Alkali-glass Membrane as Sodium Electrode

T. FØRLAND and L. U. THULIN

Institute of Physical Chemistry, The Technical University of Norway, Trondheim, Norway

The emf has been measured for the cell

$Cl_2(g)|NaCl(l)|Na,K\text{-glass}|(Na,K)Cl(l)|Cl_2(g)$

with the cell reaction

$NaCl(l) = NaCl(l)_{mix}$ at different compositions of the (Na,K)Cl melt. A liquid junction potential arises in the membrane because of transport by K^+ ions.

Aiming at a better understanding of simple ionic mixtures, it is desirable to obtain thermodynamic data for mixtures of alkali halides, since the interaction between these atomic species is dominated by coulombic forces. A convenient method for obtaining such data is emf-measurements of galvanic cells having the fused salt mixture as electrolyte. Alkali metal electrodes are of limited value as the metal will dissolve in the salt. However, glass membranes have been used as alkali-electrodes,[1,2] and the glass membranes are particularly useful if the conduction is determined primarily by one kind of ion.

For the cell

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

where A and B are alkali and X is halogen, the work carried out in the cell by the transfer of one Faraday is given by[3]

$$\Delta G = \Delta \overline{G}_{AX} + \int_{\substack{\text{over}\\\text{membrane}}} t_{B^+} d(\overline{G}_{B\text{-sil}} - \overline{G}_{A\text{-sil}}) \qquad (1)$$

where $\Delta\overline{G}_{AX}$ is the partial Gibbs free energy of mixing per mole of the fused salt component AX, t_{B^+} is the transport number of the ion B^+ in the glass referred to the walls of the cell, and $\overline{G}_{B\text{-sil}} - \overline{G}_{A\text{-sil}}$ is the difference between the molar Gibbs free energies of the two alkali silicates forming the glass membrane. It is assumed that the exchange of cations at the glass-salt interface corresponds to equilibrium.

Using the Gibbs-Duhem equation one obtains

$$\Delta G = \Delta \overline{G}_{AX} - \int_{\substack{\text{over}\\\text{membrane}}} \frac{t_{B^+}}{x_{B\text{-sil}}} d\overline{G}_{A\text{-sil}} \qquad (2)$$

where $x_{B\text{-sil}}$ is the cation fraction of mobile B^+ ions in the glass membrane. $x_{B\text{-sil}} + x_{A\text{-sil}} = 1$.

The integral in eqn. (2) is the work carried out in the glass membrane. This work divided by the charge transferred may be denoted as the liquid junction potential.

For a mixture AX—BX with a certain difference in partial free energy between the two components in the mixture, $\overline{G}_{AX} - \overline{G}_{BX}$, the integral over the glass membrane will be the same, independent of what kind of anion X is, as long as the glass membrane is made from the same materials each time.

The integral may be determined by measuring the emf of the type of cell shown above with an electrolyte (A,B)X with known free energy of mixing, or the integral may be determined from measurements of emf, transport number in glass, and cation exchange equilibrium between glass and salt mixture.

For systems having as cations Na^+ and K^+, the following composition has been used for the glass membrane:

SiO_2 — 80 mole %	Al_2O_3 — 10 mole %
Na_2O — 5 mole %	K_2O — 5 mole %

Low content of alkali and addition of alumina is expected to give a low Na^+-K^+ interaction, which will make the liquid junction potential a simple function of composition. However, such glasses will have a very high viscosity and are difficult to melt. The composition chosen is a compromise between the two tendencies.

The glass was used as membrane in the cell:

$Cl_2(g)|NaCl(l)|(Na,K)\text{-glass}|(Na,K)Cl(l)|Cl_2(g)$

The emf was measured for different compositions of the (Na,K)Cl electrolyte at a temperature of 885°C.

In Fig. 1 is shown the emf times the Faraday number at 885°C as a function of composition for the sodium-chloride potassium-chloride mixtures. In the same figure is shown the calculated partial free energy of mixing of sodium chloride based on the assumption of ideal mixture according to Temkin. The measured emf corresponds to large positive deviations from ideal behaviour.

The partial molar heat of mixing of sodium chloride, $\Delta\overline{H}_{NaCl}$, for the same system has been derived from measurements by Hersch and Kleppa,[4] and the

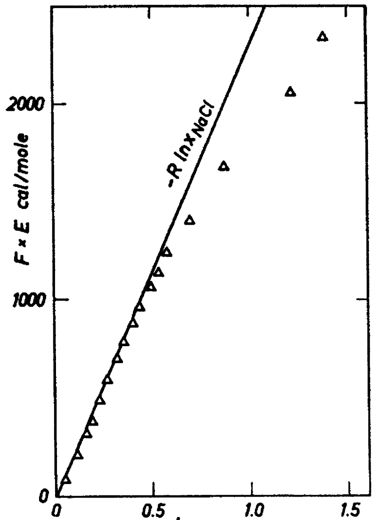

Fig. 1. Emf times the Faraday number as a function of $-\ln x_{NaCl}$ at $T = 1158°K$ for the galvanic cell

$Cl_2(g) \mid NaCl(l) \mid$ Na,K-glass $\mid (Na,K)Cl(l) \mid Cl_2(g)$.

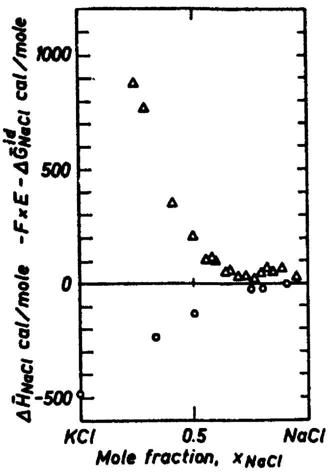

Fig. 2. Partial molar heat of mixing of sodium chloride, $\Delta\bar{H}_{NaCl}$ [O]. The expression $-F \times E - \Delta\bar{G}_{NaCl}{}^{id}$ [Δ] as a function of x_{NaCl}.

data are shown in Fig. 2. Deviations from ideal behaviour are negative. If there were no liquid junction potential in the glass membrane, *i.e.* if the transport of charge through the membrane were mainly carried out by sodium ions, the positive deviation of the partial free energy of mixing of sodium chloride would have to be explained as a significant deviation from ideal behaviour in the partial entropy of mixing of sodium chloride. For a mole fraction of sodium chloride $x_{NaCl} = 0.25$, the entropy deviation would have to be about 1 entropy unit. This seems to be an improbably large deviation, and it is more reasonable to attribute the deviation from ideal behaviour to charge transfer by potassium ions, giving a liquid junction potential. This may be decided if independent free energy measurements for this system become available.

Work is in progress to measure transport numbers in the glass and the equilibrium for exchange of sodium and potassium between glass and fused salt mixture, to determine the liquid junction potentials in galvanic cells of the type discussed in the present paper.

1. Dijkhuis, C. G. M. *An Investigation of Molten Cadmium Halide-Alkali Halide Mixtures by E.M.F. Measurements,* Rototype, Amsterdam 1964.
2. Østvold, T. *On the Application of Glass Membranes as Alkali Electrodes at Elevated Temperatures,* Licentiat thesis 1966, Institute of Physical Chemistry, The Technical University of Norway, Trondheim, Norway.
3. Førland, T. and Østvold, T. *Acta Chem. Scand.* **20** (1966) 2086.
4. Hersch, L. S. and Kleppa, O. J. *J. Chem. Phys.* **42** (1965) 11309.

Received April 7, 1967.