i^{\text{tr}} \quad \dots\dots\dots (1)$$

where,

- σ : the conductivity in $A \cdot V^{-1} \cdot cm^{-1}$
- D_i^{tr} : the tracer diffusivity of an ionic species i in $cm^2 \cdot sec^{-1}$
- n_i , z_i and t_i : concentration, valency and transference number of the ionic species, respectively
- e : the unit charge ($1.6 \times 10^{-19} A \cdot sec$)
- k : Boltzmann constant ($1.38 \times 10^{-23} V \cdot A \cdot sec \cdot ^\circ K^{-1}$)
- T : the absolute temperature
- f : the correlation factor^{2,3)} of successive jumps of the tracer.

Its validity has been proved on solid halides⁴⁾ and liquid halides.⁵⁻⁷⁾

The object of the present communication is to examine the validity of the relation on multi-component oxide slags. For this purpose, used are 29 sets of independent experimental data of the conductivity and the diffusivity at 900° to 1600°C.

II. Tracer Diffusivities, Measured and Calculated

The validity of Nernst-Einstein relation can be examined by comparing the measured tracer diffusivities of a cation with those calculated from the electrical conductivities. Here, Na_2O-GeO_2 , Na_2O-SiO_2 , $CaO-SiO_2$ and $CaO-SiO_2-Al_2O_3$ are selected with this respect. In the calculation, it is assumed that f and the transference number of Na^+ or Ca^{2+} would be unity.

Results of the calculation are shown in $D_{\text{calc.}}$ column of Table 1, while the sources of the used data are listed in Table 2. The corresponding measured tracer diffusivities are listed in $D_{\text{meas.}}$ column of Table 1, where three data from different sources are cited with respect to $CaO-SiO_2-Al_2O_3$. Data of $D_{\text{meas.}}$ are plotted against $D_{\text{calc.}}$ in Fig. 1. From the figure, one can see that every $D_{\text{meas.}}$ is smaller than $D_{\text{calc.}}$.

The relative deviations, defined by $\{(D_{\text{meas.}} - D_{\text{calc.}})/D_{\text{calc.}}\} \times 100$, are listed in the right column to $D_{\text{calc.}}$ of Table 1. From the column, it is noted that the deviations are nearly the same among binary oxide slags, i.e., $-70 \pm 20\%$, regardless of composition and temperature, and that the deviations are $-28 \pm 9\%$ in $CaO-SiO_2-Al_2O_3$. Further, it can be said that the activation energy for the tracer diffusion is larger than that for the electrical conduction.

III. An Interpretation of the Deviation

The calculation was based on many assumptions. The transference number of Na^+ or Ca^{2+} was taken as unity. According to the compilation by Adachi and Ogino,²¹⁾ t_{K^+} in K_2O-SiO_2 , t_{Li^+} in Li_2O-SiO_2 ,²²⁾ $t_{Ca^{2+}}$ in $CaO-SiO_2$ and $CaO-SiO_2-Al_2O_3$ ²³⁾ can be taken as unity. It seems quite reasonable to assume t_{Na^+} as unity in Na_2O-GeO_2 and Na_2O-SiO_2 from the data.

Correlation factor f was assumed unity, because there would be much more cation vacancies in molten slag than in solid lattice.

If the diffusivity measurement suffered from some convection in the molten slag, the apparent diffusivity would be larger than the true value. Thus, the deviation should be in the opposite direction.

Fig. 1. Comparison between tracer diffusivities, measured and calculated from the electrical conductivity data using Nernst-Einstein relation

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Table 1. Tracer diffusivity, measured and calculated from the electrical conductivity

No.	Composition (Diffusing species)	Temp. (°C)	$D_{\text{meas.}}$ (cm ² /sec)	$D_{\text{calc.}}$ (cm ² /sec)	Relative deviation* (%)	Q_d (kcal/mol)	Q_c (kcal/mol)
1	40mol%Na ₂ O-60mol%GeO ₂ (Na ⁺)	1 200	3.9×10^{-5}	13.3×10^{-5}	-71	10.5	9.6
2		1 100	2.4	7.3	-67		
3		1 000	1.7	5.9	-71		
4	30mol%Na ₂ O-70mol%GeO ₂ (Na ⁺)	1 200	2.3×10^{-5}	13.3×10^{-5}	-85	14.2	10.5
5		1 100	1.2	7.0	-83		
6		1 000	0.8	4.7	-83		
7	34wt%Na ₂ O-66wt%SiO ₂ (Na ⁺)	1 300	4.4×10^{-5}	9.6×10^{-5}	-54	12.5	11.2
8		1 100	2.5	5.6	-55		
9		900	1.1	2.9	-62		
10	24wt%Na ₂ O-76wt%SiO ₂ (Na ⁺)	1 300	2.8×10^{-5}	6.7×10^{-5}	-58	16.1	12.5
11		1 100	1.3	3.7	-65		
12		900	0.5	1.7	-71		
13	55wt%CaO-45wt%SiO ₂ (Ca ²⁺)	1 500	0.9×10^{-6}	7.0×10^{-6}	-87	50±20	35
14	54wt%CaO-46wt%SiO ₂ (Ca ²⁺)	1 600	$1.8 \times 10^{-6**}$	5.3×10^{-6}	-66	50±20	26
15		1 575	1.5	4.7	-68		
16		1 550	1.2	4.3	-72		
17	57wt%CaO-43wt%SiO ₂ (Ca ²⁺)	1 600	$1.8 \times 10^{-6**}$	5.3×10^{-6}	-66	50±20	35
18		1 575	1.5	4.7	-68		
19		1 500	1.2	4.0	-70		
20		1 350	3.3×10^{-7}	5.2×10^{-7}	-37	70±20	46
21			3.3		-37	30±15	
22			3.9		-25	50±20	
23	40wt%CaO-40wt%SiO ₂ - 20wt%Al ₂ O ₃ (Ca ²⁺)	1 400	6.8×10^{-7}	9.2×10^{-7}	-26	70±20	46
24			6.2		-33	30±15	
25			6.9		-25	50±20	
26		1 450	1.3×10^{-6}	1.6×10^{-6}	-19	70±20	46
27			9.5×10^{-7}		-37	30±15	
28			1.0×10^{-6}		-37	50±20	
29		1 500	2.1×10^{-6}	2.6×10^{-6}	-19	70±20	46

* defined by $\left(\frac{D_{\text{meas.}} - D_{\text{calc.}}}{D_{\text{calc.}}}\right) \times 100$

** These values are diffusivities of Ca²⁺ in 55wt%CaO-45wt%SiO₂.

Q_d, Q_c : activation energy for the diffusion and electrical conduction.

Table 2. Reference numbers on data sources of the tracer diffusivity, electrical conductivity and density used in Table 1.

	D^{tr}	σ	ρ
Na ₂ O-GeO ₂	9)	10)	11)
Na ₂ O-SiO ₂	12)	13)	12)
CaO-SiO ₂	14)	15)	16)
CaO-SiO ₂ -Al ₂ O ₃	14) 17)	19)	16)
	18) 20)		

If the Faradayic impedance at the interface between the electrodes and the molten slag were not negligible in the conductivity measurements, the conductivity would be smaller than the true value. Thus, the above errors would give the opposite deviation to Fig. 1.

If ionic pair movement aided the diffusion like in

liquid halides,⁴⁻⁷⁾ the measured diffusivity would be larger than that calculated from the conductivity, because the latter is not affected by the ionic pair movement.

Because all the above could not explain the deviation and the oxide slags are of multi-component, questionable is the validity of the fundamental assumption; The velocity of an ionic particle is proportional only to the force exerting upon the same ionic species, but not upon the other ionic species.

Generally, the diffusion flux of an ionic species i in multi-component oxide slag, j_i (mol·cm⁻²·sec⁻¹), is given as,⁸⁾

$$j_i = - \sum_{k=1}^n L_{ik} \frac{d\eta_k}{dx} + c_i v_o \dots\dots\dots (2)$$

where, L_{ik} : called transport coefficient in mol²·cal⁻¹·cm⁻¹·sec⁻¹

- η_k : electrochemical potential of ionic species k in cal·mol⁻¹
 c_i : molar concentration of i in mol·cm⁻³
 v_o : a local velocity of the internal reference frame in cm·sec⁻¹

Goto, Schmalzried and Nagata,^{24,25)} Nagata and Goto²⁶⁾ derived the general relationship between L_{ik} and D_i^{tr} , and also between L_{ik} and σ . According to them, the tracer diffusivity of i is given as

$$D_i^{\text{tr}} = \frac{RT}{c_i} L_{ii} \dots\dots\dots (3)$$

The partial electrical conductivity due to ionic species i is given as

$$\sigma_i = F^2 \sum_{k=0}^3 z_i z_k L_{ik} \dots\dots\dots (4)$$

where, F is Faraday constant in cal·V⁻¹·equiv.⁻¹ and A·sec·equiv.⁻¹, suffix 1, 2, 3, 0 means, for example, Ca²⁺, Si⁴⁺, Al³⁺ and O²⁻ in CaO-SiO₂-Al₂O₃ liquid slag, and z_i is the valency of i . In combination of Eq. (3) with Eq. (4), the relation, for the multi-component slags, between the electrical conductivity and the tracer diffusivity of i can be given in terms of transport coefficients, for example, CaO-SiO₂-Al₂O₃, as

$$\sigma_1 = F^2 \left(\frac{4c_1}{RT} D_{\text{Ca}}^{\text{tr}} + 8L_{12} + 6L_{13} - 4L_{10} \right) \dots\dots\dots (5)$$

In comparison of Eq. (5) with Eq. (1), it is seen that L_{12} , L_{13} and L_{10} are omitted in the Nernst-Einstein relation. Therefore, the above deviation may be interpreted due to the neglect of the cross terms of L_{12} , L_{13} and L_{10} . Also, Eq. (5) tells us that the activation energy for the conduction would not be the same as that for the diffusion because of the temperature dependence of the cross terms.

REFERENCES

- 1) A. B. Lidiard: Handbuch der Physik, Bd. XX, Springer Verlag, Berlin, (1957), 324.

- 2) J. Bardeen and C. Herring: Imperfections in Nearly Perfect Crystals, John Wiley & Sons, New York, (1952), 261.
- 3) K. Compain and Y. Haven: *Trans. Faraday Soc.*, **52** (1956), 786.
- 4) D. Mapother, H. N. Crooks and R. J. Maurer: *J. Chem. Phys.*, **18** (1950), 1234.
- 5) J. O'M. Bockris and G. W. Hooper: *Dis. Farad. Soc.*, **32** (1961), 218.
- 6) J. O'M. Bockris, S. R. Richards and L. Nanis: *J. Phys. Chem.*, **69** (1965), 1627.
- 7) G. Perkins, R. B. Escue, J. F. Lamb and J. W. Wimberley: *J. Phys. Chem.*, **64** (1960), 1792.
- 8) L. Onsager: *Trans. N.Y. Acad. Sci.*, **46** (1945), 241.
- 9) M. Sasabe and K. Kaneko: *Tetsu-to-Hagané*, **59** (1973), 190.
- 10) H. Saito: private communication (1972).
- 11) E. F. Riebling: *J. Chem. Phys.*, **39** (1963), 3022.
- 12) Y. Gupta and T. B. King: *Trans. Met. Soc. AIME*, **239** (1967), 1701.
- 13) J. R. Hutchins: dissertation of Sc. Dr, M.I.T., (1959), cited in Ref. 12).
- 14) T. Saito and K. Maruya: *J. Japan Inst. Metals*, **21** (1957), 728.
- 15) Y. Matsushita and K. Mori: *Tetsu-to-Hagané*, **38** (1952), 283.
- 16) R. Kammel and H. Winterhager: *Erzmetall.*, **18** (1965), 9.
- 17) H. Towers, M. Paris and J. Chipman: *Trans. Met. Soc. AIME*, **197** (1953), 1455.
- 18) K. Niwa: *J. Japan Inst. Metals*, **21** (1957), 304.
- 19) A. E. Martin and G. Derge: *Trans. Met. Soc. AIME*, **154** (1943), 104.
- 20) H. Towers and J. Chipman: *Trans. Met. Soc. AIME*, **209** (1957), 769.
- 21) A. Adachi and K. Ogino: *Yōyūen*, **5** (1962), 1149.
- 22) J. O'M. Bockris, J. A. Kitchener and A. E. Davies: *Trans. Farad. Soc.*, **48** (1952), 536.
- 23) O. A. Esin and A. K. Kirianov: *Izv. Akad. Nauk. SSSR Otdel. Tekh. Nauk.*, (1955), No. 12, 28.
- 24) K. S. Goto, H. Schmalzried and K. Nagata: *Tetsu-to-Hagané*, **61** (1975), 2794.
- 25) K. S. Goto, H. Schmalzried and K. Nagata: *Arch. Eisenhüttenw.*, **47** (1976), 133.
- 26) K. Nagata and K. S. Goto: *J. Electrochem.*, **123** (1976), 1814.