ACTA CHEMICA SCANDINAVICA 8 (1954) 166—174

Studies on the Electrochemistry of Silicate Melts. I

TRYGGVE BÅÅK

Division of Metallurgy of Iron and Steel, Royal Institute of Technology, Stockholm, Sweden

The validity of Faraday's Law has been studied for 2 $FeO \cdot SiO_2$, 2.5 $CoO \cdot SiO_2$, 2.75 $CoO \cdot SiO_2$ and 3 $CoO \cdot SiO_2$. It has been shown that the law holds for 2 $FeO \cdot SiO_2$, very closely for 2.5 $CoO \cdot SiO_2$ and that, in contradistinction, 2.75 $CoO \cdot SiO_2$ is a mixed conductor and 3 $CoO \cdot SiO_2$ predominantly a semiconductor.

A method to determine transport numbers in silicate melts has been worked out. Cobalt silicates possess cation conductance if the basicity is below a certain value at which semiconductance comes into play.

From the observed data, two rules for the conductance of silicate melts have been deduced. The first one gives a connexion between conductivity and composition and the second states that the ionic mobility is inversely proportional to the square of the ionic radius.

The studies on the electrochemistry of silicate melts, so far carried out, have mostly been concerned with conductance measurements and only to a lesser degree with the applicability of Faraday's Law [1]. Certain difficulties are connected with determinations of transport numbers in melts, as there is not, unlike solids and liquid solutions, any frame of reference to which changes in concentration or boundary can be referred [2]. The purpose of this work has been to determine the applicability of Faraday's Law in molten silicates of different basicities and to obtain values for the transport numbers. From transport numbers and known conductance data it is possible to get a picture of what happens when an electric current passes through a silicate melt and to obtain a quantitative connexion between conductance and composition.

EXPERIMENTS AND RESULTS

The moving boundary method was regarded as the most convenient one for this investigation. Without a frame of reference, however, the only result is a determination of the degree of applicability of Faraday's Law. However, it was found to be possible to produce a frame of reference in an orthosilicate melt by introducing an excess of a basic oxide. The transport numbers can then be obtained by analysing the volume swept out by the boundary.

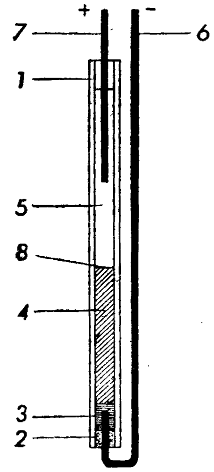

Fig. 1. 1. Alumina tube (Degussit AL23). 2. Alumina cement. 3. Silver cathode. 4. Bottom electrolyte (dark). 5. Top electrolyte (white). 6. Molybdenum wire. 7. Molybdenum anode. 8. Boundary.

The cell in the experiments was the arrangement shown in Fig. 1. After several different procedures for carrying out an experiment had been tried, the following one was found to be the best. The mixture intended as the lower electrolyte was melted in an alumina tube which was closed at one end. A narrower alumina tube of 10 cm length was pushed down to the bottom of the first tube. In this way a good meniscus was obtained. After cooling, the bottom was cut off and the solidified melt in the inner tube drilled away for a length of 1 cm. The silver with the molybdenum wire was then melted into the boring. Alumina cement was used to close the bottom end. The distance between the upper end of the tube and the meniscus was measured. The top electrolyte was introduced and the molybdenum anode inserted. The cell was placed in a furnace which was then heated to the temperature of the experiment and the electrolysing current switched on. After a certain amount of electricity had passed, the system was cooled. The tube was now cut along its length with a diamond saw and the movement of the boundary determined.

From the density and equivalent weight of the lower electrolyte, the radius of the tube and the distance travelled by the boundary (all of these quantities being measured at room temperature) it is possible to calculate the number of equivalents which the known quantity of electricity has deposited. We can formulate the following equation:

$$I \cdot \frac{f}{F} = \frac{\pi r^2 h d}{E} \tag{1}$$

where d = the density of the lower electrolyte
E = the equivalent weight =
= the molecular weight/4
r = the radius of the tube
h = the distance which the boundary has travelled
f = quantity of electricity passed
F = 96 500 coulomb
I = degree of ionic conduction

The electrolysing current, taken from a 24 volts lead storage battery whose voltage could be varied by a variable resistance, was measured by a water coulometer.

An induction furnace with an isothermal field, 7—8 cm high, was used and the temperature was measured with a Pt : Pt—10 % Rh thermocouple.

The silicates studied in these experiments are given in Table 1.

Table 1. Silicates studied.

Bottom electrolyte, dark	Top electrolyte, white
2.00 $FeO \cdot SiO_2$	$Li_2O \cdot CaO \cdot SiO_2$
1.33 $FeO \cdot 0.67\ CaO \cdot SiO_2$	$Li_2O \cdot CaO \cdot SiO_2$
2.50 $CoO \cdot SiO_2$	1.25 $CaO \cdot 1.25\ MgO \cdot SiO_2$
2.75 $CoO \cdot SiO_2$	1.25 $CaO \cdot 1.50\ BaO \cdot SiO_2$
3.00 $CoO \cdot SiO_2$	1.50 $CaO \cdot 1.50\ BaO \cdot SiO_2$

Only A. R. grade of the oxides and carbonates have been used for preparing the silicates.

The iron silicate was prepared from a carefully weighed mixture of Fe_2O_3 and SiO_2, which was melted and after cooling crushed and ground [3]. During the heating, oxygen is evolved and the Fe(II)-Fe(III)-equilibrium set up.

The cobaltous silicates were prepared from Co_2O_3 and SiO_2 in the same way as the iron silicate.

The top electrolytes have been prepared from carefully weighed mixtures of Li_2CO_3, CaO, MgO, $BaCO_3$ and SiO_2, which were heated, cooled and ground in the same way.

All experiments were performed in a purified nitrogen atmosphere.

The values for $2FeO \cdot SiO_2$ (density 4.30) are given in Table 2.

Table 2.

Temp. °C	Diameter of the tube mm	Change of boundary mm	Electricity passed coulomb	Ionic conductance
1 210	4.0	7.8	840	0.95
1 230	5.4	2.5	490	0.96
1 250	5.4	4.9	950	0.96
1 300	3.2	10.8	715	0.99
1 380	3.2	5.5	350	1.03
1 400	5.4	5.9	1 120	0.98

The degree of ionic conductance, which averaged 0.98, can in practice be put equal to 1.00 because in the computations all of the iron has been considered as ferrous (at 1 205° 2—3 % of the iron is Fe(III) [3] and at higher temperatures even less).

It cannot be deduced from these experiments which of the ions is carrying the current because there is no frame of reference. However, in the experiments on Co-silicates, only the cations are carrying the current and this, in all probability, holds true also for the other silicates.

One thing worth mentioning is that the oxygen ions have nothing to do with the current transport because in such a case a deficit of oxygen would occur at the cathode and this has not been observed either in the present work or by other authors [1].

At the cathode the iron is deposited as dendrites but is then to a greater part dissolved again in the melt (possibly as a colloid).

Around the anode oxygen and SiO_2 are set free. For this reason the resistance increases during the experiment and thus the current diminishes.

An experiment was also carried out with a mixture of 30 % by weight of $2CaO \cdot SiO_2$ and 70 % by weight of $2FeO \cdot SiO_2$, *i. e.* $1.33 FeO \cdot 0.67 CaO \cdot SiO_2$, density 3.83. The equivalent weight is computed in the usual way, Table 3.

Table 3.

Temp. °C	Diameter of the tube mm	Change of boundary mm	Electricity passed coulomb	Ionic conductance
1 250	5.0	4.6	660	1.04

Only iron is deposited, of course. It is seen that, in this case also, there is only ionic conductance.

Originally, the object of this investigation was to study the different mixtures of $FeO—SiO_2$. Unfortunately, it appeared that when the FeO content was higher than that of the orthosilicate, the corrosion of the alumina tube was too great. For this reason $CoO—SiO_2$ mixtures were tried and these melts were found not to attack the tube seriously provided that the temperature was not too high.

As previously mentioned, it is possible to determine transference numbers in melts if an excess of the basic oxide is taken as a frame of reference. If this excess is not too large, as in the mixture $2.5 CoO \cdot SiO_2$, ionic conductance was found to prevail but only 2 Co^{2+} had migrated (Fig. 2). The analysis of the

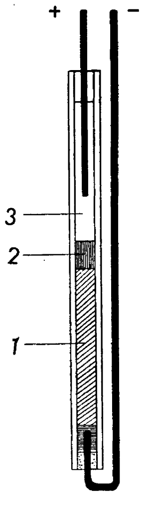

Fig. 2. 1. Bottom electrolyte. 2. 0.5 CoO + top electrolyte (the part that has migrated). 3. Top electrolyte.

volume (2 in Fig. 2) swept out by the boundary showed that 0.5 Co remained in it and had been mixed with the part of the top electrolyte that had migrated. This shows that the excess of cobalt in the bottom electrolyte must be dissolved in the orthosilicate as an unionised oxide. Possibly a slight semiconductivity occurs at this composition. The values 0.95 and 0.93 might differ from unity by more than the experimental error.

If the percentage of CoO in the melt is increased, the semiconductance will be greater until it becomes dominant in the mixture consisting of $3CoO \cdot SiO_2$.

The computations of the degree of ionic conductance have been carried out taking the equivalent weight as *e. g.* $2.5\ CoO \cdot SiO_2/4$ because only $2Co^{2+}$ are migrating.

Table 4.

No.	Substance	Temp. °C	Density	Diam. of tube mm	Change of bound. mm	Electr. passed coulomb	Ionic conductance
1	$2.5CoO \cdot SiO_2$	1440	4.36	2.0	4.7	106	0.95
2	$2.5CoO \cdot SiO_2$	1500	4.36	2.0	3.9	89.5	0.93
3	$2.75CoO \cdot SiO_2$	1450	4.52	2.0	6.0	171	0.72
4	$3.0CoO \cdot SiO_2$	1450	—	2.0	0.0	239	0.00

The analysis of the volume swept out by the boundary gave the following results:

No. 1. The gravimetric determination gave 23.2 % by weight CoO and 35.5 % by weight SiO_2, which is equivalent to a composition of $0.52\ CoO \cdot 1.00\ SiO_2$ (the rest being CaO and MgO). This means that only 1.98 Co^{2+} have migrated, which equals 2 within the experimental error. If only Mg^{2+} and Ca^{2+} ions have travelled from the top electrolyte and the CoO has been dissolved as oxide, the composition is considered to be $0.5\ CoO \cdot MgO \cdot CaO \cdot SiO_2$, which gives 19.3 % by weight CoO and 31.0 % by weight SiO_2. Now the analysis was made using a very small sample, 18.6 mg, and the determinations are therefore very uncertain. It is very probable that Al_2O_3 from the tube has dissolved in the melt and interferred with the determination of SiO_2, making the percentage too large.

To obtain the transport number of the cations in the bottom electrolyte, we must discuss both the movement of the boundary of the Co^{2+}-ions and the thickness of the layer containing 0.5 CoO between the top and bottom electrolyte (2 in Fig. 2). The movement of the first boundary, measured from the top when a given quantity of electricity has passed, is independent of the transport numbers, but the thickness of the layer 2 varies with the mobilities of the ions. If only the cations have moved ($t_+ = 1$), the thickness of the layer is equal to the movement of the boundary. But suppose only the anions had moved ($t_- = 1$), then there would be no layer containing cobaltous oxide between the top and the bottom electrolyte, both CoO and Co^{2+} being immobile. Between these two extremes ($t_+ = 1$ and $t_- = 1$) the thickness of the layer containing 0.5 CoO would be less than the movement of the boundary. In our case the transport number of the ionic conductance must be $t_+ = 1$.

No. 3. A very uncertain spectrographic determination of a very small sample gave 27 % Co, 22 % Ba and 12 % Ca (the rest being SiO_4^{4-}), which is equal to the composition $Co_{1.08} \cdot Ba_{0.38} \cdot Ca_{0.71} \cdot SiO_4$. The results of the analysis are too uncertain to allow any conclusions to be drawn concerning the transport numbers of the ionic conductance.

No. 4. The gravimetric determination gave 79 % by weight CoO for the bottom electrolyte immediately under the boundary, which means no change in the chemical composition at all (3.0 $CoO \cdot SiO_2$ equals 78.9 % CoO).

For pure CoO, Schrag [4] has shown that the melt is predominantly semiconductive with very little ionic conductance.

From these measurements of transport numbers and what is probable already from a geometrical point of view, *viz.* small cations and large anions it would appear that also in other cases apart from the orthosilicates there is unipolar conductance and $t_+ = 1$.

When the basicity is increased and free basic oxide is dissolved in the melt, we can then distinguish between two cases: 1) If the basic oxide has a high conductivity, it will increase with increasing content of the basic oxide; Ex: $FeO—SiO_2$ [5]; 2) If the basic oxide has a low conductivity, the curve will have a maximum, Ex: $CaO—SiO_2$, $MgO—SiO_2$ [5].

THE CONNEXION BETWEEN CONDUCTIVITY AND COMPOSITION OF MO-SiO$_2$-SILICATES.

It is well known that in solid ionic conductors the electrical conductance is due to defects in the lattice [6]. There are three explanations of ionic migration for solids; the two alternatives of Frenkel disorder: interstitial cations (AgCl) and interstitial anions ($PbCl_2$), and the Schottky disorder: ionic conductors deficient both in cations and anions (NaCl). It appears that Frenkel defects are likely to occur when the sizes of the cations and anions are very different, leaving appreciably large interstitial spaces.

According to the hole theory, the structure of a liquid is regarded as rather similar to that of the corresponding solid.

Now, a molten silicate is an ionic liquid with cation conductance (at any rate this is the case for Co-silicates) from which we infer that it has small cations and large anions. Here we may suppose that the electrical conductance is due to an extensive Frenkel disorder. The number of interstitial sites in the "lattice" of the melt will be dependent on the size of the anions. This size in its turn depends on the composition which can be described as follows [7].

Disilicates: Two-dimensional sheets with the composition $(Si_2O_5)^{2-}$, interstitial sites exist only between the sheets. Defect factor = 1.

Metasilicates: One-dimensional chains with the composition $(SiO_3)^{2-}$. The number of interstitial sites is twice that of the disilicates. Defect factor = 2.

Orthosilicates: Spatial restricted groups with the composition $(SiO_4)^{4-}$. The number of interstitial sites is three times that of the disilicates. Defect factor = 3.

This picture is admittedly a very crude one, but enough for our purpose.

As we have cation conductance, we will write in analogy with the customary expression for solids[8].

$$\varkappa = n \cdot z^2 e^2 \cdot u \cdot S \qquad (2)$$

$\varkappa$ = specific conductance
n = number of cations/ml
ze = the charge of the ions
u = mobility of the migrating particles in the disilicates under unit force *
S = defect factor

If we know the conductivity for, let us say, a disilicate, it is possible to compute $\varkappa$ for a meta- or an orthosilicate and, of course, any other composition, if we know the defect factor. Thus

$$\varkappa_1 = \frac{n_1}{n_2} \cdot \varkappa_2 \cdot \frac{S_1}{S_2} \qquad (3)$$

To obtain the number of cations/ml the density at the temperature in question has to be known. The densities of the molten silicates below are unknown on account of which a linear dependence on the composition is assumed and these values are then reduced by 8, 10 and 12 % for the compositions $MO \cdot 2\ SiO_2$, $MO \cdot SiO_2$ and $2\ MO \cdot SiO_2$ respectively, according to Bockris *et al.*[9].

Table 5.

Composition	Defect factor	Number of cations/ml $\cdot N^{-1}$	Conductivity ohm^{-1} cm^{-1} computed	observed	Melting point °C
$MgO \cdot 2SiO_2$	1	0.01565	—	0.23	1 750
$MgO \cdot SiO_2$	2	0.02635	0.77	0.72	1 524
$2MgO \cdot SiO_2$	3	0.03941	1.74	2.15	1 890
$CaO \cdot 2SiO_2$	1	0.01378	—	0.31	1 500
$CaO \cdot SiO_2$	2	0.02175	0.98	0.83 0.89	1 540
$2CaO \cdot SiO_2$	3	0.03044	2.05	1.15	2 130
$SrO \cdot 2SiO_2$	1	0.01275	—	0.21	1 370
$SrO \cdot SiO_2$	2	0.01925	0.63	0.63	1 580
$2SrO \cdot SiO_2$	3	0.02567	1.3	1.4	1 700
$BaO \cdot 2SiO_2$	1	0.01157	—	0.18	1 420
$BaO \cdot SiO_2$	2	0.01690	0.53	0.60	1 605
$2BaO \cdot SiO_2$	3	0.02192	1.0	1.32	1 755
$MnO \cdot 2SiO_2$	1	0.01603	—	0.55	1 700
$MnO \cdot SiO_2$	2	0.02645	1.8	1.8	1 274
$2MnO \cdot SiO_2$	3	0.03807	3.9	6.3 4.5 *	1 320
$FeO \cdot SiO_2$	2	0.02730	—	1.5 **	1 550
$2FeO \cdot SiO_2$	3	0.03946	3.2	3.25 **	1 205

All values for conductivities in Table 5 are taken from Bockris *et al.*[9], except *) and **), which are taken from Wejnarth[10], and Inouye *et al.*[11], respectively. The temperature is in all cases 1750° C except for the iron silicates for which it is 1400° C. The computations are based on those observed values for which there are no corresponding ones in the column, "computed".

---

* The mobility under a potential gradient of 1 volt/cm is equal to 300 *zeu* cm/sec.

Table 6. (1 750° C).

Composition	Conductivity ohm^{-1} cm^{-1} computed	observed	Ionic radius
$CaO \cdot 2SiO_2$	—	0.31	0.99 Å
$CaO \cdot SiO_2$	0.98	0.89	0.99 Å
$SrO \cdot 2SiO_2$	0.22	0.21	1.13 Å
$SrO \cdot SiO_2$	0.66	0.63	1.13 Å
$2SrO \cdot SiO_2$	1.3	1.4	1.13 Å
$BaO \cdot 2SiO_2$	0.14	0.18	1.35 Å
$BaO \cdot SiO_2$	0.41	0.60	1.35 Å
$2BaO \cdot SiO_2$	0.80	1.32	1.35 Å
$MnO \cdot 2SiO_2$	0.55	0.55	0.80 Å
$MnO \cdot SiO_2$	1.8	1.8	0.80 Å
$2MnO \cdot SiO_2$	3.9	6.3 4.5 *	0.80 Å
$FeO \cdot SiO_2$	2.1	1.82	0.75 Å

* Wejnarth [10].

As is seen from Table 5, the results are in fair agreement. The deviations may be caused partly by our estimations of the densities and partly by the fact that not all silicates have been measured in the molten state.

It will now be shown that the following rule holds for the binary silicate systems studied in this paper with the exception of magnesium silicates.

The ionic mobility (u) is inversely proportional to the square of the ionic radius (r) of the cation.

$$u \sim \frac{1}{r^2} \tag{4}$$

This also means that under the same conditions of temperature and potential field different cations sweep out equal volumes.

For the comparison of two systems we can write

$$\frac{u_1}{u_2} = \left(\frac{r_2}{r_1}\right)^2 \tag{5}$$

Further

$$\begin{aligned} \varkappa_1 &= n_1 \cdot z^2 e^2 \cdot u_1 \cdot S_1 \\ \varkappa_2 &= n_2 \cdot z^2 e^2 \cdot u_2 \cdot S_2 \end{aligned} \tag{6}$$

(5) and (6) give

$$\varkappa_1 = \varkappa_2 \cdot \frac{n_1}{n_2} \cdot \left(\frac{r_2}{r_1}\right)^2 \cdot \frac{S_1}{S_2} \tag{7}$$

The computed values in Table 6 are all based on the $\varkappa$-value for $CaO \cdot 2SiO_2$ and compared with the experimental values of Bockris *et al.*[9] The ionic radii are all taken from Pauling [12].

Acknowledgements. This investigation has been financed by *Jernkontoret (The Swedish Iron-Masters Association)* which support is gratefully acknowledged. The author would like to thank Professor F. M. Wiberg for his kind interest and for the facilities of his Institute. Thanks are also due to Professor A. Ölander for many valuable discussions.

REFERENCES

1. Bockris, J. O'M., Kitchener, J. A., and Davies, A. E. *J. Chem. Phys.* **19** (1951) 255; *Trans. Faraday Soc.* **48** (1952) 536.
2. Jost, W. *Diffusion in Solids, Liquids, Gases,* Academic Press, New York 1952, p. 466.
3. Bowen, N. L., and Schairer, J. F. *Am. J. Sci.* **224** (1932) 186.
4. Schrag, G., and Steiner, H. *Z. Metallkunde* **42** (1951) 24.
5. Tomlinson, J. W. *The Physical Chemistry of Melts,* Institution of Mining and Metallurgy, London 1953, pp. 26, 27.
6. Mott, N. F., and Gurney, R. W. *Electronic Processes in Ionic Crystals,* Oxford Univ. Press, Oxford 1948, p. 26.
7. Slater, J. C. *Introduction to Chemical Physics,* McGraw-Hill, New York 1939, p. 435.
8. Jost, W. *Diffusion in Solids, Liquids, Gases,* Academic Press, New York 1952, p. 180.
9. Bockris, J. O'M., Kitchener, J. A., Ignatowicz, S., and Tomlinson, J. W. *Trans. Faraday Soc.* **48** (1952) 75.
10. Wejnarth, A. *Rapport till Statens Tekniska Forskningsråd,* 20 jan. 1950.
11. Inouye, J., Tomlinson, J. A., and Chipman, J. *Trans. Faraday Soc.* **49** (1953) 796.
12. Pauling, L. *Nature of the Chemical Bond,* 2nd ed., Cornell University Press, Ithaca, N. Y. 1940, p. 350.

Received November 4, 1953.