

Alkali Glass as Electrodes at Elevated Temperatures

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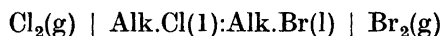
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The applicability of alkali glass as alkali electrodes is discussed and equations are derived correlating the electrode potential and the chemical work due to transport of ions in the glass.

Aiming at a better understanding of the thermodynamic properties of fused salts and their mixtures, studies of the alkali halide systems are of particular interest since these compounds are considered to be the most typical ionic compounds. The heat of mixing for many binary mixtures of alkali halides has a low value, and one might expect that the thermodynamic properties can be described by simple equations.

Galvanic cells are well suited for determining the free enthalpy of fused salt mixtures, as the measurements are usually rapid and only require simple instruments. Reversible chlorine, bromide and iodine electrodes are known for quite a long time. It is, however, difficult to make a reversible alkali electrode. The alkali metal will partly dissolve in the alkali halide.

The difference in free enthalpy between two pure alkali halides is obtained from emf measurements of the cell:



The cell has a liquid junction, and transport numbers must be known to correct for the liquid junction potential. The liquid junction potential can be eliminated by inserting a glass or porcelain membrane between the two fused alkali halides. If the current transport through the membrane is performed exclusively by the Alk.^+ ions in the glass, no change takes place in the glass and no chemical work is carried out in the junction.¹

In a similar way a cell of the type



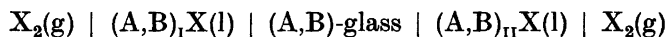
is used to investigate the free enthalpy of the Alk.(Cl, Br) mixture. The left part of the cell including the glass has the function of an alkali electrode.² The glass must contain the same alkali ion as the fused halides.

If the fused salt mixture contains two kinds of cations which transport current through the glass, a liquid junction potential will be created in the

glass. Membranes of glass or porcelain have been used for many years, but in many cases the composition of the membranes was arbitrary and the unknown junction potential was assumed to be small.³⁻⁹

This paper presents a calculation of the junction potential or the chemical work in a glass membrane containing two kinds of mobile ions A^+ and B^+ .

A concentration cell is considered where the two electrolytes are separated by a glass membrane.



The electrolytes consist of a fused mixture of two salts AX and BX (A^+ and B^+ forming cations and X^- forming the anion) the A^+/B^+ ratio being different on the two sides of the cell. The electrodes are reversible to the anion only.

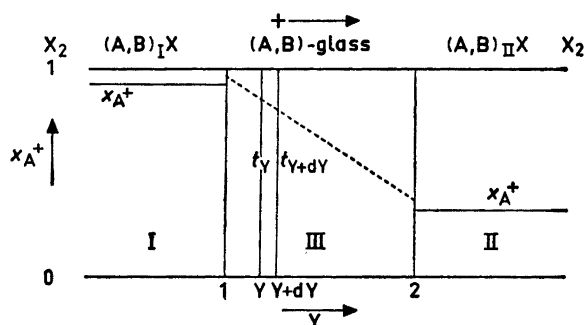


Fig. 1. Schematic diagram of the galvanic cell:

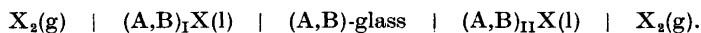


Fig. 1 shows the ionic fraction x_{A^+} and x_{B^+} as a function of the distance y from one side of the cell. The ionic fractions are defined as

$$x_{A^+} = \frac{n_{A^+}}{n_{A^+} + n_{B^+}} \quad \text{and} \quad x_{B^+} = \frac{n_{B^+}}{n_{A^+} + n_{B^+}}$$

where n with subscript indicates the number of moles of an ion.

The walls of the container are chosen as a frame of reference.

Diffusion of A^+ and B^+ through the glass membrane, is assumed to be slow compared to the diffusion of these ions in the liquid phase and compared to the exchange of ions at the glass-liquid interphase. This means that equilibrium is obtained for the exchange of A^+ and B^+ between fused salt and glass at the contact between the two phases.

By the calculation of the change in free enthalpy by the transfer of an electric charge, ΔQ , it is assumed that there is a linear relation between fluxes and forces in the glass membrane (compare calculation by Førland¹⁰). It is further assumed that the electrostatic energy of dipol layers in the concentration gradient does not change significantly by the charge transfer.¹¹

The change in free enthalpy in the glass membrane by the charge transfer is given by:

$$\Delta G_{\text{III}} = -\frac{\Delta Q}{F} \int_1^2 (\bar{G}_{\text{A-sil}} dt_{\text{A}^+} + \bar{G}_{\text{B-sil}} dt_{\text{B}^+})$$

where $\bar{G}_{\text{A-sil}}$ and $\bar{G}_{\text{B-sil}}$ are the partial free enthalpy per mole of the A-silicate and B-silicate respectively, and t_{A^+} and t_{B^+} are the transport numbers of the two mobile ions in the glass membrane. F is Faraday's number.

Using electrodes reversible to X, the content of AX increases with $(\Delta Q/F)t_{\text{A}^+(2)}$ moles in the right compartment of the cell where $t_{\text{A}^+(2)}$ is the transport number of A^+ at the right side of the glass membrane. Similarly the content of AX decreases with $(\Delta Q/F)t_{\text{A}^+(1)}$ moles in the left compartment. The content of BX changes with $(\Delta Q/F)t_{\text{B}^+(2)}$ moles and $-(\Delta Q/F)t_{\text{B}^+(1)}$ moles in the respective compartments.

The total change in free enthalpy in the cell due to the transfer of the charge ΔQ becomes

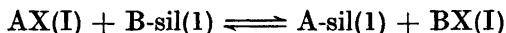
$$\begin{aligned} \Delta G = \frac{\Delta Q}{F} [& -\bar{G}_{\text{AX(I)}}t_{\text{A}^+(1)} - \bar{G}_{\text{BX(I)}}t_{\text{B}^+(1)} + \bar{G}_{\text{AX(II)}}t_{\text{A}^+(2)} + \bar{G}_{\text{BX(II)}}t_{\text{B}^+(2)} \\ & + \int_1^2 (\bar{G}_{\text{A-sil}} - \bar{G}_{\text{B-sil}}) dt_{\text{B}^+}] \end{aligned} \quad (1)$$

where $t_{\text{A}^+} + t_{\text{B}^+} = 1$ has been introduced.

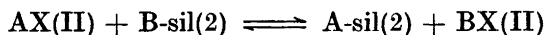
Integration by parts gives for the integral:

$$\begin{aligned} \int_1^2 (\bar{G}_{\text{A-sil}} - \bar{G}_{\text{B-sil}}) dt_{\text{B}^+} = & (\bar{G}_{\text{A-sil}(2)} - \bar{G}_{\text{B-sil}(2)})t_{\text{B}^+(2)} \\ & - (\bar{G}_{\text{A-sil}(1)} - \bar{G}_{\text{B-sil}(1)})t_{\text{B}^+(1)} - \int_1^2 t_{\text{B}^+} d(\bar{G}_{\text{A-sil}} - \bar{G}_{\text{B-sil}}) \end{aligned} \quad (2)$$

It was assumed that equilibrium is obtained for the exchange of A^+ and B^+ between fused salt and glass in the contact between the two phases:



in the left compartment, and



in the right compartment. Thus

$$\bar{G}_{\text{AX(I)}} - \bar{G}_{\text{BX(I)}} = \bar{G}_{\text{A-sil(1)}} - \bar{G}_{\text{B-sil(1)}} \quad (3)$$

$$\bar{G}_{\text{AX(II)}} - \bar{G}_{\text{BX(II)}} = \bar{G}_{\text{A-sil(2)}} - \bar{G}_{\text{B-sil(2)}} \quad (4)$$

Introducing eqns. (2), (3), and (4) into eqn. (1) gives

$$\Delta G = \frac{\Delta Q}{F} [\bar{G}_{\text{AX(II)}} - \bar{G}_{\text{AX(I)}} - \int_1^2 t_{\text{B}^+} d(\bar{G}_{\text{A-sil}} - \bar{G}_{\text{B-sil}})] \quad (5)$$

Since the transfer of the charge ΔQ is connected with no other chemical work in the cell than ΔG (eqn. 5), the emf, E , of the cell is given by:

$$E \Delta Q + \Delta G = 0$$

or

$$E = -\frac{1}{F} [\bar{G}_{\text{AX(II)}} - \bar{G}_{\text{AX(I)}} - \int_1^2 t_{\text{B}^+} d(\bar{G}_{\text{A-sil}} - \bar{G}_{\text{B-sil}})] \quad (6)$$

which gives with the Gibbs-Duhem equation:

$$E = -\frac{1}{F} [\bar{G}_{\text{AX(II)}} - \bar{G}_{\text{AX(I)}} - \int_1^2 \frac{t_{\text{B}^+}}{x_{\text{B-sil}}} d\bar{G}_{\text{A-sil}}] \quad (7)$$

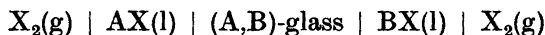
Applying a glass membrane with a much higher mobility for A^+ than for B^+ , the emf would be

$$E = -\frac{1}{F} (\bar{G}_{\text{AX(II)}} - \bar{G}_{\text{AX(I)}})$$

and the membrane functions as an electrode reversible to A.

When the mobility of both kinds of ions is high, the integral in eqn. (6) can be found if the difference $\bar{G}_{\text{AX(II)}} - \bar{G}_{\text{AX(I)}}$ is known from other measurements.

For a cell containing only one salt component in each compartment:



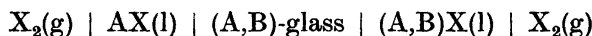
the total change in free enthalpy in the cell due to the transport of a charge of one Faraday is:

$$\Delta G = G^\circ_{\text{BX}} - G^\circ_{\text{AX}} - G^\circ_{\text{B-sil}} + G^\circ_{\text{A-sil}} - \int_1^2 (\Delta \bar{G}_{\text{B-sil}} - \Delta \bar{G}_{\text{A-sil}}) dt_{\text{B}^+} \quad (8)$$

where $\Delta \bar{G}_{\text{B-sil}} = \bar{G}_{\text{B-sil}} - G^\circ_{\text{B-sil}}$ and G° refers to pure component.

The integral is zero for no interaction between the A^+ and B^+ ions in the silicate lattice, and the total change in free enthalpy equals the free enthalpy for the exchange equilibria between A^+ and B^+ in the pure fused salts and A^+ and B^+ in the pure A- and B-silicate.

For the special cell:



the total change in free enthalpy when passing one Faraday of electric charge is:

$$\Delta G = \Delta \bar{G}_{\text{AX}} + \int_1^2 t_{\text{B}^+} d(\bar{G}_{\text{B-sil}} - \bar{G}_{\text{A-sil}}) = \Delta \bar{G}_{\text{AX}} - \int_1^2 \frac{t_{\text{B}^+}}{x_{\text{B-sil}}} d\bar{G}_{\text{A-sil}} \quad (9)$$

The left part of the cell including the glass membrane may be regarded as the electrode reversible to A. The integral in eqn. (9) is the chemical work

carried out in the glass membrane. This work divided by Faraday's number may conveniently be called the liquid junction potential.

The integral in eqn. (9) can be calculated when the transport number of the ions in the glass and the free enthalpy of alkali silicate are known. In some cases one may go the other way and calculate the integral from independent data on the partial free enthalpy of mixing of the salt component and the emf of the cell. From emf measurement on cells having an electrolyte of a AX—BX salt mixture with known thermodynamic properties, one can therefore obtain the value of the integral for any composition of the glass.

With this knowledge the free enthalpy of mixing for another system AY—BY can be obtained from emf measurements of cells similar to the one above if the same kind of glass is used as membrane.

For this reason it would be convenient to select certain standard compositions for glasses to be used as membranes. The liquid junction will be small if the transport number of one cation dominates largely, and the concentration and temperature dependence of the liquid junction potential is expected to be a simple function if cations form a very dilute solution in the structure of the glass membrane. Work on such glass membranes is in progress.

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