A Silver/Silver Chloride, Sodium Chloride/Pythagoras Membrane-Electrode as a Reference Electrode in Melts with Sodium Chloride

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A silver/silver chloride electrode in sodium chloride inside a porcelain diaphragm has been used as a reference electrode in galvanic cells containing sodium chloride.

The electrode was shown to be reproducible and stable and with a transference number of sodium ions through the membrane equal one. This makes it possible to determine sodium chloride activities in the melt outside the membrane. Such determinations have been performed for the sodium chloride/magnesium chloride system using the cell:

Glasses¹⁻⁷ and other ceramic materials⁸⁻¹⁰ have been extensively used as membranes in EMF-measurements in concentration cells. The response of electrodes with such membranes in relation to the transport properties of the membranes has been discussed by several authors.^{2,5,11-16}

Capsule type electrodes with a glass or porcelain-membrane possess some advantages, the main of which is that the membrane prevents the interdiffusion of the melts in the two compartments. The function of this electrode, however, depends on the transport properties of the membrane.

We have for some time used an electrode consisting of a silver wire in a mixture of silver chloride and sodium chloride inside a porcelain membrane, as a reference electrode for studying electrode reactions in magnesium chloride/sodium chloride melts.

In these cells the sodium ion is the only common cation in the system, and the EMF can only be calculated from the thermodynamic properties of the melts if all the electric charge

is transported through the membrane by sodium ions. That charge should be transported by chloride ions is very unlikely.

In order to establish whether the electrode behaves in a predictable manner we have measured the EMF response of the cell:

by varying the composition in compartment II.

THE MEMBRANE

The membranes were made of commercial grade "Pythagoras" tubes from Haldenwanger A/G with the following composition: Al_2O_3 , 60 wt. %; SiO_2 , 37 wt. %; Na_2O , 3 wt. %, and with traces of other alkali and alkaline-earth oxides. The electric charge has been found to be transported only by sodium ions in this type of membrane.¹⁷

THE EMF OF CELL A

If the membrane is in equilibrium with the melt at both interphases, then the total change in free energy when one Faraday of positive charge is transported through the cell from left to right is:

$$\Delta G = \bar{G}_{\text{AgCl(I)}} + \sum_i^{\text{II}} t_i d\bar{G}_i \quad (1)$$

Here t_i is the transference number of the component i and $\bar{G}_i$ is the corresponding partial free energy of this component. If the charge is transported only by sodium ions in the mem-

brane then the total change in free energy is equivalent to:

$$\begin{aligned}\Delta G &= \bar{G}_{\text{AgCl(I)}} + \bar{G}_{\text{NaCl(II)}} - \bar{G}_{\text{NaCl(I)}} \\ &= G^\circ_{\text{AgCl}} + RT \ln a_{\text{AgCl(I)}} + RT \ln \frac{a_{\text{NaCl(II)}}}{a_{\text{NaCl(I)}}} \quad (2)\end{aligned}$$

To calculate the activity of sodium in compartment II one has to know the activities in compartment I. The EMF for the formation of pure silver chloride has been determined by some authors^{18,19} and also by us, using the formation cell:

The partial free energy of silver chloride in mixtures with sodium chloride was determined by Pelton and Flengas¹⁹ using the same type of formation cell. To calculate the activity of sodium chloride in this melt from those measurements, one can use the Gibbs-Duhem equation in the form:

$$\ln \frac{a_{\text{NaCl}}}{X_{\text{NaCl}}} = - \int_0^{X_{\text{AgCl}}} \frac{X_{\text{AgCl}}}{X_{\text{NaCl}}} d \ln \frac{a_{\text{AgCl}}}{X_{\text{AgCl}}} \quad (3)$$

EXPERIMENTAL

The membrane. The membranes used were in the form of tubes with diameter of either 5 × 7 mm or 4 × 8 mm. Before use the tubes were washed in concentrated hydrochloric acid, then in distilled water and acetone. Afterwards they were dried at 300 °C for 24 h.

The melts. *Magnesium chloride* was pure grade from Merck AG. It was dehydrated by slowly heating under HCl-atmosphere to 420 °C, and maintaining it at this temperature for 24 h. Afterwards it was melted and filtered through silica wool under HCl-atmosphere.

Pure grade *sodium chloride* from Merck AG was pre-dried at 350 °C and at a pressure of 10 Pa. *Silver chloride* from Riedel de Haën AG was not dried before use. Its hygroscopicity is rather insignificant.

The melt in compartment I, which contained 81.7 mol % silver chloride in all the measurements, was placed inside the Pythagoras tube. The melt in half-cell II was placed in an alumina crucible. The composition in this compartment was changed by adding premelted weighed pieces of sodium chloride.

The electrodes. The chlorine electrode is shown in Fig. 1. The active electrode was made of spectrographic AGKSP-graphite from Union Carbide. The chlorine gas was pre-dried by passing it through dehydrite (magnesium

Fig. 1. Chlorine/carbon reference electrode. 1 Spec-pure graphite. 2 Silica tube. 3 Graphite. 4 Chlorine inlet (pvc). 5 O-ring seal (pvc).

perchlorate). The silver electrode was a wire with 99.99 % silver content.

Procedure. The crucible was placed in a wire wound laboratory furnace, which was temperature controlled to within ± 1 °C.

After the salt mixture was melted, the chlorine/carbon electrode was equilibrated by passing a DC current of 100 mA through it for half an hour. After a change in composition the EMF stabilized and became constant after about 1 h. Changes in composition were made at intervals of 3–4 h.

The EMF was measured with a Solartron digital multimeter with an accuracy of ± 0.1 mV. The stability of the EMF was 0.2–0.3 mV during a run. However, it was observed a small drift of the potential with time probably because of changes in the composition in compartment II due to vaporization. The EMF was therefore registered at the same moment as samples for analysis were taken from the melt.

The melts were analyzed using a Varian Techtron Atomic Absorption analyzer. Within the experimental error no silver or magnesium ions were found to be carried through the membrane.

RESULTS AND DISCUSSION

The formation cell B. The EMF for formation cell B as a function of temperature is shown in Fig. 2. The measurements were corrected for the thermopotential between silver and carbon. The results of Pelton and Flengas¹⁹ are also plotted in. The EMF measured by us is a few mV lower and has a somewhat higher temperature coefficient than found by them.

The concentration cell A. The results from the

Fig. 2. Emf of cell B as a function of the temperature. 1 Present work. 2 Pelton and Flengas.¹⁹

EMF-measurements of cell A are shown in Tables 1 and 2 for 750 °C and 850 °C, respectively. Using the data of Pelton and Flengas¹⁹ for the free energy of silver chloride, we have calculated the partial free energy of mixing of sodium chloride in silver chloride using eqn. (3). The partial free energy of mixing of sodium chloride in magnesium chloride has then been calculated using eqn. (2). The values of $\Delta\bar{G}_{\text{NaCl}}$ and of $\Delta\bar{G}_{\text{NaCl}}^{\text{E}}$ (E=excess) are tabulated in Table 1 for 750 °C and in Table 2 for 850 °C.

At 750 °C the measurements were performed only to $X_{\text{NaCl}}=0.9$ because of the solidification of sodium chloride at higher concentrations. In Figs. 3 and 4 the activity of sodium chloride in mixture with magnesium chloride is shown as a function of the composition at 750 °C and 850 °C, respectively. The values of Østfold⁵ have been plotted in for comparison in Fig. 4. The deviation seems rather small. At $X_{\text{NaCl}} > 0.5$ we have found a somewhat greater negative deviation, and at $X_{\text{NaCl}} < 0.5$

Table 1. Thermodynamic data for the NaCl–MgCl₂ system. Temp. 750 °C.

X_{MgCl_2}	EMF(V)	$-\Delta\bar{G}_{\text{NaCl}}$ (J/mol)	$-\Delta\bar{G}_{\text{NaCl}}^{\text{E}}$ (J/mol)
0.17	0.7572	2940	1470
0.28	0.7931	6500	3800
0.39	0.8391	10900	6700
0.50	0.8851	15500	9400
0.62	0.9311	19700	11500
0.72	0.9811	24700	13800
0.80	1.0611	32200	18400
0.89	1.1221	38100	19700

Table 2. Temp. 850 °C.

X_{MgCl_2}	EMF(V)	$-\Delta\bar{G}_{\text{NaCl}}$ (J/mol)	$-\Delta\bar{G}_{\text{NaCl}}^{\text{E}}$ (J/mol)	$\Delta\bar{S}_{\text{NaCl}}$ (J/mol K)
0.027	0.6891	290	0	—
0.058	0.6919	540	40	—
0.14	0.7027	1460	250	1.05
0.22	0.7300	3900	2000	2.43
0.32	0.7706	7500	4600	3.85
0.42	0.8161	11300	7500	3.56
0.54	0.8679	15900	10500	4.02
0.65	0.9168	20500	12600	5.05
0.77	0.9624	24300	13000	5.86
0.87	1.0274	30100	13800	9.21
0.97	1.1262	38900	9200	—

Fig. 3. The activity of sodium chloride in the sodium chloride/magnesium chloride melt, 750 °C.

a smaller deviation from ideality than was found by Østvold.

The partial entropy of mixing. To examine the deviation from Østvold's data more closely we have calculated the partial entropy of mixing of sodium chloride by using our data for the partial free energy of mixing, and the enthalpy data found by Kleppa and McCarthy.²¹ The results for 850 °C are shown in Table 2 and are

Fig. 4. The activity of sodium chloride in the sodium chloride/magnesium chloride melt, 850 °C. ○ Present work. ◇ From Østvold.⁵

Fig. 5. The partial entropy of mixing of sodium chloride in the sodium chloride/magnesium chloride melt, 850 °C. 1 Present work. 2 From Østvold.⁵ 3 $\Delta\bar{S} = -R \ln X_{\text{NaCl}}$.

plotted *vs.* the composition in Fig. 5. In the same diagram we have also plotted the results of Østvold,⁵ and the curve for the ideal partial entropy:

$$\Delta\bar{S}_{\text{NaCl}} = -R \ln N_{\text{Na}^+} N_{\text{Cl}^-} = -R \ln X_{\text{NaCl}} \quad (4)$$

This relation is based upon a random distribution of all the cations in a quasi cation lattice and the chloride ions in a quasi anion lattice. Our results show a more pronounced deviation from ideality than the data of Østvold.⁵ At $X_{\text{MgCl}_2} < 0.3$ there is found a slightly positive deviation from the ideal plot. At $X_{\text{MgCl}_2} \sim 0.3$ an abrupt decrease in the slope of the curve, or even a small maximum is found. Such an arrest is also slightly indicated in the results of Østvold. A maximum or an inflection in the partial entropy curve, reflects a corresponding local inflection in the integral entropy of mixing curve as found by Ikeuchi and Krohn.²⁰ This is probably due to the ordering of the melt by the formation of MgCl_4^{2-} -groups. Such groups have been proposed in all the systems with alkali cations with ionic radii greater than that for sodium ions.^{5,21,22} The "complex" formation

becomes more pronounced the smaller the polarizing strength of the cation. The results from this work indicate that such a grouping is present also in the sodium chloride/magnesium chloride system as proposed by Ikeuchi and Krohn, who calculated a dissociation constant for the complex of about 10^{-2} .²⁰

The transport properties of the membrane and the accuracy of the determined quantities

The difference in EMF of cell A using two equal membrane electrodes was 1–2 mV in most of the composition range, with a maximum deviation of 4 mV at one composition.

It is of course necessary for knowing the exact cell reaction that the transference number of sodium ions in the membrane is constant and equals one. If the transference numbers of magnesium or silver ions are significant although undetectable, the contributions to the total free energy from the work done in the membrane are very difficult to evaluate. Both the magnitude of the work done, and the sign of it, would depend on the relative variations of the transference numbers through the membrane and the concentrations of these ions present as impurities in the other melt. Contributions from transport both of magnesium and silver ions should tend to cancel each other. Contributions from transport of silver ions should not vary significantly with the composition in compartment II, whereas contributions from transport of magnesium ions should increase with increasing content of magnesium chloride in compartment II.

In evaluating the accuracy of the determined quantities we have estimated the mean deviation of the EMF of cell A to be 2 mV, and the accuracy in the determination of X_{NaCl} to vary from 0.001 at $X_{\text{NaCl}} \sim 0.1$ to 0.01 at $X_{\text{NaCl}} \sim 0.9$. Using the estimated accuracy of the literature data,^{19,21} we found the precision in the determined values of the free energy to vary from ± 100 J/mol to ± 1000 J/mol in the concentration range mentioned above. The corresponding precision in the partial entropy of mixing values varies from ± 0.1 to ± 1 J/mol K. The basis for this is of course that the free energy change in cell A can unambiguously be described by eqn. 2.

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CONCLUSION

A silver/silver chloride electrode in sodium chloride, enclosed by a porcelain tube membrane, was found to give a rather stable and reproducible EMF when introduced in melts containing sodium chloride. Within the experimental error it was established that the electric charge was transported through the membrane only by sodium ions. The electrode therefore, is very simple and useful in such melts.

The partial free energy and entropy of mixing of sodium chloride in mixtures with magnesium chloride was calculated using EMF values from measurements in concentration cells of the type

The results indicate a pronounced ordering of the melt corresponding to MgCl_4^{2-} -groups.

REFERENCES

1. Bockris, J. O'M., Hills, G. J., Inman, D. and Young, L. *J. Sci. Instrum.* **33** (1956) 438.
2. Littlewood, R. *Electrochim. Acta* **3** (1971) 270.
3. Førland, T. and Østvold, T. *Acta Chem Scand.* **20** (1966) 2068.
4. Førland, T. and Thulin, L. U. *Acta. Chem. Scand.* **21** (1967) 1121.
5. Østvold, T. *Thesis*, NTH, Trondheim 1971.
6. Stern, K. H. and Meador, S. E. *J. Res. Nat. Bur. Stand. A* **69** (1965) 553, No. 6.
7. Bartlett, H. E. and Crowther, P. *Electrochim. Acta* **15** (1970) 681.
8. Labrie, R. J. and Lamb, V. A. *J. Electrochem. Soc.* **106** (1959) 895.
9. Danner, D. and Rey, M. *Electrochim. Acta* **4** (1961) 274.
10. Kolotii, A. A. and Delimarskii, Yu. K. *J. Appl. Chem. USSR (English Transl.)* **39** (1966) 2342.
11. Stern, K. H. *J. Phys. Chem.* **67** (1963) 893.
12. Suzuki, T. *Denki Kagaku* **5** (1965) 380.
13. Doremus, R. H. *J. Phys. Chem.* **72** (1968) 2877.
14. Doremus, R. H. *J. Electrochem. Soc.* **115** (1968) 924.
15. Stern, K. H. *J. Phys. Chem.* **72** (1968) 1963.
16. Garfinkel, H. M. *J. Phys. Chem.* **73** (1969) 1766.
17. Engseth, P. B. *Thesis*, NTH, Trondheim 1973.
18. Panish, M. B., Blankenship, F. F., Grimes, W. R. and Newton, R. F. *J. Amer. Chem. Soc.* **62** (1958) 1325.

19. Pelton, A. D. and Flengas, S. N. *J. Electrochem. Soc.* **117** (1970) 1130.
20. Ikeuchi, H. and Krohn, C. *Acta Chem. Scand.* **23** (1969) 2230.
21. Kleppa, O. J. and McCarthy, F. G. *J. Phys. Chem.* **70** (1966) 1249.
22. Flood, H. and Urnes, S. *Z. Elektrochem.* **59** (1955) 834.

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