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Determinations of the Thermodynamic Functions of NaBr in NaBr-KBr Mixtures from Concentration Cell Measurements

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The partial Gibbs energies of mixing of NaBr in liquid mixtures with KBr have been determined by emf measurements of the following cell:

$$C(s)Br_2(g)\,|\,NaBr(l)\,|\,Na\text{-}K\ \text{glass}\,|\,NaBr(l)KBr(l)\,|\,Br_2(g)C(s)$$

and measurements of transport number of the alkali ion in the Na-K glass membrane used to separate the two half cells in the above concentration cell.

From the values obtained for the partial free energies of mixing of NaBr, the Gibbs energies of mixing in the NaBr-KBr system were determined, and the excess Gibbs energies of mixing and excess entropies of mixing calculated. The results indicate small excess entropies of mixing.

In the present work the change in the chemical potentials of mixing of NaBr in molten NaBr-KBr mixtures were obtained using a concentration cell with Na-K glass membrane. The emf of this cell is dependent upon the transport properties in the membrane, *i.e.* "the liquid junction potential". Therefore the transport numbers of the two alkali ions in the glass were determined.

The following galvanic cell was studied:

$$C(s)Br_2(g)\,|\,NaBr(l)\,|\,Na\text{-}K\ \text{glass}\,|\,NaBr(l)KBr(l)\,|\,Br_2(g)C(s)$$

The electrolyte consisted of a fused mixture of NaBr and KBr on the right hand side, and pure fused NaBr on the left hand side of the glass membrane. The membrane is a cation exchange membrane and it contains the two mobile ions Na^+ and K^+. The bromine over graphite electrodes are reversible to the Br^+ ions only.

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EXPERIMENTAL

The cell used in the present investigation is similar to the one described in previous papers.[1],[2] The composition of the glass was 80 mol % SiO_2, 10 mol % Al_2O_3, 5 mol % Na_2CO_3 and 5 mol % K_2CO_3. All the components of the glass, obtained from E. Merck, Germany, were ground together and melted. The glass was then crushed and remelted to assure uniform composition. The emf of the above cell was investiged over a concentration range $x_{NaBr}=0.06$ to $x_{NaBr}=0.8$ at 800°C. The temperature and emf were recorded on a dual channel Philips recorder (type PR 2212A/00). Both were compensated by bucking potentials supplied from a thermostatically housed reference voltage supply and divider built by Sintef, Norway. These were calibrated daily against a Tinsley "Thermoelectric Free" potentiometer. The analytical reagent grade salts, NaBr and KBr, obtained from E. Merck, Germany, were melted before use in order to remove moisture and crushed into suitable fragments before weighed out to give the wanted compositions.

The above cell was also used for the determination of the transport numbers of K^+ and Na^+ ions in the glass membrane. The course of a typical experiment was as follows. The cathode compartment, containing the glass membrane at the bottom, was filled with about 6 g of pure NaBr and then immersed in the fused NaBr-KBr mixture. Bromine gas was bubbled over the graphite electrodes and a positive current of about 10 mA passed through the cell from the mixture to the pure salt for about 8 h. The amount of charge passing through the cell was measured with a digital coulombmeter. The amount of potassium which had migrated into the cathode compartment through the glass membrane was determined by flame photometry.

RESULTS AND DISCUSSION

The emf as function of composition of the galvanic cell

$$C(s)Br_2(g)\,|\,NaBr(l)\,|\,Na\text{-}K\ \text{glass}\,|\,NaBr(l)KBr(l)\,|\,Br_2(g)C(s)$$

is shown in Fig. 1. The emf is related to the change in Gibbs energy for the cell reaction by the equation [3]

$$\Delta G = -EF = \Delta\bar{G}_{NaBr} - \int_1^2 t_{K^+}\mathrm{d}(\bar{G}_{Na\text{-sil.}} - \bar{G}_{K\text{-sil.}}) \quad (1)$$

over membrane

Using Gibbs-Duhem equation one obtains

$$\Delta G = -EF = \Delta\bar{G}_{NaBr} - \int_1^2 \frac{t_{K^+}}{x_{K\text{-sil.}}}\,\mathrm{d}\bar{G}_{Na\text{-sil.}} \quad (2)$$

over membrane

where $\Delta\bar{G}_{NaBr}=\bar{G}_{NaBr}-G^{\circ}_{NaBr}$ is the change in chemical potential on mixing, t_{K^+} is the transport number of potassium in the glass membrane and $x_{K\text{-sil.}}$ is the mol fraction of K^+ ions in the glass.

Since the emf and the Gibbs energy changes for the cell reaction are dependent on the transport properties of the ions in the glass membrane separating the two half cells, one has to know the value of the integral in eqn. (2) before the partial quantities of mixing can be calculated. For this reason the transport number of the K^+ ions in the glass membrane was measured at 800°C.

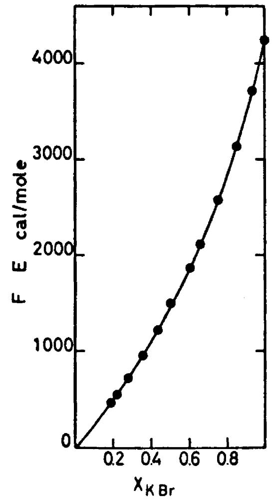

Fig. 1. Variation of emf with composition of NaBr-KBr melt at 800°C for the galvanic cell:

$C(s)Br_2(g)|NaBr(l)|Na\text{-}K\ glass|NaBr(l)\ KBr(l)|Br_2(g)C(s)$.

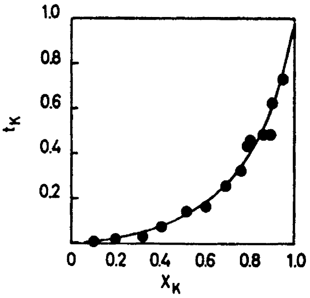

Fig. 2. Dependence of transport numbers in Na-K glass with composition of NaBr-KBr melt at 800°C.

From the concentration of KBr in the pure NaBr melt after electrolysis, the transport number of K^+ ions in the glass membrane can be calculated from eqn. (3):

$$t_{K^+} = \frac{n_{KBr}}{\Delta Q/F} \tag{3}$$

where n_{KBr} is the number of equivalent of KBr found in the pure NaBr melt after electrolysis and ΔQ is the amount of charge transferred through the cell measured in Coulomb.

The concentration dependence of the transport number is shown in Fig. 2.

In the above cell the pure NaBr in the left hand side compartment is used as the standard state for NaBr in the mixture. Therefore, for a small change in composition of the NaBr-KBr mixture the change in emf of the cell is given by

$$F\mathrm{d}E = -\,\mathrm{d}\bar{G}_{NaBr} + t_{K^+}\mathrm{d}(\bar{G}_{Na\text{-}sil.} - \bar{G}_{K\text{-}sil.}) \tag{4}$$

Equilibrium is assumed at the interface between Na^+ and K^+ ions in solution and Na^+ and K^+ ions in the silicate. For a small change in composition of the NaBr-KBr mixture the change in the equilibrium conditions is described by the following equation:

$$\mathrm{d}\bar{G}_{NaBr(2)} + \mathrm{d}\bar{G}_{K\text{-}sil.(2)} = \mathrm{d}\bar{G}_{KBr(2)} + \mathrm{d}\bar{G}_{Na\text{-}sil.(2)} \tag{5}$$

Combining eqns. (4) and (5) one obtains

$$F\mathrm{d}E = -\,\mathrm{d}\overline{G}_{\mathrm{NaBr}} + t_{\mathrm{K^+}}\mathrm{d}(\overline{G}_{\mathrm{NaBr}} - \overline{G}_{\mathrm{KBr}}) = -\,t_{\mathrm{Na^+}}\mathrm{d}\overline{G}_{\mathrm{NaBr}} - t_{\mathrm{K^+}}\mathrm{d}\overline{G}_{\mathrm{KBr}} \tag{6}$$

Using the Gibbs-Duhem equation, eqn. (6) takes the form

$$\Delta\overline{G}_{\mathrm{NaBr}} = F\int_1^2 \frac{x_{\mathrm{KBr}}}{t_{\mathrm{K^+}} - x_{\mathrm{KBr}}}\,\mathrm{d}E \tag{7}$$

where x_{KBr} is the mol fraction of KBr in the mixture. A similar equation has been derived by Førland and Thulin [4] for a similar system. For a given composition of the mixture NaBr-KBr, one can measure the emf, E, of the cell and the transport number of K^+ ions in the glass, $t_{\mathrm{K^+}}$, in equilibrium with the bromide mixture. By plotting corresponding values of $x_{\mathrm{KBr}}/(t_{\mathrm{K^+}} - x_{\mathrm{KBr}})$ and FE, the change in chemical potential of NaBr on mixing, ΔG_{NaBr}, is obtained as the area under the curve.

Hersh and Kleppa [5] give the following equation for the molar enthalpies of mixing in the liquid mixture of KBr and NaBr at 770°C:

$$\Delta H_{\mathrm{mix}} = x_1x_2(-510 - 60x_1) \tag{8}$$

where x_1 and x_2 are the mol fractions of NaBr and KBr, respectively. The enthalpy of mixing measured by Hersh and Kleppa were performed at lower temperatures than the emf measurements presented in this work. The enthalpy of mixing for simple alkaili halides and nitrates is not much temperature dependent. The entropies of mixing calculated by using Gibbs energies and enthalpies measured at different temperatures are therefore quite reliable.

From the values obtained for $\Delta\overline{G}_{\mathrm{NaBr}}$, $\Delta\overline{G}_{\mathrm{KBr}}$ was calculated using the Gibbs-Duhem equation and ΔG_{mix} could thus be determined by the equation

$$\Delta G_{\mathrm{mix}} = x_{\mathrm{NaBr}}\Delta\overline{G}_{\mathrm{NaBr}} + (1 - x_{\mathrm{NaBr}})\Delta\overline{G}_{\mathrm{KBr}} \tag{9}$$

Differences between experimentally observed quantities and quantities to be expected for a Temkin [6] mixture or ideal mixture are given by the excess quantities:

$$\Delta G^{\mathrm{E}}{}_{\mathrm{mix}} = \Delta G^{\mathrm{obs}}{}_{\mathrm{mix}} - \Delta G^{\mathrm{id}} \tag{10}$$

Table 1. Thermodynamic data for the NaBr-KBr mixtures calculated from emf and transport number measurements at 1073 K.

x_{KBr}	$t_{\mathrm{K^+}}$	FE cal/mol	$\Delta\overline{G}_{\mathrm{KBr}}$ cal/mol	$\Delta\overline{G}_{\mathrm{NaBr}}$ cal/mol	ΔG_{mix} cal/mol	$\Delta G^{\mathrm{E}}{}_{\mathrm{mix}}$ cal/mol	ΔH_{mix} cal/mol	$\Delta S^{\mathrm{E}}{}_{\mathrm{mix}}$ cal/deg. mol
0.1	0.01	190	−230	−5460	−753	−59	−50.8	0.01
0.2	0.02	470	−500	−3852	−1170	−103	−89.3	0.01
0.3	0.04	760	−825	−2874	−1440	−137	−115.9	0.02
0.4	0.07	1090	−1225	−2164	−1601	−166	−131.0	0.03
0.5	0.12	1450	−1650	−1613	−1632	−154	−135.0	0.02
0.6	0.18	1850	−2225	−1169	−1591	−156	−128.2	0.03
0.7	0.27	2280	−2875	−800	−1423	−120	110.9	0.01
0.8	0.40	2810	−3850	−496	−1167	−100	−83.5	0.02
0.9	0.60	3450	−5375	−230	−745	−51	−46.4	0.00

The excess entropy of mixing and the excess enthalpy of mixing are defined in an analogous way.

The data of the excess quantities together with the transport numbers and emf's as function of composition are listed in Table 1.

The results indicate that there are small excess entropies of mixing which means that the deviation from regular solution behaviour for the NaBr-KBr mixture is very small.

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