

Conductivity of melts in the system CaO—FeO—Fe₂O₃—SiO₂

V. DANĚK, T. LIČKO, and Z. PÁNEK

*Institute of Inorganic Chemistry, Centre for Chemical Research,
Slovak Academy of Sciences, CS-842 36 Bratislava*

Received 21 December 1984

*Dedicated to the memory of Professor Ing. M. Malinovský, DrSc.,
April 2, 1926—December 15, 1984*

Conductivity of the CaO—FeO—Fe₂O₃—SiO₂ melts in the temperature range 1530 K to 1920 K and in the atmosphere of air increases with the increasing temperature and with the increasing concentration of the iron oxides. The presence of iron in two oxidation states, Fe(II) and Fe(III), results in a partial electronic conductance which is due to the jumping electron. The dependence of logarithm of the conductivity value on the reciprocal temperature was described by the third order polynomial. The dependence of conductivity on the composition was described by the equation

$$\kappa = \sum_i z_i F u_i (c_i - c_{i,0})$$

From the above equation mobilities and diffusion coefficients for Ca²⁺, Fe²⁺, and Fe³⁺ cations and for electrons at 1723 K and 1823 K were calculated by the multiple linear regression. The concentration of the electrons in the melt is proportionate to 2x(Fe₂O₃) · x(FeO). Both mobility and diffusion coefficient of the present conductive particles increase in the order

$$u(\text{Fe}^{3+}) < u(\text{Fe}^{2+}) < u(\text{Ca}^{2+}) < u(e^-)$$

Удельная электропроводность расплава CaO—FeO—Fe₂O₃—SiO₂ в промежулке температур 1530 К—1920 К в воздушной атмосфере возрастает при увеличении температуры и при увеличении концентрации окислов железа. Присутствие железа в двух степенях окисления Fe(II) и Fe(III) ведет к частичной электронной проводимости, возникающей благодаря скачущему электрону. Зависимость логарифма величины удельной электропроводности от обратной температуры описана с помощью полинома третьего порядка. Зависимость удельной электропроводности от состава описана уравнением

$$\kappa = \sum_i z_i F u_i (c_i - c_{i,0})$$

Исходя из данного уравнения посредством многократной линейной регрессии были рассчитаны величины подвижностей и коэффициентов диффузии катионов Ca^{2+} , Fe^{2+} и Fe^{3+} и электронов при 1723 К и 1823 К. Концентрация электронов в расплаве пропорциональна $2x(\text{Fe}_2\text{O}_3) \cdot x(\text{FeO})$. Величины подвижностей и коэффициентов диффузии присутствующих проводящих частиц возрастают в ряду

$$u(\text{Fe}^{3+}) < u(\text{Fe}^{2+}) < u(\text{Ca}^{2+}) < u(e^-)$$

The system $\text{CaO—FeO—Fe}_2\text{O}_3\text{—SiO}_2$ is the basic system of metallurgical slags. The ratio of two- and threevalent iron in the melt is dependent on the oxygen partial pressure, the temperature and on the total melt composition. When the melt is held in equilibrium with metallic iron, and in an inert atmosphere, only Fe^{2+} cations are present in the melt. *Toropov* and *Bryantsev* [1] used such conditions in measuring conductivity of MgO—FeO—SiO_2 melts. The atmosphere of air is another atmosphere with the defined oxygen partial pressure. In this case the content of two- and threevalent iron is dependent on the temperature and on the melt composition. Conductivity of $\text{FeO}_y\text{—CaO—SiO}_2$ melts in the air was measured by *Dancy* and *Derge* [2], and by *Engell* and *Vygen* [3]. Conductivity of the melts in the atmosphere of pure oxygen, when only threevalent iron is present in the melt, was measured in [4—7].

For investigation of properties of the $\text{CaO—FeO}_y\text{—SiO}_2$ melts in the air it is necessary to know the equilibrium melt composition as a function of the temperature and of the total melt composition. Phase diagram of the system was studied in [8, 9], where the equilibrium contents of two- and threevalent iron in the melt were determined in quenched samples. The presence of the ions of the same kind in two oxidation states results in an increase of melt conductivity due to the electronic conductance contribution caused by the electrons jumping between the two ions in the different oxidation states. Such phenomenon was observed in molten salts, e.g. in the systems metal—metal halide [10, 11], and in the system CuCl—CuCl_2 [12]. The above mechanism for charge transport in melts was supposed by *Rice* [13] and it was elaborated by *Raleigh* [14] to explain the exponential conductivity increase with the increasing metal content in the system Bi—BiCl_3 ; in this case the electron jumps between Bi^+ and Bi^{3+} ions.

In the present work conductivity of $\text{CaO—FeO—Fe}_2\text{O}_3\text{—SiO}_2$ melts in the air, and in the temperature range 1530 K to 1920 K was investigated. The experimental results were used for the calculation of the electronic conductance contribution. The mobilities and the diffusion coefficients of the conductive particles were also calculated.

Experimental

Conductivity was measured by an alternative current using the device for measuring the physical properties of silicate melts described in [15, 16]. Resistance was measured by the semi-automatic bridge Tesla BM-484 with built in a.c. generator (frequency 1592 Hz) employed. Electrodes — discs 5 mm in diameter with the leads 1 mm in diameter, all made of PtRh40 alloy — were immersed for 7 mm into the melt. The depth of immersion was adjusted using a micrometer screw. The sample was placed in the PtRh20 crucible in the electrical resistance furnace. The temperature was measured with an accuracy ± 5 K with a PtRh6—PtRh30 thermocouple which was immersed into the melt. The cell was calibrated with the KCl aqueous solutions. For the experimental temperatures the cell constant was then corrected using the known data on PtRh40 alloy dilatation. Because of the calibration method used (and because of possibility of cell deformation at the elevated temperatures) the relative error of conductivity measurements was ± 4 %.

The samples were made from calcined CaCO_3 , SiO_2 , and Fe_2O_3 (all of anal. grade) by melting in PtRh20 crucible. The composition of samples was selected to follow, as possible, the change in the slag composition in the model system $\text{CaO—Fe}_2\text{O}_3\text{—SiO}_2$ during the steel-making process in the basic oxygen-furnace. The curve is represented in Fig. 1

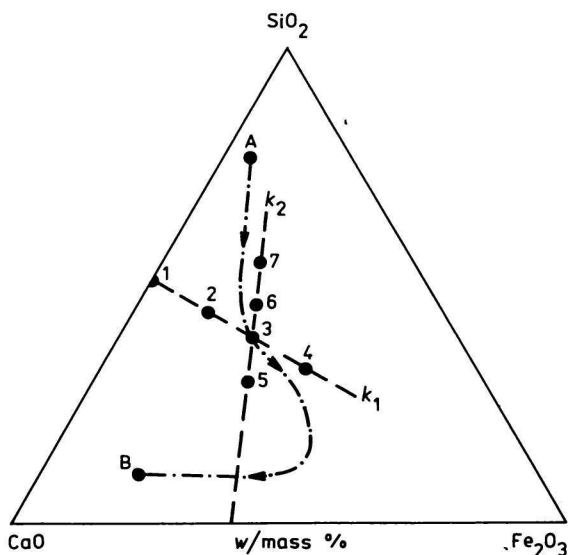


Fig. 1. The chosen sections in the system $\text{CaO—Fe}_2\text{O}_3\text{—SiO}_2$.

1—7: The weighed compositions of the investigated samples; A—B: the path of the slag composition during the steel-making process [17].

according to the data given in [17]. The compositions of the investigated samples are also represented in Fig. 1. The points correspond to two sections with constant mole ratio $k_1 = x(\text{CaO})/x(\text{SiO}_2) = 1$ and $k_2 = x(\text{CaO})/x(\text{Fe}_2\text{O}_3) = 4$. The equilibrium compositions of melts at the given experimental temperature were calculated according to

$$r = 1.7273 - 6.592 \times 10^{-4} T/\text{K} + 0.223k_1 + 0.116x'(\text{Fe}_2\text{O}_3) \quad (1)$$

where $r = x(\text{Fe}_2\text{O}_3)/[x(\text{FeO}) + x(\text{Fe}_2\text{O}_3)]$, T is the thermodynamic temperature, and $x'(\text{Fe}_2\text{O}_3)$ is the mole fraction of Fe_2O_3 in the weighed mixture. Eqn (1) was derived in the present work using the data taken from [8, 9]. The contents of two- and threevalent iron were also determined experimentally in the quenched samples after measurements. The analyses were carried out by titration and also by the atomic absorption spectroscopy and were in good agreement with equilibrium compositions calculated according to eqn (1).

Results and discussion

The temperature dependences of conductivity of the $\text{CaO}-\text{FeO}-\text{Fe}_2\text{O}_3-\text{SiO}_2$ melts in the form $\log \{\kappa\} = f(K/T)$ were described by the third order polynomial using the least squares method. The parameters of this dependence together with standard deviations of the experimental conductivity values are given in Table 1.

Table 1

Coefficients of the temperature dependence of conductivity of the investigated melts

$$\log \{\kappa\} = a + b \cdot \frac{K}{T} + c \cdot \left(\frac{K}{T}\right)^2 + d \cdot \left(\frac{K}{T}\right)^3$$

Sample	$a \cdot 10^{-1}$	$b \cdot 10^{-5}$	$c \cdot 10^{-8}$	$d \cdot 10^{-11}$	$\sigma \cdot 10^3$	T/K
1 ^a	-11.3610	6.0350	-10.6230	6.1720	4.4	1790—1920
2	-4.5336	2.2548	-3.6575	1.9063	4.5	1670—1850
3	-12.5581	6.3807	-10.7278	5.9524	7.3	1660—1830
4	-7.7777	3.8855	-6.3745	3.4296	5.8	1530—1830
5	-10.3900	5.3522	-9.1058	5.1051	6.3	1640—1880
6	-8.9731	4.5810	-7.7122	4.2592	3.8	1570—1870
7	-9.7800	5.0290	-8.5443	4.7605	4.9	1650—1890

a) According to Ref. [16].

The equilibrium melt compositions and conductivities at 1723 K are given in Table 2. Conductivities of the investigated melts increase with the increasing concentration of calcium oxide and of iron oxides (Fig. 2) and with the increasing temperature. The exponential increase of melt conductivities with the increasing content of iron oxides indicates a presence of other conductive particles in the melt. Free electrons jumping from Fe(II) to Fe(III) atoms are suggested to contribute to

Table 2

Equilibrium composition, conductivity, and molar volume of the investigated melts at 1723 K

Sample	$x(\text{CaO})$	$x(\text{FeO})$	$x(\text{Fe}_2\text{O}_3)$	$x(\text{SiO}_2)$	$\frac{\kappa(1723 \text{ K})}{\text{S cm}^{-1}}$	$\frac{V(1723 \text{ K})^b}{\text{cm}^3 \text{ mol}^{-1}}$
1*	0.500	—	—	0.500	0.304	21.790
2	0.472	0.010	0.046	0.472	0.394	22.611
3	0.444	0.019	0.092	0.444	0.566	23.422
4	0.412	0.030	0.146	0.412	1.142	24.071
5	0.517	0.009	0.120	0.353	0.650	23.649
6	0.383	0.022	0.074	0.521	0.425	23.556
7	0.312	0.023	0.055	0.610	0.215	23.915

a) According to Ref. [16]; b) according to Ref. [21].

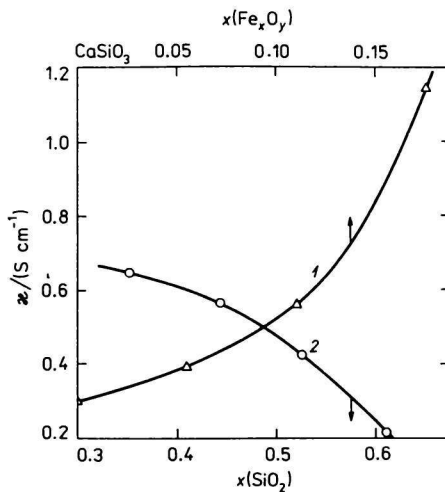


Fig. 2. The dependence of the conductivity on the composition of the investigated melts at 1723 K.

1. The section with the constant ratio $k_1 = x(\text{CaO})/x(\text{SiO}_2) = 1$;
2. the section with the constant ratio $k_2 = x(\text{CaO})/x(\text{Fe}_2\text{O}_3) = 4$.

conductance. As it was mentioned above, the charge transport by electrons was observed in numerous inorganic molten systems containing atoms in different oxidation states, e.g. Cu(I) and Cu(II) [12], Bi(I) and Bi(III), Nd(II) and Nd(III) [18], Co(II) and Co(III) [19] or V(IV) and V(V) [20], respectively.

In the previous work [16] the conductivity of ionic silicate melts was shown to be proportionate to the product of mobilities and concentrations of conductive particles

$$\kappa = \sum_i z_i F u_i (c_i - c_{i,0}) \quad (2)$$

where c_i are the molar concentrations of conductive particles with charge numbers z_i , $c_{i,0}$ are the molar concentrations of that part of cations which do not participate in the charge transport, F is the Faraday's constant, and u_i are the mobilities of the conductive particles. It was shown in [16] that in silicate melts with high SiO_2 contents (min. 40 mole %) the charge is transported exclusively by cations. In the system $\text{CaO—FeO—Fe}_2\text{O}_3\text{—SiO}_2$ the contribution of electrons has also be included. Eqn (2) then can be written

$$\kappa = F\{2u(\text{Ca}^{2+}) [c(\text{Ca}^{2+}) - c_0(\text{Ca}^{2+})] + 2u(\text{Fe}^{2+}) [c(\text{Fe}^{2+}) - c_0(\text{Fe}^{2+})] + 3u(\text{Fe}^{3+}) [c(\text{Fe}^{3+}) - c_0(\text{Fe}^{3+})] + u(e^-) c(e^-)\} \quad (3)$$

Eqn (3) can be solved by multiple linear regression when concentrations c_i of all conductive particles in the melt are known. Concentrations of Ca^{2+} and Fe^{2+} cations can be calculated from melt densities measured in [21]. In [22] the calculation of liquidus surface of CaSiO_3 in the system $\text{CaO—Fe}_2\text{O}_3\text{—SiO}_2$ was carried out. On the calculations it was stated in [22] that a half of Fe(III) atoms is coordinated tetrahedrally, *i.e.* it behaves as a network former. It follows that only other part of Fe(III) atoms, which is more highly coordinated and which behaves as a network modifier, can participate in the charge transport. Concentration of conductive Fe^{3+} cations is then given by

$$c(\text{Fe}^{3+}) = \frac{x(\text{Fe}_2\text{O}_3)}{V_{\text{melt}}} \quad (4)$$

where V_{melt} is the molar volume of the melt and $x(\text{Fe}_2\text{O}_3)$ is the mole fraction of Fe_2O_3 in the melt.

Concentration of electrons in the melt was determined as follows. *Rice* [13] and *Raleigh* [14] supposed that the concentration of electrons is proportionate to the concentration of the component in lower oxidation state, *i.e.* to $x(\text{FeO})$ in the investigated system. Such suggestion is fulfilled well in systems metal—metal halide in the range of high concentrations of metal halide (when the metal is a minor component). However, in the systems with comparable concentrations of both the cations the situation will be somewhat different. Electron can jump only when a donor (Fe^{2+}) has an acceptor (Fe^{3+}) in its neighbourhood. The probability that such an acceptor is available is equal to $2x(\text{Fe}_2\text{O}_3)$. Concentration of electrons is then equal to

$$c(e^-) = \frac{2x(\text{Fe}_2\text{O}_3) \cdot x(\text{FeO})}{V_{\text{melt}}} \quad (5)$$

The dependence of conductivity on the concentration of the conductive particles in the system $\text{CaO—FeO—Fe}_2\text{O}_3\text{—SiO}_2$ was determined by multiple linear regression. The dependence has the form

$$\kappa = -A + B_1c(\text{Ca}^{2+}) + B_2c(\text{Fe}^{2+}) + B_3c(\text{Fe}^{3+}) + B_4c(e^-) \quad (6)$$

where $B_i = z_iFu_i$. Standard deviation of the experimental values from the calculated ones is $\sigma = 3 \times 10^{-2} \text{ S cm}^{-1}$. The calculated constants A and B_i for 1723 K and 1823 K are given in Table 3. Comparing eqns (3) and (6) it follows for A

$$A = B_1c_o(\text{Ca}^{2+}) + B_2c_o(\text{Fe}^{2+}) + B_3c_o(\text{Fe}^{3+}) \quad (7)$$

Table 3

Constants A , B_i , mobilities, and diffusion coefficients of the conductive particles in the $\text{CaO—FeO—Fe}_2\text{O}_3\text{—SiO}_2$ melts at 1723 K and 1823 K

Parameter	T/K	Ca^{2+}	Fe^{2+}	Fe^{3+}	e^-
B_i $\text{S cm}^2 \text{ mol}^{-1}$	1723	38.6	35.1	32.7	2170
	1823	41.9	38.4	35.6	2050
$\frac{\mu_i \cdot 10^4}{\text{cm}^2 \text{ s}^{-1} \text{ V}^{-1}}$	1723	2.0	1.8	1.1	225
	1823	2.2	2.0	1.2	212
$\frac{D_i \cdot 10^5}{\text{cm}^2 \text{ s}^{-1}}$	1723	1.5	1.4	0.56	334
	1823	1.7	1.6	0.61	315
$\frac{A}{\text{S cm}^{-1}}$	1723			0.61	
	1823			0.53	

In the previous work [16] the limit concentration $c_{i,o}$ was regarded to be the part of cations, which did not participate in the charge transport. Those cations were supposed to be bonded into larger structural units, clusters, which could be composed of silicate polyanions connected by cations with polar covalent bond. In the system $\text{CaO—FeO—Fe}_2\text{O}_3\text{—SiO}_2$ such bonding occurs especially in the case of Fe(III) atoms. However, the part of nonconductive Fe(III) atoms was already excluded in the calculations (eqn (4)). As regards the other conductive particles, a tendency towards such behaviour can be expected at Fe(II) and less at Ca(II) atoms. A partial tetrahedral coordination of Fe(II) atoms could not be excluded either at the calculation of the liquidus surface of CaSiO_3 in the system CaO—FeO—SiO_2 [22]. Limit concentrations of Ca(II) and Fe(II) atoms in the investigated system can be estimated from the value of the absolute term A . Provided that $c_o(\text{Ca}^{2+})/c_o(\text{Fe}^{2+}) = r(\text{Fe}^{2+})/r(\text{Ca}^{2+})$, where r_i are the ionic radii (similarly it holds for concentration regions of miscibility gaps in the systems

CaO—SiO₂ and FeO—SiO₂), the values of $c_o(\text{Ca}^{2+}) \doteq 6 \times 10^{-3} \text{ mol cm}^{-3}$ and $c_o(\text{Fe}^{2+}) \doteq 7.5 \times 10^{-3} \text{ mol cm}^{-3}$ can be obtained; the values correspond to ca. 15 mole % CaO and 18 mole % FeO in the corresponding systems.

The mobilities of conductive particles, *i.e.* Ca²⁺, Fe²⁺, and Fe³⁺ cations and electrons, were calculated from B_i coefficients in eqns (6) and (7); calculations were carried out for 1723 K and 1823 K. From the obtained mobilities corresponding values of diffusion coefficients were calculated using Nernst—Einstein's equation. The calculated values are given in Table 3. The mobilities as well as diffusion coefficients of the cations were found to decrease in the order $u(\text{Ca}^{2+}) > u(\text{Fe}^{2+}) > u(\text{Fe}^{3+})$, which can be explained by different forces effective between the cations and the nonbridging oxygens on SiO₄ tetrahedrons. When a cation has a higher value of the ratio z/r (z is a charge number and r is a cationic radius) a stronger bond between the cation and nonbridging oxygens arises; from sterical reasons the coordination number of the cation becomes lower. Such cation is stronger bonded in its position and the Me—O bond becomes more covalent, which results in the decrease of mobility of the cation.

The mobilities of the electrons were found to be two orders higher comparing to that of the cations. For electron jump some fluctuation in the composition or a different arrangement of the ionic atmosphere of both the exchange cations is needed. Fe(II) and Fe(III) atoms present in silicate melts are differently coordinated and the distances from the nearest neighbours (*i.e.* oxygen atoms) are also different. The distances between the exchange sites are relatively long and that is why for jump frequency the values close to the mean value of vibration frequencies of the ionic thermal movement in the melt can be expected. The mobility of such electron is defined in Ref. [14]

$$u(e^-) = \frac{e}{6kT} \nu_R \cdot R^2 \quad (8)$$

where e is the electron charge, ν_R is the jump frequency, and R is the mean distance between the exchange sites given by

$$R \doteq \left(\frac{V}{N_A} \right)^{1/3} \quad (9)$$

where V is the molar volume and N_A is the Avogadro's constant. From the mobilities the jump frequency of electron can be calculated according to eqn (8). For 1723 K and $V \doteq 23 \text{ cm}^3 \text{ mol}^{-1}$ one obtains $\nu_R \doteq 1.7 \times 10^{13} \text{ s}^{-1}$, which is real value comparable to the vibration frequency of thermal movement. The reciprocal frequency value is the mean lifetime of the given arrangement $\tau \doteq 6 \times 10^{-14} \text{ s}$. The high degree of the symmetry of oxygen covers of both exchange cations is indicated by the ν_R and τ values. Energy levels of the excited states of the electron in both oxidation states of Fe atoms are probably close to each other.

References

1. Toropov, N. A. and Bryantsev, B. A., *Strukturnye prevrashcheniya pri povyshennykh temperaturakh*, p. 205. Moscow—Leningrad, 1965.
2. Dancy, E. A. and Derge, G. J., *Trans. Met. Soc. AIME* 236, 1642 (1966).
3. Engell, H. J. and Vygen, P., *Ber. Bunsenges. Phys. Chem.* 72, 5 (1968).
4. Hirashima, H. and Yoshida, T., *Yogyo Kyokai Shi* 80, 75 (1972).
5. Lopatin, V. M., Nikitin, Yu. P., and Barmin, L. N., *Izv. Vyssh. Ucheb. Zaved., Cher. Met.* 1973, 17.
6. Morinaga, K., Suginoara, Y., and Yanagase, T., *Nippon Kinzoku Gakkaishi* 39, 1312 (1975).
7. Shcheglova, M. D. and Kholovskii, M. F., *Khim. Tekhnol. (Kiev)* 1977, 12.
8. Larson, H. and Chipman, J., *Trans. Met. Soc. AIME* 197, 1089 (1953).
9. Timucin, M. and Morris, A. E., *Met. Trans.* 1, 3193 (1970).
10. Bronstein, H. R., Dworkin, A. S., and Bredig, M. A., *J. Chem. Phys.* 37, 677 (1962).
11. Grantham, L. F., *J. Chem. Phys.* 43, 1415 (1965).
12. Grantham, L. F. and Yosim, S. J., in *Molten Salts, Characterisation and Analysis*, p. 409 (Mamantov, G., Editor.) M. Dekker, New York, 1969.
13. Rice, S. A., *Discuss. Faraday Soc.* 32, 181 (1961).
14. Raleigh, D. O., *J. Chem. Phys.* 38, 1677 (1963).
15. Daněk, V. and Ličko, T., *Silikáty* 25, 153 (1981).
16. Ličko, T. and Daněk, V., *Silikáty* 27, 55 (1983).
17. Berghauer, Z., Rusnák, J., Stračár, S., and Škoda, E., *Zbor. X. konf. oceliarov a magnezitárov.* (Proceedings of the Xth Conference of Steel-makers and Producers of Refractories.) Košice, 1980.
18. Dworkin, A. S., Bronstein, H. R., and Bredig, M. A., *J. Phys. Chem.* 67, 2715 (1963).
19. Balajka, J. and Daněk, V., *Werkstoffe und Korrosion* 25, 513 (1974).
20. Daněk, V., Votava, I., Matiašovský, K., and Balajka, J., *Chem. Zvesti* 28, 728 (1974).
21. Ličko, T., Daněk, V., and Pánek, Z., *Chem. Papers* 39, 599 (1985).
22. Daněk, V., *Chem. Zvesti* 38, 379 (1984).

Translated by T. Ličko