Tracer Diffusivity of Ca^{45} and Electrical Conductivity in CaO-SiO_2 Melts

HELMUT KELLER, KLAUS SCHWERDTFEGER, AND KLAUS HENNESEN

The tracer diffusivity of Ca^{45} has been measured in CaO-SiO_2 melts in the temperature range 1500 to 1700°C. In addition the electrical conductivity has been determined. Both properties decrease with increasing silica content. The activation energies (~30 kcal $g \cdot atom^{-1}$) are of the same order of magnitude. The electrical conductivity as computed from the diffusivity on the assumption that the total current is transported exclusively by divalent calcium ions and that the usual Nernst-Einstein relationship is valid, is somewhat lower than the measured electrical conductivity with the difference increasing with increasing silica content.

THE rate of many slag/metal reactions is controlled by transport in the slag, and in order to compute the rate of such reactions the mechanism of transport in the slag must be understood. Slags are multicomponent oxide mixtures which are dissociated into ions and which usually contain considerable amounts of silica. Only few and contradictory data are available on the mobilities of the various ions in the technically important slags. Usually, it is assumed that the silicate melts are cation conductors. This, however, is not in keeping with the self-diffusivity of oxygen which is reported to be in the same order of magnitude or higher than that of calcium.[6-8] Also the self-diffusivity of silicon is, although lower than that of the cations, still rather high.[1,2] Hence, the transport mechanism is not well understood and it is not clear how the electrical transport properties and diffusivities are interrelated and how flux equations should be formulated.

In order to improve this situation, self-diffusivities, chemical diffusivities, transference numbers and electrical conductivities should be measured, using the best experimental techniques available, to obtain sets of data as complete as possible for specific slag systems. The present authors have started such an investigation on CaO-SiO_2 melts. This system is the binary bounding system for most slags in iron and steelmaking. In the following paper the results will be reported on the tracer diffusivity of Ca^{45} and on the electrical conductivity. A subsequent paper will deal with the tracer diffusion of Si^{31}.

EXPERIMENTAL TECHNIQUE

The diffusivity of Ca^{45} was determined in the temperature range 1500 to 1700°C using the capillary technique. Active and inactive rods of the same chemical compositions and of 1.2 cm length were placed in a capillary over each other. The capillaries were machined from molybdenum and had internal diam of 2 mm. In order to avoid convection the capillaries were suspended in the lower half of the hot zone of the furnace during the diffusion experiment.

The slags were prepared from high purity calcium carbonate (Merck, Darmstadt) and silica (Koch-Light, Colnbrook). The mixture was first annealed at 1200°C for 12 h and then melted at 1600°C in a platinum crucible. In order to ensure homogenization the melt was stirred with a platinum-rhodium rod at regular intervals. Subsequently, the melts were vacuum degassed. The rods were prepared by sucking the melt into graphite tubing of 2 mm ID. The tubes were then quenched in a copper block. The rods could easily be pushed out of the bore. Pieces 1.2 cm in length were cut off, and the transverse surfaces of their extremities were ground and polished to obtain perfectly flat surfaces for joining the diffusion couples. The radioactive rods were made, in the same way, from the same starting mixture by adding "carrier free" Ca^{45} tracer. The tracer was purchased in the form of an aqueous $Ca^{45}Cl_2$ solution. After the addition to the slag mixture, concentrated ammonia was added and the mixture was heated to drive off the chlorine as ammonium chloride. In some experiments oxalic acid was added to convert the calcium chloride to calcium oxalate. There was no difference in the diffusivities as obtained with the rods prepared by these two procedures.

The diffusion experiments were carried out in a molybdenum wound tube furnace. Forming gas (95 pct N_2, 5 pct H_2) was used as atmosphere. In some experiments the forming gas was passed through a mixture of oxalic acid and oxalic acid anhydrate, held at 20°C in a thermostatically controlled bath to obtain a defined H_2O/H_2 ratio and oxygen pressure. These experiments yielded the same results. The temperature of the furnace was controlled electronically within ±1°C.

At the end of the diffusion run the sample was drawn into the cold top of the furnace. The capillary was embedded in mounting material and a longitudinal section of the sample was prepared by grinding and polishing. The concentration profile was determined with a measuring device which was built in this laboratory (Fig. 1). It consisted of a support table with a slit, the sample holder which could be moved over the slit with a micrometer and a methane counter with a gold window which was placed under the slit. The width of the slit was chosen at 0.5 mm. The β-radiation passing through the slit was measured in the samples each 0.5 mm.

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The activity A of β-radiation at distance x is given by:

$$A = \frac{A_o}{2} \operatorname{erfc} \frac{x}{2\sqrt{Dt}} \qquad [1]$$

where A_o is the unchanged activity at the end of the radioactive rod, D the diffusion coefficient of Ca^{45} and t the diffusion time. By plotting the ratio A/A_o against distance on probability paper, straight lines are obtained and the diffusivity is computed from the slopes. During solidification and cooling the samples contract

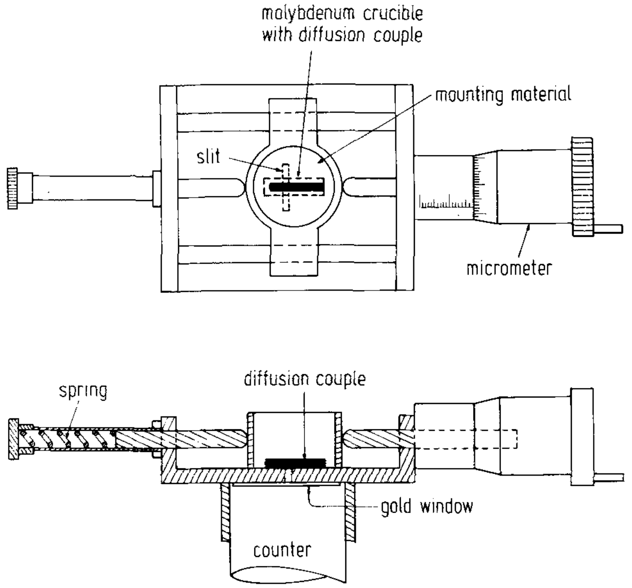

Fig. 1—Sketch of apparatus used to measure the concentration profiles of Ca^{45}.

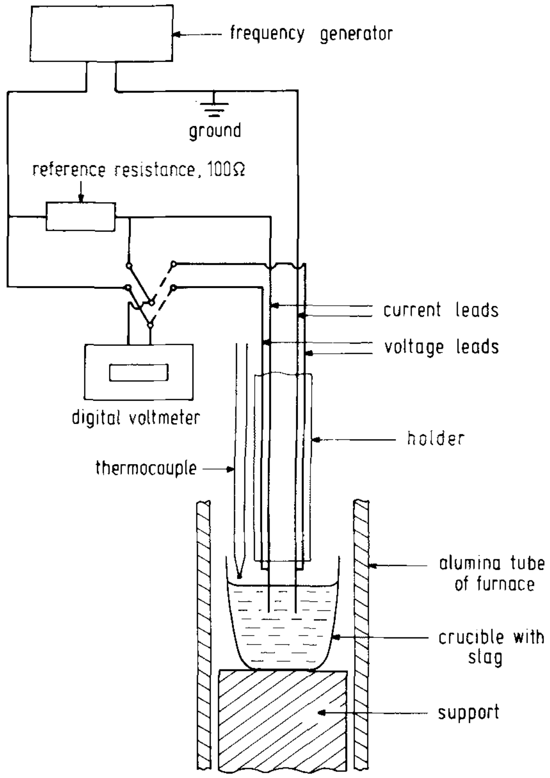

Fig. 2—Conductivity cell and measuring circuit (schematical).

Table 1. Experimental Results on Tracer Diffusion of Ca^{45} in $CaO\text{-}SiO_2$ Melts as Obtained in This Work

Composition of Melt, N_{SiO_2}	Temperature, °C	$D_{Ca^{45}} \times 10^6$, $cm^2 s^{-1}$	Activation Energy $E_{D_{Ca^{24}}}$, kcal g-atom^{-1}
0.634	1500	1.7	35
	1550	2.2 2.1 2.1	
	1560	2.0 2.0 1.9	
	1600	2.8 2.8 3.0	
	1610	3.0 2.7	
	1650	3.2 3.3 3.8	
0.587	1560	2.8 2.8 3.0 2.7	30
	1600	3.6 3.6	
	1650	3.8 4.5 4.2	
0.530	1550	3.1 3.4 3.6	34
	1600	5.0 4.0 5.1	
	1700	6.4 7.4	
0.488	1550	4.2	34
	1560	4.7 4.2	
	1600	5.1 5.7 5.3	
	1650	6.9 6.9	
0.448	1500	4.3 4.7 4.5	29
	1600	5.7 6.8 6.2	
	1700	10.5 9.9	

Table II. Electrical Conductivity of $CaO\text{-}SiO_2$ Melts as Determined in this Work

Composition of Melt, N_{SiO_2}	Temperature, °C	Electrical Conductivity, $\Omega^{-1} cm^{-1}$		Activation Energy, E_κ, kcal g-atom^{-1}
0.634	1500	0.108	0.107	26
	1519	0.118	0.116	
	1538	0.125	0.125	
	1560	0.138	0.139	
	1580	0.148	0.149	
	1600	0.161	0.157	
	1607	0.163		
0.587	1519	0.153		26
	1531	0.161		
	1540	0.166	0.166	
	1550	0.173	0.175	
	1560	0.188	0.180	
	1580	0.192	0.195	
	1600	0.211	0.212	
0.546	1550	0.226		27
	1553	0.231		
	1566	0.240		
	1569	0.245		
	1585	0.258	0.262	
	1600	0.276	0.277	
	1605	0.281		
	1618	0.297		
	1622	0.300		
0.486	1550	0.327	0.328	25
	1560	0.338		
	1577	0.360	0.358	
	1600	0.393	0.390	
	1615	0.415		
	1618	0.418		
0.448	1499	0.307	0.297	27
	1524	0.344	0.335	
	1550	0.375	0.380	
	1580	0.425	0.425	
	1600	0.456	0.457	

somewhat. The obtained diffusivity values were thus corrected to take into account the changes in density of the slag. The contraction was taken to be mainly in the length direction. Consequently, the diffusivity value at reaction temperature is determined by multiplying the room temperature value with the square of the ratio $\rho(20°\text{C})/\rho(T)$ of the densities at room temperature and diffusion temperatures. The room temperature densities were measured with a pycnometer. The densities of the melt were taken from the literature.[10,11] The difference between the densities at room temperature and diffusion temperature is in the order of 10 pct.

The electrical conductivities were measured with AC current of variable frequency using the four pole method. The melt was contained in a platinum crucible. A Tammann furnace was used. The atmosphere consisted of forming gas which was passed through a mixture of oxalic acid and oxalic acid anhydrate. Some experiments were conducted under argon or argon oxygen gas mixtures yielding the same results. The sketch of the cell and of the measuring circuit is shown in Fig. 2. The electrodes consist of two platinum wires, parallel to each other at a distance of 10 and 0.5 mm in diam. The electrodes are attached to a holder made of an alumina tube. The holder is fastened to a gear with which the electrodes can be immersed into the slag. The immersion depth was 10.0 mm. An AC current is passed through these electrodes. The voltage is measured with two other leads which are welded to the electrode wires. Hence, the voltage drop in the current carrying wires is eliminated. The current was produced by a high frequency generator and was measured as the potential drop at a reference resistance of 100 Ω. Measurements were taken as a function of frequency. With increasing frequency the polarization voltage drop at the interface of the electrodes decreases, and at a sufficiently high frequency (30 to 100 kHz) the ratio voltage/current becomes independent of frequency and equal to the ohmic resistance of the slag. The cell was calibrated with aqueous 1 N KCl, 0.02 N KCl, saturated NaCl solutions at 20°C and with KCl melt at 850°C.

EXPERIMENTAL RESULTS AND DISCUSSION

The experimental results are listed in Tables I and II. Several diffusion experiments were performed with different diffusion times for each slag composition and temperature. As shown in Table I excellent reproducibility of the diffusivity values was obtained. As an example, Fig. 3 shows the concentration curves obtained with slags of $N_{\text{SiO}_2} = 0.634$ at 1560°C from which the following diffusivity values were derived: 2.0×10^{-6} cm^2 s^{-1} for 1 h, 2.0×10^{-6} cm^2 s^{-1} for 3 h, and 1.9×10^{-6} cm^2 s^{-1} for 5 h. Figure 4 shows the diffusivities for various slag compositions as a function of reciprocal temperature.

The electrical conductivity data given in Table II are plotted in Fig. 5 as a function of reciprocal temperature. The activation energies for diffusion of Ca^{45} (average 32 kcal g-atom^{-1}) and for electrical conduction (average 26 kcal g-atom^{-1}) as determined from the slopes of the straight lines in Figs. 4 and 5 deviate only little from each other. The diffusivity as well as the electrical conductivity decrease with increasing silica content.

The tracer diffusivity of Ca^{45} and electrical conductivity have been measured previously in silicate slags. In most of the former determinations of $D_{\text{Ca}^{45}}$ there is a considerable scatter between individual measurements. The present values agree best, at the same basicity CaO/SiO$_2$, with those measured by Towers and Chipman[1,2] in slag with approximately 40 pct CaO, 40 pct SiO$_2$ and 20 pct Al$_2$O$_3$. But they are higher than those determined by Saitô and Maruya[4] and by Niwa[3] and lower than those obtained by Johnston, Stark and Taylor.[9] For instance, at 1500°C the datum of Chipman and Towers or Saitô and Maruya (extrapolated from somewhat lower temperature) is (2.2

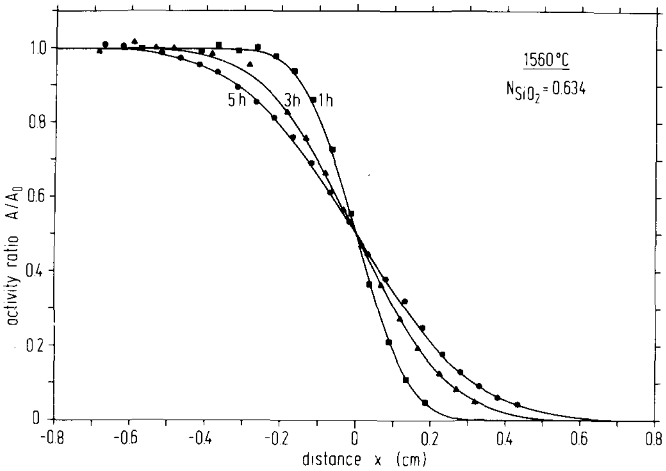

Fig. 3—Typical examples for concentration curves of Ca^{45} as obtained in this work.

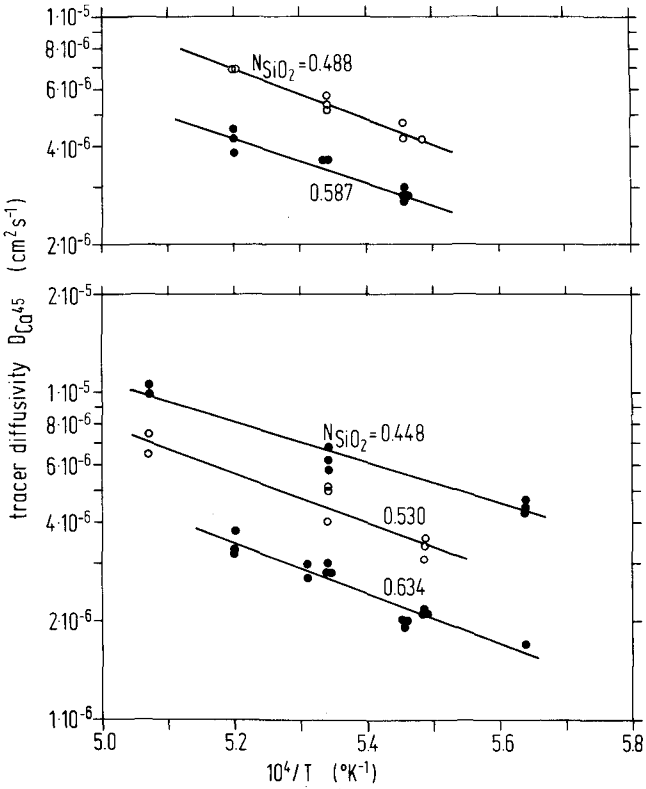

Fig. 4—Tracer diffusivity of Ca^{45} in CaO-SiO$_2$ melts as a function of temperature.

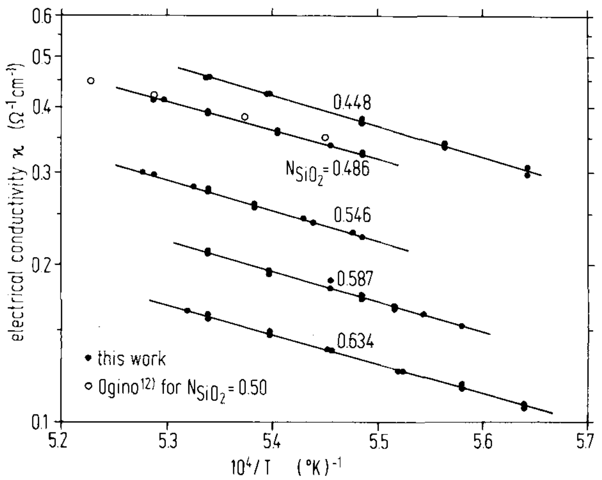

Fig. 5—Electrical conductivity of CaO-SiO$_2$ melts as a function of temperature.

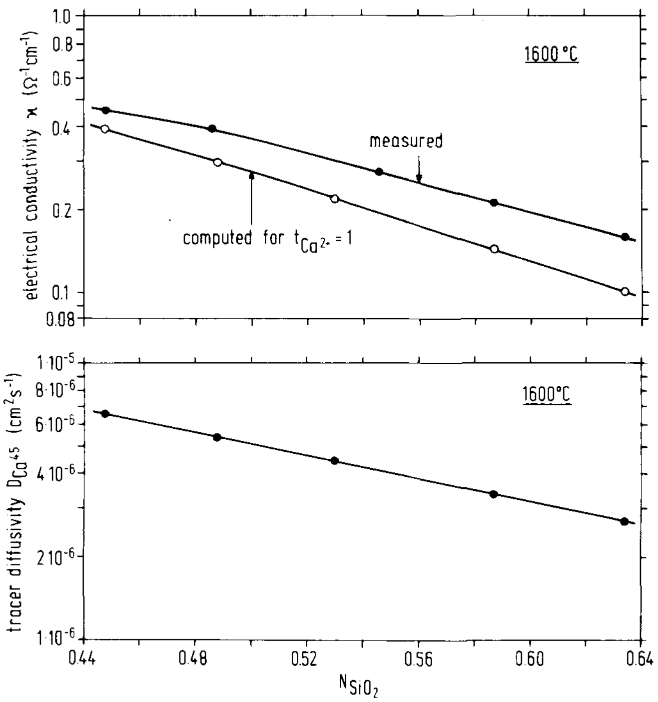

Fig. 6—Electrical conductivity (upper diagram) and tracer diffusivity of Ca^{45} (lower diagram) as a function of mole fraction of silica for 1600°C.

± ~1.3) × 10^{-6} and 1.6 × 10^{-6}, respectively, the datum of Johnston is (5.2 ± ~2.5) × 10^{-6} and that of Niwa 6.5 × 10^{-7} cm^2 s^{-1} (1400°C) for the 40 pct CaO, 40 pct SiO$_2$, 20 pct Al$_2$O$_3$ slag. Our datum for the binary slag of same CaO/SiO$_2$ ratio as extrapolated to 1500 or 1400°C is 3.1 × 10^{-6} or 1.7 × 10^{-6} cm^2 s^{-1}, respectively. The present data on electrical conductivity are very close to those measured recently in CaO-SiO$_2$ melts by Ogino and Nishiwaki[12] (see Fig. 5), but they are lower (factor of 1.6 to 1.3 at 1550°C) than those of Bockris *et al*,[13] and of Morinago *et al*[14] (factor of about 1.6 at 1600°C) and higher (factor of about 1.2) than those of Mori and Matsushita.[15]

The tracer diffusivities were used to compute the electrical conductivity assuming that conduction is solely by motion of Ca^{2+} ions and that the Nernst-Einstein equation is valid. The following equation applies when the transference number of the calcium ions t_{Ca} is one:

$$\kappa\,(t_{Ca}=1)=\frac{z_{Ca}^2\,c_{Ca}\,D_{Ca}\,F^2}{RT}\qquad[2]$$

where z_{Ca} (= 2) is the charge of the Ca^{2+} ion, c_{Ca} the concentration in moles cm^{-3} of the Ca^{2+} ions, and F the Faraday constant. In Fig. 6 the computed values of κ are compared to those measured, for a temperature of 1600°C. It is seen that the calculated values are lower than measured. The difference, however, is small at low SiO$_2$ content, but it increases with increasing SiO$_2$ content. Hence, it appears that at least in the CaO rich slag most of the current is indeed transported by Ca^{2+} ions and this is in agreement with the transference numbers of the cations which are claimed to be close to one in such melts by various authors.[16-18]

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