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# Analysis of Lippmann Diagrams: Binary Alkali Halide Systems

**Erich Königsberger**

Abteilung für Physikalische Chemie, Montanuniversität Leoben, A-8700 Leoben, Austria

**Summary.** From the analysis of solubility diagrams information on excess $G$ functions at 298.15 K of binary common ion alkali halide mixed crystals can be obtained. With additional data on enthalpies of mixing and $G$ values derived from the liquidus curve, a correlation between excess enthalpies and entropies is established which can be employed to predict phase diagrams of other systems.

**Keywords.** Alkali halides; Phase diagrams; Solubility; Thermodynamic functions; Bayesian estimation.

**Analyse von Lippmann-Diagrammen: Binäre Alkalihalogenidsysteme**

**Zusammenfassung.** Aus der Analyse von Löslichkeitsdiagrammen kann man Informationen über Excess-$G$-Funktionen binärer Alkalihalogenid-Mischkristalle bei 298.15 K erhalten. Zusammen mit experimentellen Mischungsenthalpien und $G$-Werten, die aus den Liquiduskurven abgeleitet wurden, läßt sich eine Korrelation zwischen Excessenthalpien und -entropien aufstellen, die zur Vorhersage von Phasendiagrammen anderer Systeme verwendet werden kann.

## Introduction

The evaluation of excess functions of binary common ion alkali halide systems is of current interest [1–7] and was recently stressed in a comprehensive review [8].

Oonk et al. [6] proposed a relationship between excess Gibbs energies $G^{E(s)}$ and enthalpies of mixing $H^{E(s)}$ of the solid phase, at $x = 0.5$,

$$G^{E(s)} = H^{E(s)}(1 - T/T_0), \tag{1}$$

where $T_0 = 2\,631$ K was found to be a "common vanishing point" of $G^{E(s)}$ for five common anion systems. The calculations were based on experimental data of liquidi and regions of solid phase demixing. Eq. (1) corresponds to

$$G^{E(s)} = H^{E(s)} - TS^{E(s)} \tag{2}$$

with temperature-independent excess enthalpies and entropies. Since it was found experimentally that $H^{E(s)}$ of binary alkali halide mixtures is always positive, $S^{E(s)} = H^{E(s)}/T_0$ will also be positive, which has been predicted previously as a consequence of vibrational contributions to the entropy of mixing [9]. For ordinary metallic solutions Eq. (1) with $T_0 = 3\,000 \pm 1\,000$ K was suggested [10].

Recently a geometrical model (3) for the enthalpy of mixing of binary NaCl type alkali halides was proposed [11],

$$H^{E(s)} = 1\,600\,x(1-x)[(1-x)\Delta_A^2 + x\Delta_B^2]\,\mathrm{kJ\,mol^{-1}}, \tag{3}$$

where $\Delta_i = (r_i - r_j)/r_i$ and $r_i$ denotes the nearest-neighbour distance of component $i = \mathrm{A, B}$, and $j \neq i$. When Eq. (3) was combined with Eq. (1) a common temperature $T_0 = 2\,100\,\mathrm{K}$ has been found appropriate to reproduce the phase diagrams of all binary alkali halide systems with a region of complete solid miscibility in good agreement with experimental data [12].

Some systems exhibit complete solid miscibility even at room temperature so that regions of demixing cannot be exploited for the evaluation of $G^{E(s)}$. In this case, solubility equilibria of mixed crystals with aqueous solutions provide most valuable thermodynamic information for an additional check of Eq. (1).

### *Lippmann Diagrams*

In order to depict the aqueous solubility of binary mixed crystals $\mathrm{B}_{(1-x)}\mathrm{C}_x\mathrm{A}$ Lippmann [13] proposed a new type of phase diagrams and defined the total solubility constant

$$\sum K = (\{\mathrm{B}^+\} + \{\mathrm{C}^+\})\{\mathrm{A}^-\} = a_{\mathrm{BA}}K_{\mathrm{BA}} + a_{\mathrm{CA}}K_{\mathrm{CA}} \tag{4}$$

and activity fractions

$$x_{\mathrm{act}} = \{\mathrm{C}^+\}/(\{\mathrm{B}^+\} + \{\mathrm{C}^+\}) = \{\mathrm{C}^+\}\{\mathrm{A}^-\}/\sum K = a_{\mathrm{CA}}K_{\mathrm{CA}}/\sum K. \tag{5}$$

In Eqs. (4) and (5) braces denote aqueous activities; the $a_i$'s and $K_i$'s are activities in the solid phase and solubility constants of components $i$, respectively. For common cation systems the equations can be modified accordingly. In Lippmann diagrams [13], $\sum K$ is plotted vs. mole fractions $x$ of the solid phase and activity fractions $x_{\mathrm{act}}$ of the aqueous phase at thermodynamic equilibrium.

Stable and metastable solubility equilibria have been discussed within a unifying thermodynamic framework [14–17]. Lippmann diagrams which actually refer to ternary $\mathrm{BA-CA-H_2O}$ systems were shown to become quasi-binary phase diagrams when for the aqueous phase activity fractions are introduced instead of mole fractions [17].

Since aqueous activity coefficients of mixed salt solutions can be modelled with the Pitzer equation [18] up to saturation, analysis of Lippmann diagrams will lead to excess Gibbs energies of the solid phase.

## Results and Discussion

### *Analysis of Lippmann Diagrams*

The Pitzer equation with $\beta_0$, $\beta_1$ and $c$ parameters [19] was used to convert original solubility data of $\mathrm{KCl-RbCl}$ [20], $\mathrm{KCl-KBr}$, $\mathrm{KBr-RbBr}$, and $\mathrm{RbCl-RbBr}$ [21] to $x - x_{\mathrm{act}} - \log\sum K$ values. The Pitzer parameters $\theta$ and $\psi$ of $\mathrm{KCl-KBr}$ equal zero [18]; values for the other systems are not given. Since it can be expected that they are also close to zero, they have been neglected in the present calculations. For the system $\mathrm{KBr-KI-H_2O}$ aqueous activity coefficients obtained by the iso-

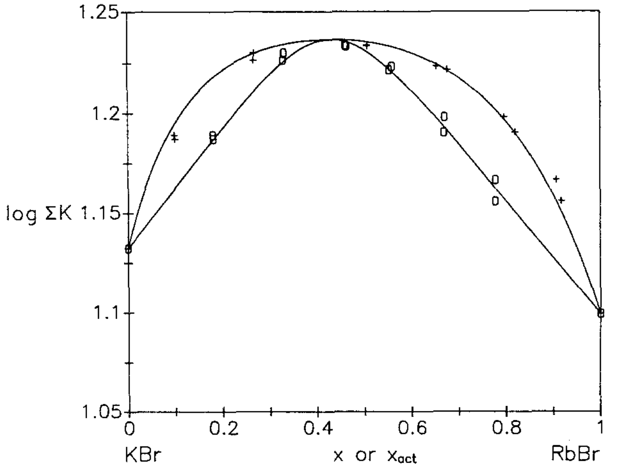

**Fig. 1.** Lippmann diagram of the system KBr−RbBr−$H_2O$; + solidus, ○ solutus points [21]

**Table 1.** Excess parameters at 298.15 K from fits to Lippmann diagrams

| System | $G_1^{E(s)}$/J mol$^{-1}$ | $G_2^{E(s)}$/J mol$^{-1}$ |
|---|---|---|
| KBr−KI | 6100 ± 125 | −350 ± 175 |
| KCl−KBr | 3460 ± 15 | 205 ± 30 |
| RbCl−RbBr | 2915 ± 75 | 120 ± 170 |
| KCl−RbCl | 3345 ± 175 | 250 ± 270 |
| KBr−RbBr | 2705 ± 35 | 390 ± 85 |

**Table 2.** Enthalpies of mixing (see [8]) and $G_1^{E(s)}$ values estimated from liquidus minima

| System[a] | $H_1^{E(s)}$/J mol$^{-1}$ | $H_2^{E(s)}$/J mol$^{-1}$ | $G_1^{E(s)}$/J mol$^{-1}$ |
|---|---|---|---|
| KBr−KI | 7055 ± 175 | −1215 ± 265 | 4450 ± 50 |
| KCl−KBr | 3905 ± 60 | −190 ± 170 | 2500 ± 500 |
| RbCl−RbBr | ... | ... | 2000 ± 500 |
| KCl−RbCl | 3700 ± 55 | 300 ± 155 | 2250 ± 100 |
| KBr−RbBr | ... | ... | 2000 ± 200 |
| NaCl−NaBr | 5545 ± 65 | 330 ± 130 | ... |
| NaBr−NaI | 9610 ± 240 | 800 ± 395 | ... |
| NaCl−KCl | 18080 ± 335 | 495 ± 600 | ... |
| NaBr−KBr | 14660 ± 200 | 1250 ± 430 | ... |
| NaI−KI | 10360 ± 210 | 1415 ± 355 | ... |
| KI−RbI | 2685 ± 20 | −770 ± 35 | ... |

[a] $H_1^{E(s)}$ and $G_1^{E(s)}$ of systems 1-5 have been used in the fit to Eq. (1), whereas both excess enthalpy parameters of the other systems were inserted in Eq. (8) and led to the results presented in Tables 4 and 5

piestic method [22] have been used; the respective solubility diagram is given in [17]. The Lippmann diagram of the system KBr−RbBr−$H_2O$ is shown in Fig. 1, whereas diagrams of the system KCl−KBr−$H_2O$ were given by Glynn et al. [23, 24].

A recently developed method of Bayesian excess parameter estimation [25] was applied to the analysis of Lippmann diagrams. The algorithm uses $\log \sum K$ as independent and $x$ and $x_{\mathrm{act}}$ as dependent variables. When available, experimental miscibility limits at 298.15 K can be employed as *a priori* information (KBr − KI). The solid solutions were modelled by the excess Gibbs function

$$G^{E(s)} = x(1-x)\left[G_1^{E(s)} + G_2^{E(s)}(1-2x)\right], \tag{6}$$

where $x$ is the mole fraction of the second component. Results of this evaluation are given in Table 1.

## *Estimation of $G^{E(s)}$ at Melting Temperature*

Since for some systems agreement of liquidus data from different sources is poor, only the first parameter of function (6) was estimated from reported liquidus minima [8]. Enthalpies of mixing in the liquid state (reviewed in Ref. [8]) have been assumed temperature-independent and equal to $G^{E(l)}$ in these calculations; parameters of the function $\Delta_s^l G^*(T)$ for the pure components were taken from [8]. Results of this estimation together with parameters for enthalpies of mixing (7), if available, are given in Table 2.

$$H^{E(s)} = x(1-x)\left[H_1^{E(s)} + H_2^{E(s)}(1-2x)\right]. \tag{7}$$

**Table 3.** Results of fit to Eq. (1)

| System | $H_1^{E(s)}$/J mol$^{-1}$ | $S_1^{E(s)}$/J K$^{-1}$ mol$^{-1}$ |
|---|---|---|
| KBr − KI | 6975 ± 72 | 2.693 ± 0.072 |
| KCl − KBr | 3909 ± 17 | 1.509 ± 0.031 |
| RbCl − RbBr | 3279 ± 78 | 1.266 ± 0.051 |
| KCl − RbCl | 3700 ± 37 | 1.429 ± 0.037 |
| KBr − RbBr | 3064 ± 39 | 1.183 ± 0.034 |

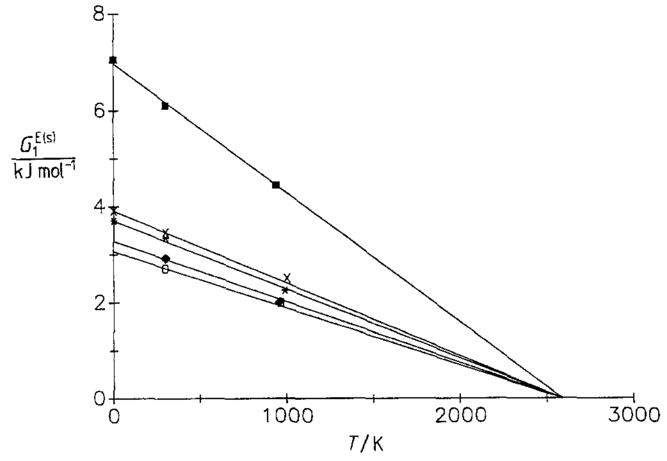

**Fig. 2.** $G_1^{E(s)}$ vs. $T$ leading to a correlation between excess enthalpies and entropies; ○ KBr − RbBr, ◆ RbCl − RbBr, ✳ KCl − RbCl, × KCl − KBr, ■ KBr − KI

### *Evaluation of $T_0$*

In order to establish a correlation between excess enthalpies and entropies, Eq. (1) was used with $G_1^{E(s)}$ values at 298.15 K (Table 1) and at melting temperature (Table 2) as input. In a Bayesian treatment, $H_1^{E(s)}$ parameters were calculated for each system; experimental values were taken as *a priori* information, whenever they were available. A value of $T_0 = 2\,590 \pm 41$ K common to all systems was obtained as a consequence of an *a priori* estimation of $T_0 = 2\,600 \pm 50$ K. All pertinent results are given in Table 3 and a plot of $G_1^{E(s)}$ vs. $T$ is shown in Fig. 2.

Whereas the results for KBr – KI agree within the uncertainty limits with those of Sangster and Pelton [8], the temperature-independent $G^{E(s)}$ functions proposed by the authors [8] for the systems RbCl – RbBr, KBr – RbBr, and KCl – RbCl are not consistent with experimental solubility equilibria at 298.15 K.

The results of Table 3 have been used to re-calculate the positions of the minima of solidus and liquidus which are compared with experimental values in Table 4.

**Table 4.** Minima of liquidus and solidus[a]

| System | $T_{\text{calc}}$/K | $x_{\text{calc}}$ | $T_{\text{exp}}$/K | $x_{\text{exp}}$ |
|---|---|---|---|---|
| KBr – KI | 937 | 0.667 | 936– 937 | 0.65–0.68 |
| KCl – KBr | 1 000 | 0.713 | 993–1 007 | 0.68–0.70 |
| RbCl – RbBr | 954 | 0.610 | 959– 963 | ≈0.5 |
| KCl – RbCl | 988 | 0.796 | 988– 989 | 0.60–0.75 |
| KBr – RbBr | 963 | 0.764 | 946– 959 | 0.60–0.95 |
| NaCl – NaBr | 1 012 | 0.727 | 1 011–1 017 | 0.60–0.84 |
| NaBr – NaI | 915 | 0.686 | 908– 923 | 0.65–0.76 |
| NaCl – KCl | 922 | 0.524 | 918– 931 | ≈0.5 |
| NaBr – KBr | 897 | 0.496 | 899– 917 | 0.46–0.54 |
| NaI – KI | 850 | 0.445 | 853– 858 | 0.58–0.62 |
| KI – RbI | 913 | 0.749 | ≈899 | ≈0.7 |

[a] Experimental values are reviewed in Ref. [8]

**Table 5.** Consolute points of solid-solid demixing[a]

| System | $T_{\text{calc}}$/K | $x_{\text{calc}}$ | $T_{\text{exp}}$/K | $x_{\text{exp}}$ |
|---|---|---|---|---|
| NaCl – NaBr | 297 | 0.456 | <298 | |
| NaBr – NaI | 478 | 0.440 | >298 | |
| NaCl – KCl | 767 | 0.480 | 763–775 | 0.30–0.50 |
| NaBr – KBr | 666 | 0.493 | ≤668 | 0.35–0.50 |
| NaI – KI | 518 | 0.408 | 513 | 0.38 |

[a] Experimental values are reviewed in Ref. [8]

*Prediction of Phase Diagrams*

In addition, the following version of model (1)

$$G^{E(s)} = x(1-x)[H_1^{E(s)} + H_2^{E(s)}(1-2x)](1 - T/2\,590\,\mathrm{K}) \qquad (8)$$

was employed to calculate liquidus minima (Table 4) and consolute points of solid-solid demixing (Table 5) from experimental $H_j^{E(s)}$ parameters (Table 2) of some other systems. The agreement with experimental data is convincing, even the asymmetry of the regions of demixing is reproduced.

The success of model (1) leads to the conclusion that for binary common ion alkali halide systems temperature-independent $G^{E(s)}$ functions are an oversimplification, whereas the introduction of $C_p^{E(s)}$ functions, as proposed by Sangster and Pelton [8] for the systems NaCl–KCl, NaBr–KBr, and NaI–KI, is probably not necessary.

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