Activity Coefficients and Excess Molar Gibbs Functions of Liquid Alkali Halide + Silver Halide Mixtures at Varying Temperature and Composition *

J. Richter, R. Conradt, and R. Becker
Institute of Physical Chemistry of the Rheinisch-Westfälischen Technischen Hochschule Aachen

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In certain temperature ranges, the e.m.f. of binary molten salt concentration cells without transference can be described by a mole fraction expansion with three constants depending linearly on temperature.

With the six constants it is possible to calculate the activity coefficients, the thermodynamic factor, and the excess molar Gibbs function of liquid alkali halide + silver halide mixtures at given temperatures and compositions. The precision of the representation corresponds to an accuracy in the e.m.f. data of 0.5 mV to 1.2 mV.

Thermodynamics

Let Φ be the e.m.f. of a cell with a binary molten salt of the type

$$\mathrm{Ag}\,|\,\mathrm{Alk\,X} + \mathrm{Ag\,X}\,|\,\mathrm{X} \tag{1a}$$

or

$$\mathrm{Ag}\,|\,\mathrm{Ag\ \ Y} + \mathrm{Ag\,X}\,|\,\mathrm{X}, \tag{1b}$$

where X and Y denote halogenes. The halogen electrode is composed of graphite as matrix for the halogen gas. Measurements on the cell

$$\mathrm{Ag}\,|\,\mathrm{Ag\,X}\,|\,\mathrm{X} \tag{1c}$$

give the e.m.f. $\Phi^{\cdot}$. Then $\Phi - \Phi^{\cdot}$ is the e.m.f. of a concentration cell without transference, for which the relation

$$RT \ln f_2 = -F(\Phi - \Phi^{\cdot}) - RT \ln x_2 \tag{2}$$

holds. Here f_2 is the activity coefficient and x_2 the mole fraction of AgX. On the other hand the relation

$$\mu_i^{\mathrm{E}} = RT \ln f_i, \quad i = 1, 2 \tag{3}$$

is valid, where μ_i^{E} is the excess chemical potential of component i.

From (2) and (3) we obtain

$$\mu_2^{\mathrm{E}} = -F(\Phi - \Phi^{\cdot}) - RT \ln x_2 . \tag{4}$$

Using the series expansion [1]

$$\mu_2^{\mathrm{E}} = B_2 x_1^2 + B_3 x_1^3 + B_4 x_1^4 + \cdots \tag{4a}$$

and truncating the series after the third term we get

$$\Phi - \Phi^{\cdot} = -\frac{1}{F}(B_2 x_1^2 + B_3 x_1^3 + B_4 x_1^4) - \frac{RT}{F} \ln x_2 . \tag{5}$$

Plotting the published e.m.f.-data for molten alkali halide + silver halide mixtures (see references in Table 1), measured at constant x_2 and at various temperatures, versus T, one obtains a linear relationship of the form

$$\Phi - \Phi^{\cdot} = a + bT . \tag{6}$$

The same relation also exists for alkali nitrate + silver nitrate melts [1]. From (5) and (6) we find

$$a + bT = -\frac{1}{F}(B_2 x_1^2 + B_3 x_1^3 + B_4 x_1^4) - \frac{RT}{F} \ln x_2 . \tag{7}$$

Thus B_2, B_3, and B_4 have to depend linearly on $T\,(P = \mathrm{const})$:

$$\begin{aligned} B_2 &= \alpha_0 + \beta_0 T , \\ B_3 &= \alpha_1 + \beta_1 T , \\ B_4 &= \alpha_2 + \beta_2 T . \end{aligned} \tag{8}$$

From (7) and (8) we derive

$$-Fa = \alpha_0 x_1^2 + \alpha_1 x_1^3 + \alpha_2 x_1^4 \tag{9}$$

and

$$-Fb - R \ln x_2 = \beta_0 x_1^2 + \beta_1 x_1^3 + \beta_2 x_1^4 , \tag{10}$$

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Reprint requests to Prof. Dr. J. Richter, Institut für Physikalische Chemie der Technischen Hochschule Aachen, Templergraben 59, D-5100 Aachen.

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i.e. by the axis intersections and the slope of $\Phi - \Phi^{\cdot}$ vs. T plots at least three compositions the six constants are fixed.

With these six constants, which are independent of temperature and composition, the following thermodynamic properties can be calculated:

1) The activity coefficients f_1 and f_2 of components 1 and 2 result from (3), (4a), (8), and the Gibbs-Duhem equation:

$$RT \ln f_1 = [(\alpha_0 + \beta_0 T) + \tfrac{3}{2}(\alpha_1 + \beta_1 T) + 2(\alpha_2 + \beta_2 T)] x_2^2 - [(\alpha_1 + \beta_1 T) + \tfrac{8}{3}(\alpha_2 + \beta_2 T)] x_2^3 + (\alpha_2 + \beta_2 T) x_2^4, \quad (11)$$

$$RT \ln f_2 = (\alpha_0 + \beta_0 T) x_1^2 + (\alpha_1 + \beta_1 T) x_1^3 + (\alpha_2 + \beta_2 T) x_1^4. \quad (12)$$

2) The thermodynamic factor Γ

$$\Gamma \equiv 1 + (\partial \ln f_2 / \partial \ln x_2) \quad (13)$$

is given by

$$\Gamma = 1 - \frac{x_1 x_2}{RT} [2(\alpha_0 + \beta_0 T) + 3(\alpha_1 + \beta_1 T) x_1 + 4(\alpha_2 + \beta_2 T) x_1^2] \quad (14)$$

as seen from (12).

3) The excess molar Gibbs function can be shown to be

$$\bar{G}^{\mathrm{E}} = x_1 x_2 \{(\alpha_0 + \beta_0 T) + \tfrac{1}{2}(\alpha_1 + \beta_1 T) + \tfrac{1}{3}(\alpha_2 + \beta_2 T) + [\tfrac{1}{2}(\alpha_1 + \beta_1 T) + \tfrac{1}{3}(\alpha_2 + \beta_2 T)] x_1 + \tfrac{1}{3}(\alpha_2 + \beta_2 T) x_1^2\}. \quad (15)$$

The excess molar enthalpy $\bar{H}^{\mathrm{E}}$ can be determined more exactly by calorimetric measurements, and with that it is possible to calculate the excess molar entropy $\bar{S}^{\mathrm{E}}$ from (15):

$$\bar{S}^{\mathrm{E}} = (\bar{G}^{\mathrm{E}} - \bar{H}^{\mathrm{E}})/T. \quad (16)$$

The molar enthalpies of mixing $\bar{H}^{\mathrm{E}}$ of the systems considered here have been measured by Dantzer and Kleppa [2], excluding molten iodides for which, at present, there are no calorimetric data.

Up to the middle of 1980, e.m.f.-measurements on concentration cells without transference have been published on the systems listed in Table 1. The measured e.m.f.-data for all these systems were compiled by Becker [21] as functions of temperature and composition.

Table 1. Binary liquid alkali halide + silver halide mixtures with references, the e.m.f. of which were measured on concentration cells without transference.

Mixture	Reference	Mixture	Reference
LiCl + AgCl	[3, 4]	LiI + AgI	[12]
NaCl + AgCl	[5, 6, 7, 8]	NaI + AgI	[12]
KCl + AgCl	[9, 10, 11]	KI + AgI	[13]
RbCl + AgCl	[5]	RbI + AgI	[12]
CsCl + AgCl	[5]	CsI + AgI	[12]
LiBr + AgBr	[14]	AgBr + AgI	[18]
NaBr + AgBr	[15]	AgCl + AgI	[18]
KBr + AgBr	[16]	AgCl + AgBr	[19, 20]
RbBr + AgBr	[17]		

Criterion of Consistency

To obtain an idea on the compatibility of the e.m.f.-data with those leading to "a" and "b" in (6), we have developed a relation between calorimetric and electrochemical measurements. This is referred to as "criterion of consistency" or briefly as "consistency test". The starting-points are the calorimetrically determined enthalpies of mixing quoted by Kleppa and his coworkers [2], which they represent by

$$\bar{H}^{\mathrm{E}} = x_1 x_2 (a^* + b^* x_2 + c^* x_1 x_2). \quad (17)$$

x_2 is again the mole fraction of the silver halogen; the coefficients a^*, b^*, and c^* are given for binary fused chlorides, bromides and nitrates.

The partial excess molar enthalpies $\bar{H}_2^{\mathrm{E}}$ of component 2 is given by

$$\bar{H}_2^{\mathrm{E}} = \bar{H}^{\mathrm{E}} - x_1 (\partial \bar{H}^{\mathrm{E}} / \partial x_1), \quad (18)$$

and from this and (17) we derive

$$\bar{H}_2^{\mathrm{E}} = (a^* + 2b^* - c^*) x_1^2 + (-2b^* + 4c^*) x_1^3 - 3c^* x_1^4. \quad (19)$$

Furthermore, we have

$$\mu_2^{\mathrm{E}} \equiv \bar{G}_2^{\mathrm{E}} = \bar{H}_2^{\mathrm{E}} - T \bar{S}_2^{\mathrm{E}}. \quad (20)$$

From (4) and (6) there follows

$$\bar{G}_2^{\mathrm{E}} = -Fa - [Fb + R \ln x_2] T. \quad (21)$$

Comparing the coefficients of (20) and (21), we obtain

$$-\bar{H}_2^{\mathrm{E}}/F = a. \quad (22)$$

(22) implies that $\bar{H}_2^{\mathrm{E}}$ is independent of temperature. But actually, looking at the experimental data of Dantzer and Kleppa [2], there is a slight tempera-

ture dependence of $\bar{H}_2^{\mathrm{E}}$, so that we have to take two factors into consideration.

1. The variation of $\bar{H}_2^{\mathrm{E}}$ with temperature is comparatively small. This is due to the fact that $\Phi - \Phi^{\cdot}$ is not strictly linear in T but can be approached by a linear function within experimental accuracy. Thus, according to (22), "a" is equivalent to $-\bar{H}_2^{\mathrm{E}}/F$.
2. The effect of temperature on $\bar{H}_2^{\mathrm{E}}$ illustrates that the values of "a" and $\bar{H}_2^{\mathrm{E}}/F$ are not identical at any given temperature.

The consistency between measurements from calorimetric and electrochemical investigations indicate that (22) is essentially satisfied. Although this formulation lacks a quantitative statement, it has proved to be a reliable test for the reliability of electrochemical measurements.

The consistency test is illustrated in Fig. 1 by the example of NaCl + AgCl. It shows the similarity of the concentration curves of the calorimetrically determined values of Dantzer and Kleppa [2] at 660 °C and 810 °C, and the "a"-values of Pelton and Flengas [5], which are independent of temperature and have been determined electrochemically. This example also shows that the measurements of Panish et al. [6], Stern [7], and Sternberg [8] are not of the same consistency as compared with the calorimetric measurements. In view of this, the e.m.f.-data of Pelton and Flengas [5] were chosen for further evaluation.

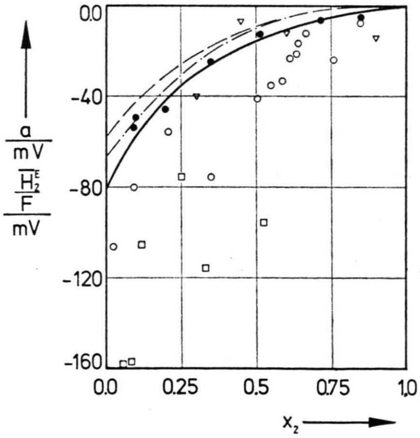

Fig. 1. Criterion of consistency for the system NaCl + AgCl. ——— $(-\bar{H}_2^{\mathrm{E}}/F)$ at 810 °C, –·–·– $(-\bar{H}_2^{\mathrm{E}}/F)$ at 660 °C after Kleppa [2] [Eq. (19)], — "a" from Eq. (9) with the constants from Tab. 2. Measured data: ● Pelton and Flengas [5], ○ Panish et al. [6]. □ Stern [7], ▽ Sternberg and Gheorghiu [8].

We used this consistency test to check the reliability of the e.m.f.-data of all systems in Table 1 (except the iodide systems for which $\bar{H}^{\mathrm{E}}$-measurements do not exist). When data were available from more than one source, only one was used in view of the above relationship.

Results and Discussion

The e.m.f.-data of the selected references are plotted vs. temperature for certain mole fraction and least-squares fitted to linear functions, or taken directly from the references. The factors "a" and "b" of (6), depending on concentration result from this. The six constants α_0, α_1, α_2; β_0, β_1, β_2 result from equations (9) and (10) by means of a polynominal approach with the least-squares method. The constants of the selected systems, obtained in this way, are listed in Table 2.

With the six constants it is possible to calculate the activity coefficients of various systems, according to (11) and (12), as well as the activities $a_i = x_i f_i$, the thermodynamic factor Γ according to (14), and the excess molar Gibbs function $\bar{G}^{\mathrm{E}}$ according to (15), at any given temperature and composition above the liquidus.

Column 9 of Table 2 shows the mean square deviations of single values

$$\delta(\Phi - \Phi^{\cdot})_{\mathrm{abs}} = \sqrt[2]{\frac{\sum\limits_{i=4}^{n}(\Delta\Phi_{\mathrm{Author}} - \Delta\Phi_{\mathrm{cal}})^2}{n-3}}\,. \quad (23)$$

$\Delta\Phi_{\mathrm{Author}}$ is the e.m.f.-difference $\Phi - \Phi^{\cdot}$ measured by the author in the cited paper, $\Delta\Phi_{\mathrm{cal}}$ the corresponding difference calculated with the six constants, and n the number of composition points measured by the author. The deviations are given in mV, since the absolute measurements and thus the relative percentage deviation depend strongly on the composition. Starting with the assumption that the deviation of e.m.f.-measurement on a concentration cell without transference is about 0.5 mV, the representation of the e.m.f. by the six constants is very satisfactory. At a composition of $x_2 = 0.8$ it causes a relative deviation of 2–5%, and at $x_2 = 0.3$ it is always less than 1% for all systems, except LiBr + AgBr and LiI + AgI. This is the effect of the Li$^+$-ion itself. Besides that, the e.m.f.-

Table 2. System constants α_0, α_1, α_2, β_0, β_1 and β_2 of binary fused alkali halide + silver halide mixtures for evaluation of thermodynamic data.

System	Ref.	$\alpha_0 \cdot 10^{-3}$ / J mol^{-1}	$\alpha_1 \cdot 10^{-3}$ / J mol^{-1}	$\alpha_2 \cdot 10^{-3}$ / J mol^{-1}	β_0 / J K^{-1} mol^{-1}	β_1 / J K^{-1} mol^{-1}	β_2 / J K^{-1} mol^{-1}	$\delta(\Phi - \Phi')_{abs}$ / mV
LiCl + AgCl	[3]	18.294	− 20.290	8.776	− 3.8789	− 2.4927	11.0179	1.18
NaCl + AgCl	[5]	11.736	− 19.031	15.062	− 8.4382	19.3226	− 14.3330	0.53
KCl + AgCl	[5]	− 10.666	5.531	− 1.471	1.8836	− 2.1684	0.7523	0.54
RbCl + AgCl	[5]	− 4.217	− 29.694	21.977	− 3.4664	17.4171	− 11.6930	1.11
CsCl + AgCl	[5]	− 29.627	13.436	− 0.919	23.8681	− 44.2570	23.9039	0.97
LiBr + AgBr	[14]	20.792	− 55.068	48.673	− 22.1259	83.5288	− 69.7510	5.25
LiI + AgI	[12]	− 4.274	29.067	− 24.127	15.6290	− 34.1856	25.2321	1.71
NaI + AgI	[12]	− 4.552	23.096	− 22.490	6.2098	− 20.4442	19.9730	0.36
KI + AgI	[13]	− 52.645	148.828	− 115.386	34.3845	− 120.4933	99.1237	1.15
RbI + AgI	[12]	− 43.801	73.337	− 40.475	26.1677	− 59.1525	37.4561	0.57
CsI + AgI	[12]	− 82.110	194.264	− 137.083	59.3143	− 186.9028	147.1619	1.81
AgBr + AgI	[18]	24.281	− 95.630	105.368	− 12.3552	70.0671	− 83.2581	1.10
AgCl + AgI	[18]	− 14.133	34.587	− 13.217	19.7235	− 44.2172	17.9838	0.72
AgCl + AgBr	[19]	74.922	− 202.546	138.096	− 49.3890	140.5233	− 83.7505	0.31

measurements on the system LiBr + AgBr show limited reliability only in the consistency test.

In Table 3 the $\bar{G}^E_{author}$, after Pelton and Flengas [5], and $\bar{G}^E_{cal}$, after (15), of the system CsCl + AgCl at 800 °C are listed as a function of composition.

All deviations of $\bar{G}^E$ are insignificant, i.e. the $\bar{G}^E$ values of the measured systems can be calculated with great accuracy also at temperatures and compositions different from those to which the measurements refer.

In Fig. 2 the excess molar Gibbs functions of alkali chloride + silver chloride melts are plotted against the mole fraction of silver chloride at 810 °C. For all systems there is a strong dependence of $\bar{G}^E$ on the mole fraction, and all curves are nearly symmetrical in composition (Haase's Symmetry Rule [22]). But there is also a clear dependence on the cation. The high negative values for CsCl + AgCl, which become smaller for RbCl + AgCl and KCl + AgCl, indicate a good miscibility relative to the ideal melt ($\bar{G}^E = 0$); the increasing positive values of NaCl + AgCl and LiCl + AgCl indicate a poorer miscibility. The change from negative to positive sign of $\bar{G}^E$ is obviously correlated to the radius of the cation (see Figure 4). $\bar{G}^E$ is positive when the alkali ion has a smaller radius than Ag$^+$, and viceversa. The $\bar{G}^E$ of the systems LiCl + AgCl, LiI + AgI, and LiBr + AgBr at 810 °C depending

x_2	$\bar{G}^E_{author}$ / J mol^{-1}	$\bar{G}^E_{cal}$ / J mol^{-1}
0.0	0	0
0.1	1262	1262
0.2	2327	2328
0.3	3129	3131
0.4	3622	3624
0.5	3780	3782
0.6	3596	3598
0.7	3083	3085
0.8	2274	2276
0.9	1223	1223
1.0	0	0

Table 3. Excess molar Gibbs function $\bar{G}^E$ of the system CsCl + AgCl at 800 °C after Pelton and Flengas [5] ($\bar{G}^E_{author}$), and calculated with Eq. (15) ($\bar{G}^E_{cal}$) depending on the mole fraction of silver chloride.

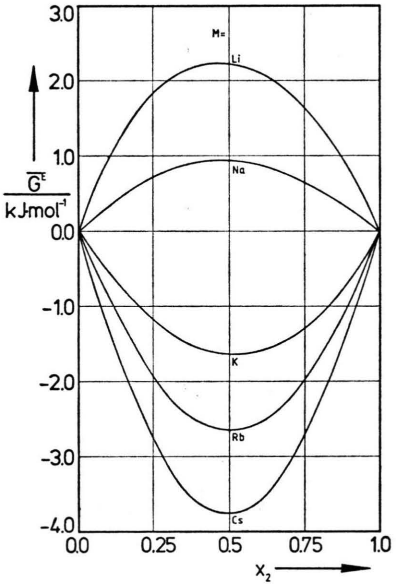

Fig. 2. Excess molar Gibbs functions $\bar{G}^E$ for liquid alkali chloride + silver chloride mixtures MCl + AgCl (M = Li, Na, K, Rb, Cs) at 810 °C as function of the mole fraction x_2 of silver chloride.

on the composition are plotted in Figure 3. It shows clearly that the $\bar{G}^E$ of binary molten halides are nearly independent of the anion, that is the Li$^+$-ion behaves more or less in the same way for the different ionic melts Cl$^-$-AgCl, I$^-$-AgI, and Br$^-$-AgBr, which might be considered as various "solvents".

The dependence of $\bar{G}^E$ upon the cation, mentioned above, is proved in Figure 4. Here the extrema of the $\bar{G}^E$-curves of Fig. 2 and of the iodide curves are plotted versus the cation radius r_C. The correlation to the cation radius is approximately linear. This has been proved and used already on other thermodynamic functions of ionic pure melts [23]. The intersection of the two lines at $r_C \approx 1.08$ Å, corresponding to $\bar{G}^E = 0$ kJ mol^{-1}, is to be interpreted as the radius of a (hypothetical) alkali ion, the chloride and iodide of which behaves ideal in a mixture with AgCl and AgI, respectively.

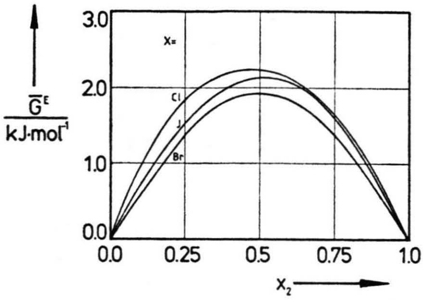

Fig. 3. Excess molar Gibbs functions $\bar{G}^E$ for the systems LiX + AgX (X = Cl, J, Br) at 810 °C as function of the mole fraction x_2 of silver chloride.

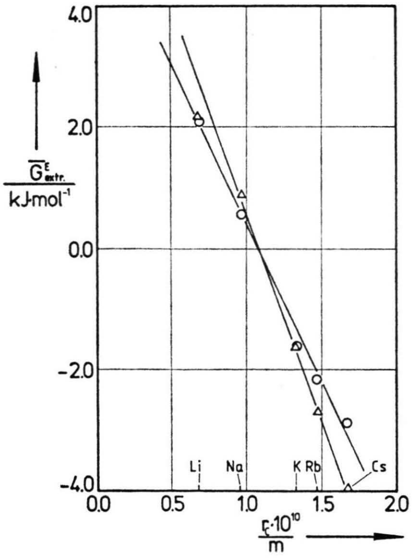

Fig. 4. Extrema of the excess molar Gibbs functions of alkali chloride + silver chloride melts (△) and alkali iodide + silver iodide melts (○) at 810 °C as functions of the cation radius r_C.

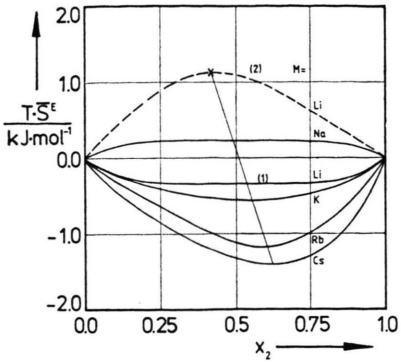

Fig. 5. Excess molar entropy $T\bar{S}^E$ of the alkali chloride + silver chloride melts MCl + AgCl (M = Li, Na, K, Rb, Cs) at 810 °C as function of the mole fraction x_2 of silver chloride (—— from experimental $\bar{G}^E$ and $\bar{H}^E$ determined curves, --- curve found out the extrapolation of the extrema in r_C and x_2).

This linear behaviour of the cation radius is also shown in the function $T\bar{S}^E$ in Figure 5. First we see that the negative $T\bar{S}^E$ values calculated from (16), i.e. the increase of the enthalpy during the mixing, is smaller than it would be in an ideal mixture. In the system NaCl + AgCl, $T\bar{S}^E$ is, as assumed, slightly positive, as the poor miscibility of the system corresponds to a greater excess entropy. An exception is the system LiCl + AgCl, where we find a slightly negative $T\bar{S}^E$ from the measurements [according to (16)] (curve 1), instead of a positive $T\bar{S}^E$. Extrapolation of the minima and maxima of $T\bar{S}^E$ versus r_C as well as the linear connection of the extreme values, drawn in Fig. 5, locates exactly the excepted maximum of the $T\bar{S}^E$-curve of LiNO$_3$ + AgNO$_3$. Curve 2 shows the qualitatively expected $T\bar{S}^E$-curve of LiCl + AgCl. The decrease of $T\bar{S}^E$ in the actually measured curve might be expalined by the strong polarizing effect of the small Li$^+$-ion on the structure of the liquid.

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