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On the Application of Glass Membranes as Alkali Electrodes at Elevated Temperatures

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The transport numbers of alkali and alkaline earth ions are determined at 800–950°C in a sodium and potassium silicate containing alkaline earth oxide. The result shows that the alkali ions carry practically all current through the glass. These glasses can therefore be used as electrodes reversible to the alkali ions only in galvanic cells of the type:

$$X_2(g) \mid AX(l) \mid (A,B)\text{-glass} \mid (A,B)X(l) \mid X_2(g)$$

where A = Na or K, B = Mg, Ca, Sr, or Ba and X_2 is a halogen.

In a previous paper Førland and Østvold[1] calculated the chemical work done in glass membranes when an electrical charge passes through the membranes. The calculations were based on the assumption of two kinds of mobile monovalent ions in the glass. It was found that the chemical work or the liquid junction potential depended on the transport numbers of the mobile ions in the membrane and on the activities of the corresponding silicates.

It is the purpose of this work to give a method for measuring alkali halide activities in fused mixtures of alkali and alkaline earth halides by galvanic cells without introducing any significant liquid junction potential.

We will consider the following concentration cell

$$X_2(g) \mid AX(l) \mid (A,B)\text{-glass} \mid (A,B)X(l) \mid X_2(g)$$

where the electrolyte consists of a fused mixture of two salts AX and BX_2 (A^+, B^{2+}, and X^-) on the right side and the pure fused salt AX on the left side of the glass membrane which is assumed to contain two kinds of mobile ions, A^+ and B^{2+}. The electrodes are reversible to the anion only.

The change in free enthalpy due to the transport of a charge of one Faraday from the left to the right side in the cell may be calculated assuming that equilibrium is obtained for the exchange of A^+ and B^{2+} ions between fused salt and glass at the contact between the two phases, and that no significant concentration gradients are present in the fused salt mixture. The change in free enthalpy by the charge transfer is

$$\Delta G = -G^{\circ}_{\mathrm{AX}} + \bar{G}_{\mathrm{AX}} t_{\mathrm{A^+}} + \tfrac{1}{2}\bar{G}_{\mathrm{BX_2}} t_{\mathrm{B^{2+}}} - \int_{\substack{\text{over}\\ \text{gradient}}} (\bar{G}_{\mathrm{A—sil}} \mathrm{d} t_{\mathrm{A^+}} + \tfrac{1}{2}\bar{G}_{\mathrm{B\text{-}sil}} \mathrm{d} t_{\mathrm{B^{2+}}})$$

where $t_{\mathrm{A^+}}$ and $t_{\mathrm{B^{2+}}}$ refer to the transport numbers in the glass membrane of $\mathrm{A^+}$ and $\mathrm{B^{2+}}$ ions, respectively. As a frame of reference the walls of the container are chosen. $\bar{G}$ and G° with index refer to the partial free enthalpy per mole of the different components and the free enthalpy for the pure salts, respectively.

Using the above assumption that equilibrium is reached between salt and silicate

$$\mathrm{AX(l)} + \tfrac{1}{2}\mathrm{B\text{-}sil(s)} \rightleftharpoons \tfrac{1}{2}\mathrm{BX_2(l)} + \mathrm{A\text{-}sil(s)}$$

the total change in free enthalpy due to the transport of a charge of one Faraday through the cell is given by

$$\Delta G = \Delta \bar{G}_{\mathrm{AX}} + \int_{\substack{\text{over}\\ \text{gradient}}} t_{\mathrm{B^{2+}}} \mathrm{d}(\tfrac{1}{2}\bar{G}_{\mathrm{B—sil}} - \bar{G}_{\mathrm{A—sil}}) \tag{1}$$

where $\Delta \bar{G}_{\mathrm{AX}} = \bar{G}_{\mathrm{AX}} - G^{\circ}_{\mathrm{AX}}$.

Using the Gibbs Duhem equation eqn. (1) attains the form

$$\Delta G = \Delta \bar{G}_{\mathrm{AX}} - \int_{\substack{\text{over}\\ \text{gradient}}} \frac{t_{\mathrm{B^{2+}}}}{x'_{\mathrm{B—sil}}} \mathrm{d}\bar{G}_{\mathrm{A—sil}} \tag{2}$$

where $x'_{\mathrm{B—sil}}$ is the ionic fraction of mobile ions in the glass membrane.

If $t_{\mathrm{B^{2+}}} = 0$ and $t_{\mathrm{A^+}} = 1$ in the glass membrane, the total change in free enthalpy is given by

$$\Delta G = \Delta \bar{G}_{\mathrm{AX}} \tag{3}$$

and the liquid junction potential is eliminated. Sodium or potassium containing glasses of specific compositions have a transport number for alkali very close to unity. Thus the glasses serve as sodium and potassium electrode, respectively, in galvanic cells of the type mentioned above when $\mathrm{B^{2+}}$ is $\mathrm{Mg^{2+}}$, $\mathrm{Ca^{2+}}$, $\mathrm{Sr^{2+}}$, or $\mathrm{Ba^{2+}}$.

Table 1. Composition of the two most useful glasses (mole percent).

Components	Sodium glass	Potassium glass
$\mathrm{SiO_2}$	70	64.8
$\mathrm{Na_2O}$	12.3	
$\mathrm{K_2O}$		15.—
$\mathrm{Al_2O_3}$	12.7	15.2
$\mathrm{TiO_2}$	2	2
$\mathrm{ZrO_2}$	2	2
$\mathrm{Ce_2O_3}$	1	1

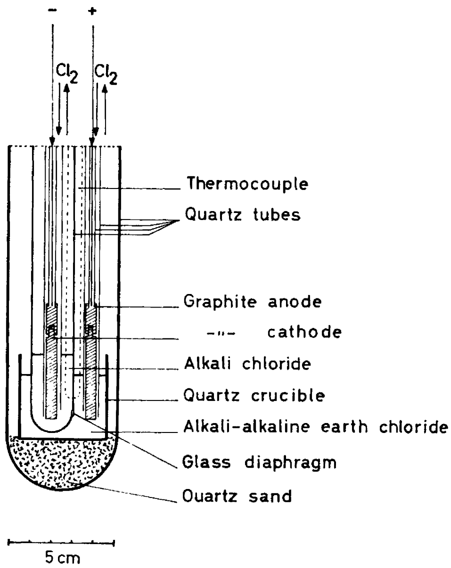

Fig. 1. Cell used for the determination of transportnumbers of alkaline earth ions in glass membranes.

A diagram of the cell used for the determination of the transport numbers of the alkali earth ions in the glass membrane is shown in Fig. 1.

The course of a typical experiment was as follows: A quartz crucible was filled with alkali chloride * and alkaline earth chloride,** dried in vacuum, in the ratio 30:70 mole percent and placed in a quartz tube. The mixture was melted in an HCl atmosphere to prevent formation of alkaline earth oxide. A little piece of the alkali-glass ($\approx$0.05 g) was melted into a hole, 2 mm in diameter, in the bottom of a quartz tube forming the cathode compartment. (The glass was prepared by melting a mixture of Alk.$_2$CO$_3$, Al_2O_3, TiO_2, ZrO_2, Ce_2O_3, and SiO_2. After cooling the glass was crushed and remelted to assure homogeneity). The cathode compartment was filled with 8—10 g of pure alkali chloride, the salt was melted, and the quartz tube was immersed into the fused alkali alkaline earth chloride mixture. Chlorine gas was bubbled over the graphite electrodes during the experiment. The temperature in the cell was measured with a Pt/Pt 10Rh thermocouple. A current of $\approx$ 15 mA was passed through the cell during 5—6 h. This represents an electrical charge about ten times the total charge of the mobile ions in the glass.

The amount of charge passing through the cell was measured with a silver coulombmeter. (Silver was deposited on a silver cylinder from a 10 % $AgNO_3$ solution). The amount of alkaline earth which had migrated into the cathode compartment were determined. Mg and Ca were found by EDTA-titration.[2] Ba and Sr were determined spectroscopically. Because of the high content of

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* NaCl and KCl, *pro analysi* grade from Merck, Germany.

** $CaCl_2$ and $BaCl_2 \cdot 2H_2O$ *pro analysi* grade from Merck, Germany. $SrCl_2 \cdot 6H_2O$ *pro analysi* grade from Riedel De Haën, Germany. $MgCl_2$, chemisch rein, entwässert, Riedel De Haën, Germany.

alkali in the mixture, the amount of alkaline earth found by the EDTA-titration was too high, and a correct result was obtained by comparing these results with EDTA-titrations of standard mixtures of alkali and alkaline earth.

The concentration of alkaline earth is approximately constant throughout the membrane during the electrolysis, and equal to the equilibrium concentration of alkaline earth at the interphase between the fused salt mixture and the glass membrane. In a thin layer on the silicate-side of the interphase between the glass and the pure fused alkali chloride the concentration of alkaline earth ions falls to approximately zero.

The transport number for alkaline earth in the glass membrane is given by the equation

$$t_{\mathrm{B}^{2+}} = \frac{2n_{\mathrm{B}^{2+}}}{\Delta Q} \tag{3}$$

where $t_{\mathrm{B}^{2+}}$ is the transport number of B^{2+} in the membrane, $n_{\mathrm{B}^{2+}}$ is the number of moles B^{2+} transferred through the glass and ΔQ is the amount of charge passed through the cell.

The amount of alkaline earth in the membrane is different from zero after the electrolysis. Some experiments were therefore performed with ΔQ ten times greater than the normal amount of charge passed through the cell. No significant change in $t_{\mathrm{B}^{2+}}$ was observed.

No significant change in the transport numbers of alkaline earth in the two most useful glasses tested was observed in the temperatur range 800°—950°C.

It is assumed that the transport number of alkaline earth is approximately proportional to the concentration of alkaline earth in the membrane. The correction term in eqn. (2) will then be equal to:

$$\begin{aligned}\text{Corr.term} &= -\underset{\text{gradient}}{\text{over}} \int \frac{t_{\mathrm{B}^{2+}}}{x'_{\mathrm{B-sil}}}\, \mathrm{d}\bar{G}_{\mathrm{A-sil}} \\ &= -\frac{t_{\mathrm{B}^{2+}}}{x'_{\mathrm{B-sil}}} \left[(\bar{G}_{\mathrm{A-sil(right)}} - \bar{G}_{\mathrm{A-sil(left)}}\right]\end{aligned} \tag{4}$$

Table 2. Transport numbers of alkali and alkaline earth ions in sodium and potassium containing glass membranes measured with pure fused alkali chloride in the cathode compartment and fused alkali alkaline earth chloride mixture in the ratio 30—70 mole percent in the anode compartment.

System investigated			t_{alkali}	$t_{\text{alkaline earth}}$
$KCl, MgCl_2$	K-glass	KCl	> 0.998	< 0.002
$KCl, CaCl_2$	K-glass	KCl	> 0.998	< 0.002
$KCl, SrCl_2$	K-glass	KCl	0.992	0.008
$KCl, BaCl_2$	K-glass	KCl	> 0.999	< 0.001
$NaCl, MgCl_2$	Na-glass	NaCl	0.996	0.004
$NaCl, CaCl_2$	Na-glass	NaCl	> 0.999	< 0.001
$NaCl, SrCl_2$	Na-glass	NaCl	> 0.999	< 0.001
$NaCl, BaCl_2$	Na-glass	NaCl	> 0.999	< 0.001

As an approximation it is assumed that the concentration of alkaline earth in the membrane is changing linearly from the equilibrium value at the alkaline earth rich side to zero at the side where the membrane is in contact with the pure fused alkali chloride, and that the activity of alkali in the dilute solution of alkaline earth in the alkali-silicate is ideal. Eqn. (4) then attains the form

$$\text{Corr.term} = -\frac{t_{B^{2+}}}{x'_{B-\text{sil}}} RT \ln x_{A-\text{sil(right)}} \tag{5}$$

With the equilibrium concentration of alkali ions in the glass known, one can thus estimate the correction therm using the data in Table 2 for the transport numbers for the alkaline earth ions in the glass membrane.

The amount of calcium in two membranes after transport number measurements was found by spectroscopic analysis. It was found that $x_{Ca-\text{sil}} = 0.05$ for the sodium containing glass, and for the potassium containing glass $x_{Ca-\text{sil}} = 0.13$.

The correction to the partial free enthalpy of NaCl in the mixture $CaCl_2$—NaCl where $x_{NaCl} = 0.3$ will be according to eqn. (5)

$$\text{Corr.term} \approx -\frac{t_{Ca^{2+}}}{x'_{Ca-\text{sil}}} RT \ln x_{Na-\text{sil}}$$

$$\approx -RT \frac{0.001}{0.05} \ln 0.95 \approx RT \times 10^{-3}$$

and the correction to the partial free enthalpy of KCl in the mixture $CaCl_2$—KCl where $x_{KCl} = 0.3$ will be

$$\text{Corr.term} \approx -\frac{t_{Ca^{2+}}}{x'_{Ca-\text{sil}}} RT \ln x_{K-\text{sil}}$$

$$\approx -RT \frac{0.002}{0.12} \ln 0.87 \approx 2\,RT \times 10^{-3}$$

These corrections are negligible compared to

$$\bar{G}_{AX}(x_{AX} = 0.3) \approx RT$$

It may thus be concluded that both the potassium and sodium containing glass membranes of the composition given in Table 1 will act as electrodes reversible only to the potassium and sodium ions, respectively, in the galvanic cells mentioned above when B^{2+} is Mg^{2+}, Ca^{2+}, Sr^{2+} or Ba^{2+}, even up to fairly large content of alkaline earth.

Work on galvanic cells of this type is in progress.

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REFERENCES

1. Førland, T. and Østvold, T. *Acta Chem. Scand.* **20** (1966) 2086.
2. Schwarzenbach, G. *Die komplexometrische Titration*, Enke, Stuttgart 1965.

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