

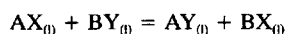
# Thermodynamics of Aqueous Reciprocal Salt Systems. I. Relationships between the Thermodynamic Behaviour of Molten and Aqueous Mixtures

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For high temperature reciprocal reactions of the type:



(all components being in the pure liquid state), where A,B stand for the cations and X,Y for the anions, the change in standard Gibbs energy is  $\Delta G_{ex}^{\circ}$ . This energy parameter enters the expression for the activity coefficients in a mixture of the four salts according to the equation by Flood, Førland and Grjotheim. The results presented in this paper demonstrate that  $\Delta G_{ex}^{\circ}$  may be considered to be a main contribution to the activity terms in concentrated solutions. Based on calculated activity coefficients by means of Pitzer's equation, the relative contributions of  $\Delta G_{ex}^{\circ}$  and of hydration effects are discussed. A criterion is proposed to estimate the predominant effect.

## Introduction

Unlike the numerous investigations of reciprocal salt pairs in their molten state,<sup>1,2</sup> the systematic work on these systems in aqueous solutions has not essentially been continued since the early works of van't Hoff,<sup>3</sup> Brønsted<sup>4,5</sup> and Jänecke.<sup>6</sup> The treatment of the thermodynamic properties of mixtures of salt solutions without common ions gives rise to the most elaborate equations within the framework of the recent methods of the specific ion interaction approach.<sup>7</sup> Usually not all of the needed interaction coefficients are available and extrapolations toward higher concentrations are doubtful.

Therefore it seems worthwhile to search for some simple relationships between the behaviour of aqueous and molten mixtures as a basis for the

development of extrapolation procedures or appropriate model equations. It is the aim of this paper, on the basis of published experimental data on aqueous reciprocal salt mixtures, to look for a correlation with the standard Gibbs energy of the corresponding reciprocal exchange reactions.

## Relations for Molten Salts

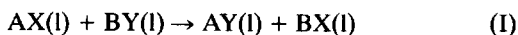
It is well-known that molten salt mixtures without common ions show a stronger non-ideality than the corresponding common ion mixtures. For simple reciprocal salt mixtures, like NaCl + KF, the deviations can be explained by pure electrostatic interactions, the so-called reciprocal Coulomb effect.<sup>8</sup> According to this, the stable salt pair is characterized by the ion combinations: small cation-anion and large cation-anion (NaF + KCl in the given example).

More generally Flood, Førland and Grjotheim<sup>9</sup> have shown that the thermodynamic mixing properties of a system  $A^+, B^+//X^-, Y^-$  can be cal-

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culated in a first approximation from the standard Gibbs energy  $\Delta G_{\text{ex}}^{\circ}$  of the exchange reaction (I).



The activity coefficients  $\gamma_{ij}$  of the salt components AX, BY, AY and BX are related to  $\Delta G_{\text{ex}}^{\circ}$  by the equations (2a, 2b).

$$\begin{aligned} \ln \gamma_{\text{AX}} &= X_{\text{B}} X_{\text{Y}} (\Delta G_{\text{ex}}^{\circ} / RT), \\ \ln \gamma_{\text{BY}} &= X_{\text{A}} X_{\text{Y}} (\Delta G_{\text{ex}}^{\circ} / RT) \end{aligned} \quad (\text{2a})$$

$$\begin{aligned} \ln \gamma_{\text{AY}} &= -X_{\text{B}} X_{\text{X}} (\Delta G_{\text{ex}}^{\circ} / RT), \\ \ln \gamma_{\text{BX}} &= -X_{\text{A}} X_{\text{Y}} (\Delta G_{\text{ex}}^{\circ} / RT) \end{aligned} \quad (\text{2b})$$

The excess Gibbs energy of mixing  $\Delta_{\text{m}} G^{\text{E}}$  for the mixtures AX-BY and AY-BX is given by the relations (3a, 3b).

$$\Delta_{\text{m}} G^{\text{E}}(\text{AX/BY}) = \Delta G_{\text{ex}}^{\circ} (X_{\text{A}} X_{\text{B}} X_{\text{X}} + X_{\text{A}} X_{\text{B}} X_{\text{Y}}) \quad (\text{3a})$$

$$\Delta_{\text{m}} G^{\text{E}}(\text{AY/BX}) = -\Delta G_{\text{ex}}^{\circ} (X_{\text{A}} X_{\text{B}} X_{\text{X}} + X_{\text{A}} X_{\text{B}} X_{\text{Y}}) \quad (\text{3b})$$

$X_i$  represents the ionic fraction of the ion  $i$  as defined by the Temkin model.<sup>8</sup>

It has been shown that Equations (2a, 2b) or (3a, 3b), respectively, can be derived as zero order approximations from a quasi-lattice model<sup>8</sup> and also from the conformal ionic solution theory.<sup>10</sup> In the case of strictly regular common ion subsystems and if  $\Delta G_{\text{ex}}^{\circ} > 0$ , the composition dependence of the activity coefficients and the excess Gibbs energy of mixing is of the type shown in Fig. 1. The mixtures of the stable pairs exhibit positive deviations that is increasing activity coefficients and  $\Delta_{\text{m}} G^{\text{E}}$  or  $\Delta_{\text{m}} H > 0$ . We find just the opposite situation for the unstable pairs.  $\Delta_{\text{m}} G^{\text{E}}$  and  $\Delta_{\text{m}} H$  give identical curves, since for regular solutions the excess entropy of mixing  $\Delta_{\text{m}} S^{\text{E}}$  is zero.

### Relation to Aqueous Solutions

As already emphasized above,<sup>11</sup> both molten salts and aqueous electrolyte solutions represent ionic liquids, the properties of which are governed by Coulombic forces. This should be reflected also in related aspects of the thermodynamics of mixing, especially for the mixtures of reciprocal salt pairs, where the largest changes of electrostatic energy occur. On the other hand the presence of

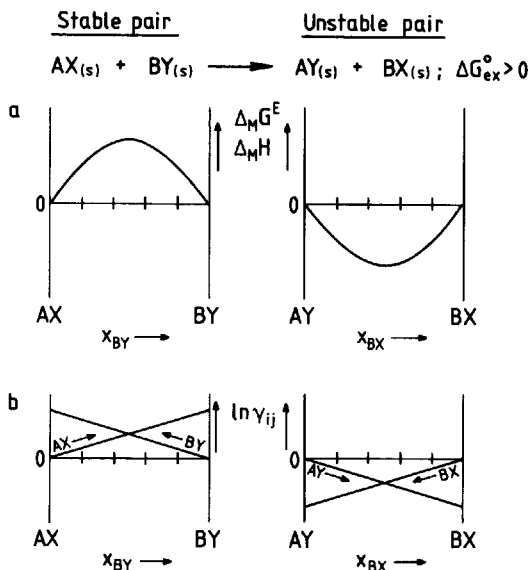
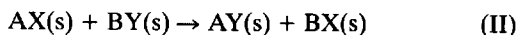


Fig. 1. General pattern of the composition dependence of some thermodynamic quantities. a) Dependence of the excess Gibbs energy of mixing  $\Delta_{\text{m}} G^{\text{E}}$  and enthalpy of mixing  $\Delta_{\text{m}} H$  on mole fractions  $x_{\text{BY}}$ ,  $x_{\text{BX}}$  for binary mixtures of the stable pair components (left side) and instable pair components (right side). b) Dependence of the logarithmic values of the activity coefficients on mole fractions  $x_{\text{BY}}$ ,  $x_{\text{BX}}$  for the same mixtures.

water will modify the ion-ion interaction due to specific ion hydration.

For the discussion of solution data we refer to  $\Delta G_{\text{ex}}^{\circ}$  of the exchange reaction in the solid state (Reaction II) at 298.15 K, because most data are available for this temperature



$\Delta G_{\text{ex}}^{\circ}$  has been calculated from standard Gibbs energies of formation and solution using references<sup>12-15</sup> as data sources. The difference between  $\Delta G_{\text{ex}}^{\circ}$  values, calculated for one and the same reaction, applying various standard data sets, never exceeded 4 kJ/mol.

### Enthalpies of Mixing at Constant Ionic Strength

Up till now the enthalpy of mixing has been published for only eight systems of reciprocal pairs.

Table 1. Enthalpies of the mixing of reciprocal salt pairs  $\Delta_m H$  (J/kg H<sub>2</sub>O) at constant ionic strength  $I$  at 298.15 K with  $y_A = y_B = 0.5$  ( $y_A, y_B$  ionic strength fraction defined as  $(I_A/I)$ , where  $I_A$  ionic strength of salt A).

| Ionic strength mol/kg H <sub>2</sub> O | Stable pair                                     | Unstable pair   | Ref. | $\Delta G_{ex}^\circ$ kJ/mol |
|--|---|---|------|------------------------------|
| 1                                      | LiCl – NaBr<br>+116                             | LiBr – NaCl<br>+65  | 16   | 11.5                         |
| 1                                      | LiCl – KBr<br>+1.5                              | LiBr – KCl<br>–133  | 16   | 14.8                         |
| 1                                      | NaCl – KBr<br>+5                                | NaBr – KCl<br>–78   | 16   | 6.5                          |
| 1                                      | NaCl – KNO <sub>3</sub><br>+331                 | NaNO <sub>3</sub> – KCl<br>–419                             | 16   | 2.2                          |
| 1                                      | MgCl <sub>2</sub> – CaBr <sub>2</sub><br>+6     | MgBr <sup>2</sup> – CaCl <sub>2</sub><br>–16                | 17   | 0.9                          |
| 3                                      | +78   |   |      |                              |
| 1                                      | NaCl – Li <sub>2</sub> SO <sub>4</sub><br>+19.1 | Na <sub>2</sub> SO <sub>4</sub> – LiCl<br>+64.4             | 18   | 26.0                         |
| 3                                      | +405  | +56.5   |      |                              |
| 6                                      | +1551   | –862  |      |                              |
| 1                                      | NaCl – MgSO <sub>4</sub><br>+60.7               | Na <sub>2</sub> SO <sub>4</sub> – MgCl <sub>2</sub><br>+206 | 19   | 41.2                         |
| 3                                      | +687  | +913  |      |                              |
| 6                                      | +1958   | +1713   |      |                              |
| 1                                      | +182  | +180  |      | 11.5                         |
| 3                                      | +1199   | +1010   |      |                              |
| 6                                      | +3027   | +1966   |      |                              |

The reported results are summarized in Table 1. The  $\Delta G_{ex}^\circ$  in the fifth column refers to the conversion of the stable into the unstable salt pair. Thereby Reaction (II) was formulated on the basis of equivalents for the salts of a higher valence type.

If there exists a relationship with  $\Delta G_{ex}^\circ$  of the exchange reaction;  $\Delta_m H$ , for the stable pairs should be positive and negative for the unstable pairs. Indeed, all mixtures of stable pairs possess endothermic enthalpies of mixing. On the other hand, not all  $\Delta_m H$  values of the unstable pairs are of negative sign. But, there is a clear tendency for  $\Delta_m H$  to be exothermic or less endothermic. In the case of the chargeasymmetric mixtures (the last three systems in Table 1) the situation becomes more complicated because, by keeping the total ionic strength constant, solutions with different molalities have to be mixed. However, at higher concentrations also for these mixtures  $\Delta_m H$  on the unstable side is less endothermic or tends toward becoming exothermic as in the example of

Na<sub>2</sub>SO<sub>4</sub>-LiCl. The authors of the original papers (see ref. Table 1) discussed their results in terms of Young's cross-square rule, which predicts that the sum of the  $\Delta_m H$  values of the four binary common ion mixtures should be equal to the sum of  $\Delta_m H$  of the two reciprocal mixtures, or in symbols  $\Sigma \square = \Sigma X$ . In this connection it is interesting to note that this rule can also be applied to reciprocal molten mixtures. This is demonstrated in Table 2 for the system Na<sup>+</sup>, K<sup>+</sup>//Cl<sup>-</sup>, Br<sup>-</sup> based on the data given by Kleppa & Toguri.<sup>21</sup> Compared with the analogous aqueous mixtures, the difference between  $\Sigma \square$  and X is larger for the molten system, but also the greater uncertainty of measurements at high temperatures must be born in mind.

#### E.M.F. Measurements

Schwabe et al.<sup>22</sup> investigated the influence of high concentrations of perchlorates on the activity coefficients of various salts without a common ion

Table 2. Enthalpies of mixing  $\Delta H_m$  in the system  $\text{Na}^+, \text{K}^+ // \text{Cl}^-, \text{Br}^-$  in the anhydrous molten state and as one molal aqueous solutions,  $\Sigma \square$  represents the sum  $\Delta H_m$  of all common ion mixtures,  $\Sigma X$  the sum of the two reciprocal mixtures.

| Salt pairs       | Melts<br>(1086 $\pm$ 2 K)*<br>J/mol | One molal<br>solutions**<br>(298.15 K)<br>J/kg H <sub>2</sub> O |
|------------------|-------------------------------------|---|
| NaCl-KCl         | - 546                               | -40   |
| NaBr-KBr         | - 565                               | -39   |
| NaCl-NaBr        | + 105                               | + 3.3   |
| KCl-KBr          | + 67                                | + 3.3   |
| $\Sigma \square$ | - 939                               | -72.4   |
| NaCl-KBr         | +1035                               | + 5.1   |
| NaBr-KCl         | -2109                               | -78   |
| $\Sigma X$       | -1074                               | -72.9   |

\*data from <sup>21</sup>, \*\*data from<sup>16</sup>.

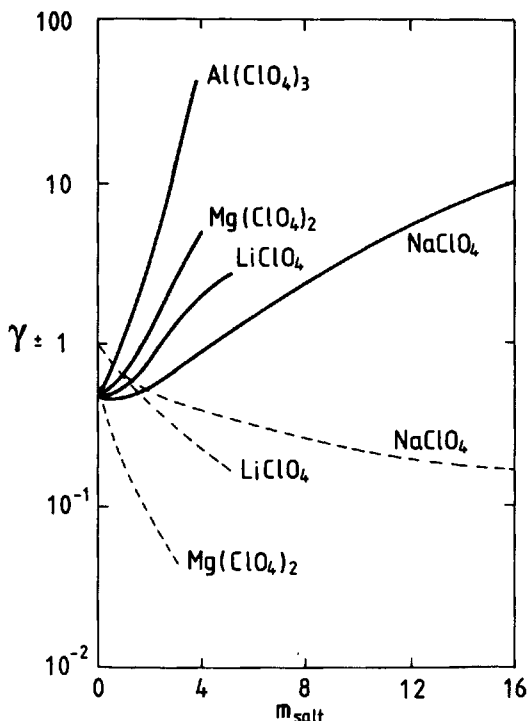


Fig. 2. Dependence of the mean ionic activity coefficient of  $\text{CdCl}_2$  and  $\text{TlF}$  on the molality of various perchlorates<sup>22</sup>. The molalities of  $\text{CdCl}_2$  and  $\text{TlF}$  are both 0.01 mol/kg H<sub>2</sub>O, —  $\text{CdCl}_2$ , ----  $\text{TlF}$ .

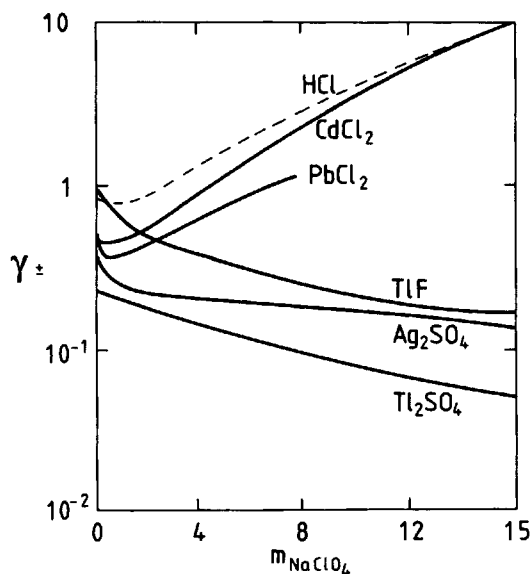


Fig. 3. The dependence of the mean ionic activity coefficient of various salts ( $m = 0.01$ ) on the molality of  $\text{NaClO}_4$ .<sup>22</sup>

by means of e.m.f. measurements with appropriate combinations of amalgam electrodes and electrodes of the second kind. Their results were only presented graphically, as shown in Figs. 2 and 3. Fig. 2 represents the mean ionic activity coefficient of  $\text{CdCl}_2$  and  $\text{TlF}$  dependent on the molality of different perchlorates. The concentration of  $\text{CdCl}_2$  and  $\text{TlF}$  was kept constant at 0.01 mol/kg H<sub>2</sub>O. The most striking feature is the fact that the addition of the perchlorates has an opposite effect on the activity coefficients of these two salts. Whereas the coefficient for  $\text{CdCl}_2$  is increased in the order  $\text{NaClO}_4 < \text{LiClO}_4 < \text{Mg}(\text{ClO}_4)_2 < \text{Al}(\text{ClO}_4)_3$ , the coefficient of  $\text{TlF}$  decreases in the same order. In general this increase of  $\gamma_{\pm}(\text{CdCl}_2)$  in the given order is explained by the growing hydration abilities of the cations within the series  $\text{Na}^+ < \text{Li}^+ < \text{Mg}^{2+} < \text{Al}^{3+}$  or by cation-cation repulsion interactions as suggested by Kelm and Schwabe.<sup>23</sup> Apart from a remark on a possible occurrence of ion association in the case of  $\text{Tl}^+$ , the authors gave no satisfactory explanation of the decrease of  $\gamma_{\pm}(\text{TlF})$ .

However, the different behaviour of  $\text{CdCl}_2$  and  $\text{TlF}$  correlates well with the values of  $\Delta G_{\text{ex}}^{\circ}$  of the corresponding exchange reactions, as summarized in Table 3. Below the chemical formula in

Table 3. Standard Gibbs energies of exchange reactions  $\Delta G_{\text{ex}}^{\circ}$  and the standard Gibbs energies of solution  $\Delta_s G^{\circ}$ , which have been taken or calculated from ref.<sup>12-15</sup>.

| Exchange Reactions                                     |   |   |   |   |   | $\Delta G_{\text{ex}}^{\circ}$ kJ/mol                  |        |
|--|---|---|---|---|---|--|--------|
| TiF<br>-11.0   | + | NaClO <sub>4</sub><br>-15.9                               | → | TiClO <sub>4</sub><br>+ 6.6*                            | + | NaF<br>+ 1.25  | - 34.7 |
| TiF<br>-11.0   | + | LiClO <sub>4</sub>  | → | TiClO <sub>4</sub><br>+ 6.6*                            | + | LiF<br>+13.8   |        |
| TiF<br>-11.0   | + | $\frac{1}{2}$ Mg(ClO <sub>4</sub> ) <sub>2</sub><br>-72.2 | → | TiClO <sub>4</sub><br>+ 6.6*                            | + | $\frac{1}{2}$ MgF <sub>2</sub><br>+20.1                | -109.9 |
| $\frac{1}{2}$ CdCl <sub>2</sub><br>+ 2.0               | + | NaClO <sub>4</sub><br>-15.9                               | → | $\frac{1}{2}$ Cd(ClO <sub>4</sub> ) <sub>2</sub><br>**  | + | NaCl<br>- 9.0  | >+15   |
| $\frac{1}{2}$ CdCl <sub>2</sub><br>+ 2.0               | + | $\frac{1}{2}$ Mg(ClO <sub>4</sub> ) <sub>2</sub><br>-72.2 | → | $\frac{1}{2}$ Cd(ClO <sub>4</sub> ) <sub>2</sub><br>**  | + | $\frac{1}{2}$ MgCl <sub>2</sub><br>-63.0               | >+12   |
| $\frac{1}{2}$ PbCl <sub>2</sub><br>+13.6               | + | NaClO <sub>4</sub><br>-15.9                               | → | $\frac{1}{2}$ Pb(ClO <sub>4</sub> ) <sub>2</sub><br>*** | + | NaCl<br>- 9.0  | >+28   |
| $\frac{1}{2}$ Ag <sub>2</sub> SO <sub>4</sub><br>+14.1 | + | NaClO <sub>4</sub><br>-15.9                               | → | AgClO <sub>4</sub><br>-19.4                             | + | $\frac{1}{2}$ Na <sub>2</sub> SO <sub>4</sub><br>+ 0.5 | + 17.1 |
| $\frac{1}{2}$ Tl <sub>2</sub> SO <sub>4</sub><br>+11.0 | + | NaClO <sub>4</sub><br>-15.9                               | → | TlClO <sub>4</sub><br>+ 6.6*                            | + | $\frac{1}{2}$ Na <sub>2</sub> SO <sub>4</sub><br>+ 0.5 | - 12.0 |
| NaCl<br>- 9.0  | + | $\frac{1}{2}$ Mg(ClO <sub>4</sub> ) <sub>2</sub><br>-72.2 | → | NaClO <sub>4</sub><br>-15.9                             | + | $\frac{1}{2}$ MgCl <sub>2</sub><br>-63.0               | - 2.3  |
| NaCl<br>- 9.0  | + | LiClO <sub>4</sub>  | → | NaClO <sub>4</sub><br>-15.9                             | + | LiCl<br>-41.5  |        |
| NaCl<br>- 9.0  | + | $\frac{1}{2}$ Ba(ClO <sub>4</sub> ) <sub>2</sub><br>-23.0 | → | NaClO <sub>4</sub><br>-15.9                             | + | $\frac{1}{2}$ BaCl <sub>2</sub><br>- 6.1               | - 10.0 |

\*Calculated from solubility<sup>28</sup> and extrapolation of the activity coefficients given by R. A. Robinson.<sup>34</sup>

\*\* $\Delta_s G^{\circ}(\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}) = -38$  kJ/mol estimated from saturated solution data with  $m_{\pm}=4.666$ ;  $\gamma_{\pm}=65.3$ <sup>35</sup> and  $a_{\text{H}_2\text{O}}=0.379$ , which is the water activity of a  $\text{MgI}_2$  solution<sup>35</sup> of the same concentration.

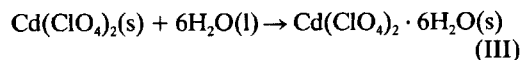
\*\*\* $\Delta_s G^{\circ}(\text{Pb}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}) = -42$  kJ/mol calculated from saturated solution data given in ref.<sup>37</sup>.

Table 3 the standard Gibbs energies of solution  $\Delta_s G^{\circ}(298)$  of the corresponding salts are given, from which  $\Delta G_{\text{ex}}^{\circ}$  was calculated by Equation (4).

$$\Delta G_{\text{ex}}^{\circ} = \Delta_s G^{\circ}(\text{AX}) + \Delta_s G^{\circ}(\text{BY}) - \Delta_s G^{\circ}(\text{AY}) - \Delta_s G^{\circ}(\text{BX}) \quad (4)$$

We find negative values for the reactions of TiF, which become numerically larger when going from NaClO<sub>4</sub> to Mg(ClO<sub>4</sub>)<sub>2</sub>. According to Equation (2a) this indicates a decrease of  $\gamma_{\pm}(\text{TiF})$  in the same order as obtained experimentally.

Unfortunately, for crystalline anhydrous cadmium perchlorate no standard data are available. Taking into account that  $\Delta G$  for the formation of a stable hydrate from the anhydrous salt must be negative (Reaction III),



$\Delta_s G^{\circ}$  for the anhydrous cadmium perchlorate will be even more negative than the value of the hydrate given in Table 3.

For the exchange reactions of CdCl<sub>2</sub> positive values of  $\Delta G_{\text{ex}}^{\circ}$  have been estimated. Therefore, both the influence of the exchange reaction and that of the hydration effect of the cations Na<sup>+</sup> and Mg<sup>2+</sup> are directed toward an increase in  $\gamma_{\pm}(\text{CdCl}_2)$ .

Likewise the curves of the activity coefficients of PbCl<sub>2</sub>, Ag<sub>2</sub>SO<sub>4</sub> and Tl<sub>2</sub>SO<sub>4</sub>, shown in Fig. 4, can be interpreted on the basis of the sign and the relative magnitude of  $\Delta G_{\text{ex}}^{\circ}$  given in Table 3. For PbCl<sub>2</sub> almost the same applies as in the case of

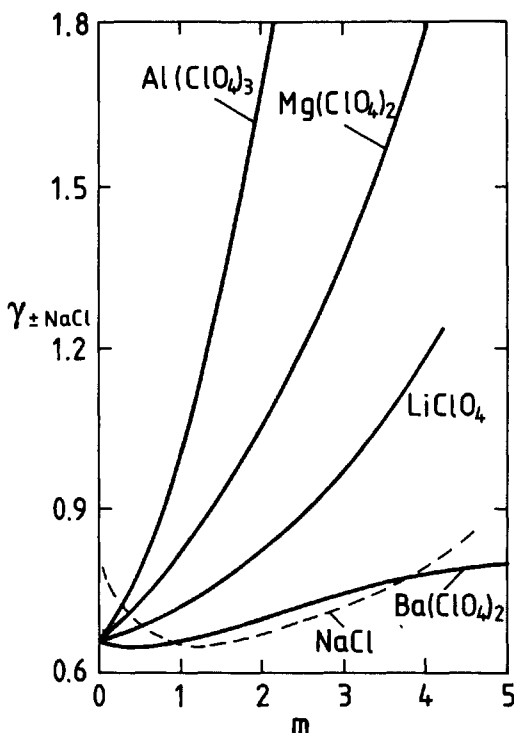


Fig. 4. The dependence of the mean ionic activity coefficient of NaCl ( $m = 1.0/\text{kg H}_2\text{O}$ ) on the molality of four perchlorates.<sup>24</sup>

$\text{CdCl}_2$ , which gives rise to a similar dependence of  $\gamma_{\pm}$  ( $\text{PbCl}_2$ ) and  $\gamma_{\pm}$  ( $\text{CdCl}_2$ ) on the content of  $\text{NaClO}_4$ . The  $\Delta G_{\text{ex}}^{\circ}$  of  $\text{Ag}_2\text{SO}_4$  and  $\text{Ti}_2\text{SO}_4$  in Table 3 are of opposite sign, but their absolute values are relatively small. Therefore the positive  $\Delta G_{\text{ex}}^{\circ}$  of  $\text{Ag}_2\text{SO}_4$  cannot overcompensate the general effect of the increasing ionic strength (Debye-Hückel term), which results in a decreasing curve for  $\gamma_{\pm}$  ( $\text{Ag}_2\text{SO}_4$ ). Corresponding with the negative sign of  $\Delta G_{\text{ex}}^{\circ}$  the curve of  $\text{Ti}_2\text{SO}_4$  shows a stronger drop at high contents of  $\text{NaClO}_4$ .

Later, measurements of the activity coefficient of NaCl in the presence of the same perchlorates were published<sup>24</sup> using sodium ion-conducting glass electrodes (Fig. 4). Again  $\Delta G_{\text{ex}}^{\circ}$  of the exchange reactions has small absolute values and hydration of the cations ( $\text{Na}^+$ ,  $\text{Li}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ba}^{2+}$ ) becomes the dominating factor reflected in an increase of  $\gamma_{\pm}$  ( $\text{NaCl}$ ).

### Influence of Hetero-ionic Salt Additions on Solubility

The background of investigations of the influence of hetero-ionic salt additions on the solubility was in most cases a test of the validity of the Debye-Hückel-Onsager equation. Therefore with few exceptions only measurements with slightly soluble salts and with electrolyte concentrations below one molal are reported. The applicability of the published solubility data for our purpose is further restricted by the fact that for a lot of salt pairs  $\Delta G_{\text{ex}}^{\circ}$  could not be calculated for reason of lacking data (especially  $\text{LiClO}_4$ , acetates, iodates, bromates, chromates). In spite of this, it seems that some solubility data are of interest to discuss from the reciprocal reaction approach.

Bozorth<sup>25</sup> determined the influence of a number of salt additions on the solubility of  $\text{KClO}_4$ . From these data the variation of the logarithm of

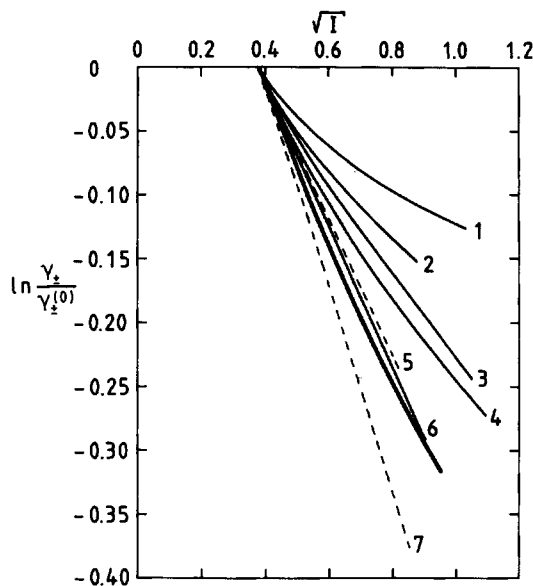


Fig. 5. Variation of the relative mean ionic activity coefficient of  $\text{KClO}_4$  as determined from solubility measurements<sup>25</sup> at 298.1 K: thick line – theoretical ionic strength's dependence according to Equation (5), continuous lines – non-common salt additions (1  $\text{BaCl}_2$ , 2  $\text{NaCl}$ , 3  $\text{Ba}(\text{NO}_3)_2$ , 4  $\text{Na}_2\text{SO}_4$ , 6  $\text{NaNO}_3$ ), dotted lines – common ion salt additions (5  $\text{KCl}$ ,  $\text{NaClO}_4$ ,  $\text{K}_2\text{SO}_4$ , 7  $\text{KNO}_3$ ).  $\gamma_{\pm}^{(0)}$  = activity coefficient of the pure  $\text{KClO}_4$  solution.

Table 4. Standard Gibbs energies of exchange reactions  $\Delta G_{\text{ex}}^{\circ}$  and standard Gibbs energies of solution  $\Delta_s G^{\circ}$  components. Values below the chemical formula denote  $\Delta_s G^{\circ}$ , which have been taken or calculated from ref.<sup>12-15</sup>.

| Exchange Reactions                                       |   |  |   |  |   | $\Delta G_{\text{ex}}^{\circ}$ kJ/mol                     |  |
|--|---|--|---|--|---|---|--|
| KClO <sub>4</sub><br>+11.3                               | + | NaCl<br>- 9.0  | → | NaClO <sub>4</sub><br>-15.9                              | + | KCl<br>- 5.2  | +23.4  |
| KClO <sub>4</sub><br>+11.3                               | + | NaNO <sub>3</sub><br>- 6.2                               | → | NaClO <sub>4</sub><br>-15.9                              | + | KNO <sub>3</sub><br>+ 0.7                                 | +20.3  |
| KClO <sub>4</sub><br>+11.3                               | + | $\frac{1}{2}$ Na <sub>2</sub> SO <sub>4</sub><br>+ 0.6   | → | $\frac{1}{2}$ K <sub>2</sub> SO <sub>4</sub><br>+ 5.0    | + | NaClO <sub>4</sub><br>-15.9                               | +22.8  |
| KClO <sub>4</sub><br>+11.3                               | + | $\frac{1}{2}$ BaCl <sub>2</sub><br>- 8.2                 | → | KCl<br>- 5.2   | + | $\frac{1}{2}$ Ba(ClO <sub>4</sub> ) <sub>2</sub><br>-23.0 | +31.3  |
| KClO <sub>4</sub><br>+11.3                               | + | $\frac{1}{2}$ Ba(NO <sub>3</sub> ) <sub>2</sub><br>+ 6.5 | → | KNO <sub>3</sub><br>+ 0.7                                | + | $\frac{1}{2}$ Ba(ClO <sub>4</sub> ) <sub>2</sub><br>-23.0 | +40.1  |
| $\frac{1}{2}$ Ba(NO <sub>3</sub> ) <sub>2</sub><br>+ 6.5 | + | NaBr<br>-17.1  | → | $\frac{1}{2}$ BaBr <sub>2</sub><br>-18.2                 | + | NaNO <sub>3</sub><br>- 6.2                                | +13.8<br>{ $\Delta H_{\text{ex}}^{\circ}$ = }<br>{+10.5} |
| $\frac{1}{2}$ Ba(NO <sub>3</sub> ) <sub>2</sub><br>+ 6.5 | + | $\frac{1}{2}$ FeCl <sub>3</sub><br>-21.3                 | → | $\frac{1}{2}$ BaCl <sub>2</sub><br>- 8.2                 | + | $\frac{1}{2}$ Fe(NO <sub>3</sub> ) <sub>3</sub>           | { $\Delta H_{\text{ex}}^{\circ}$ = }<br>{+15.5}          |
| KI<br>-11.7  | + | NaOH<br>-42.3  | → | KOH<br>-65.3   | + | NaI<br>-30.6  | +41.9  |
| $\frac{1}{2}$ CaSO <sub>4</sub><br>+12.8                 | + | NaCl<br>- 9.0  | → | $\frac{1}{2}$ CaCl <sub>2</sub><br>-32.6                 | + | $\frac{1}{2}$ Na <sub>2</sub> SO <sub>4</sub><br>+ 0.6    | +35.8  |
| $\frac{1}{2}$ CaSO <sub>4</sub><br>+12.8                 | + | LiNO <sub>3</sub><br>-14.6                               | → | $\frac{1}{2}$ Ca(NO <sub>3</sub> ) <sub>2</sub><br>-16.1 | + | $\frac{1}{2}$ Li <sub>2</sub> SO <sub>4</sub><br>- 5.0    | +19.3  |
| $\frac{1}{2}$ CaSO <sub>4</sub><br>+12.8                 | + | NaNO <sub>3</sub><br>- 6.2                               | → | $\frac{1}{2}$ Ca(NO <sub>3</sub> ) <sub>2</sub><br>-16.1 | + | $\frac{1}{2}$ Na <sub>2</sub> SO <sub>4</sub><br>+ 0.6    | +22.1  |
| $\frac{1}{2}$ Ca(OH) <sub>2</sub><br>+14.4               | + | NaCl<br>- 9.0  | → | $\frac{1}{2}$ CaCl <sub>2</sub><br>-32.6                 | + | NaOH<br>-42.3   | +80.3  |
| $\frac{1}{2}$ Ca(OH) <sub>2</sub><br>+14.4               | + | NaNO <sub>3</sub><br>- 6.2                               | → | $\frac{1}{2}$ Ca(NO <sub>3</sub> ) <sub>2</sub><br>-16.1 | + | NaOH<br>-42.3   | +66.6  |

the relative activity coefficient has been plotted against the square root of the ionic strength (Fig. 5). The thick line represents the theoretical change of the extended Debye-Hückel term given by Pitzer<sup>26</sup> (Equation 5).

$$\ln \gamma_{\pm} = -A \{ \sqrt{I} (1 + 1.2\sqrt{I}) + (2/1.2) \ln(1 + 1.2\sqrt{I}) \} \quad (5)$$

Except for the curves of KNO<sub>3</sub> and NaNO<sub>3</sub> (which are explained afterwards), the curves for common ion salt additions follow the theoretical one more closely than those for salts without a common ion. This confirms the greater non-ideality of non-common ion mixtures for aqueous

solutions as well, if other compensating effects are absent. In agreement with the positive  $\Delta G_{\text{ex}}^{\circ}$  in Table 4 all curves of the hetero-ionic additions are shifted in a positive direction. In the case of NaNO<sub>3</sub> this positive shift occasionally results in a line near to the theoretical one, because the common ion analogous curve of KNO<sub>3</sub> is situated below the Debye-Hückel curve. The stronger hydration of sodium ions cannot be considered as an explanation for the larger activity coefficient of KClO<sub>4</sub> in the presence of the hetero-ionic sodium salts, because the effect of NaClO<sub>4</sub> as a homo-ionic salt is the same as for KCl.

An investigation of a more soluble salt has been carried out by Åkerløf.<sup>27</sup> He determined the

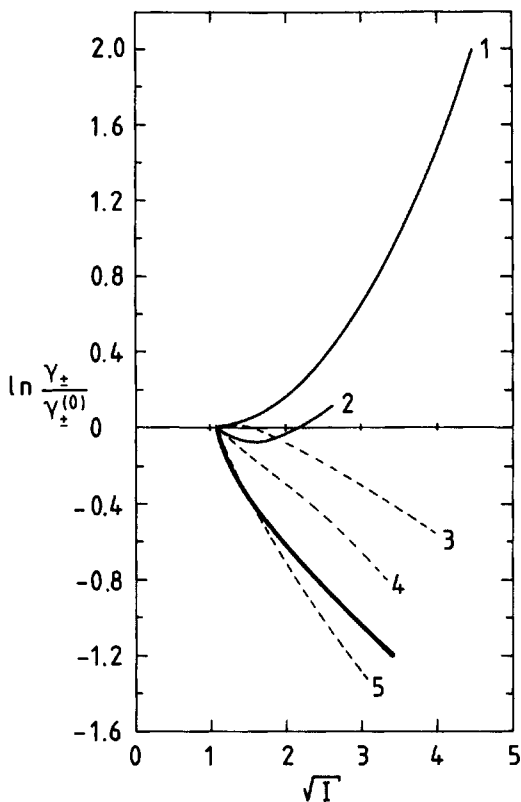


Fig. 6. Variation of the relative mean ionic activity coefficient of  $\text{Ba}(\text{NO}_3)_2$  as determined from solubility measurements<sup>27</sup> at 298.1 K, thick line – theoretical dependence according to Eq. (5), continuous lines – non-common salt additions (1  $\text{FeCl}_3$ , 2  $\text{NaBr}$ ), dotted lines – common ion salt additions (3  $\text{Al}(\text{NO}_3)_3$ , 4  $\text{BaBr}_2$ , 5  $\text{NaNO}_3$ ),  $\gamma_{\pm}^{(0)}$  – activity coefficient of the pure saturated  $\text{Ba}(\text{NO}_3)_2$  solution.

effect of various salts on the solubility of  $\text{Ba}(\text{NO}_3)_2$  up to ionic strengths of 21 molal. In Fig. 6 the activity coefficients of  $\text{Ba}(\text{NO}_3)_2$  have been plotted in the same manner as before. The hetero-ionic additions are  $\text{FeCl}_3$  and  $\text{NaBr}$ . The enthalpies of the corresponding exchange reactions are positive (see Table 4). This should also be true for  $\Delta G_{\text{ex}}^{\circ}$  of both reactions because the reaction entropies are generally small as is evidenced by the reaction of  $\text{Ba}(\text{NO}_3)_2$  with  $\text{NaBr}$  (Table 4). As expected, the reciprocal salt effect becomes more distinct at the higher salt concentrations, so that the positive  $\Delta G_{\text{ex}}^{\circ}$  values cause not only a relative positive shift, but an absolute

increase of the activity coefficient. On the other hand all salts with a common ion have a decreasing effect on  $\gamma_{\pm}$  ( $\text{Ba}(\text{NO}_3)_2$ ), although the hydration properties of the cations are similar.

The plot in Fig. 7 is based on solubility determinations of  $\text{KI}$  in the presence of  $\text{NaOH}$  or  $\text{KOH}$ , respectively<sup>28</sup>. Both hydroxides enhance the activity coefficient of  $\text{KI}$  due to their strong hydration. From this point of view  $\text{KOH}$  should give the largest salting-out effect on  $\text{KI}$ .  $\Delta_s G^{\circ}(\text{KOH}) = -65.3$  kJ/mol, whereas  $\Delta_s G^{\circ}(\text{NaOH})$  is only  $-42.3$  kJ/mol). As can be seen from Fig. 7 the reverse is obtained, again in agreement with  $\Delta G_{\text{ex}}^{\circ}$  of the reaction of  $\text{NaOH}$  with  $\text{KI}$  (Table 4), which has a large positive value.

More recently determinations<sup>29-31</sup> of the influence of  $\text{NaNO}_3$ ,  $\text{NaCl}$  and  $\text{LiNO}_3$  on the solubility of  $\text{CaSO}_4$  (anhydrite) and  $\text{Ca}(\text{OH})_2$  have been performed at enhanced temperatures ( $T \geq 125^{\circ}\text{C}$ ) and up to salt concentrations of 6 molal. At a given ionic strength the solubility of  $\text{CaSO}_4$  decreases in the order  $\text{NaNO}_3 \approx \text{LiNO}_3 > \text{NaCl}$ . Similarly, higher solubilities of  $\text{Ca}(\text{OH})_2$

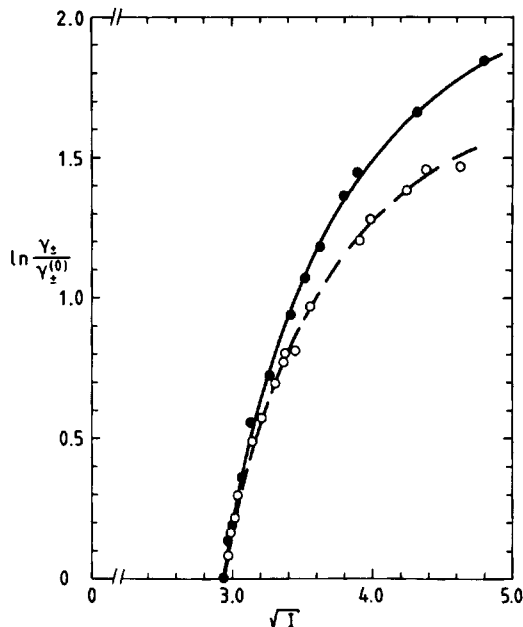


Fig. 7. Dependence of the relative mean ionic activity coefficient of  $\text{KI}$  on the addition of  $\text{NaOH}$  (●) and  $\text{KOH}$  (○) from solubility measurements<sup>23</sup> at 293 K.



in NaNO<sub>3</sub> than in NaCl solutions have been reported<sup>31</sup>. This behaviour is also consistent with the  $\Delta G_{\text{ex}}^{\circ}$  values given in the last part of Table 4. In the reactions with NaCl,  $\Delta G_{\text{ex}}^{\circ}$  is more positive, which gives a larger salting-out effect. The exchange reactions of NaNO<sub>3</sub> and LiNO<sub>3</sub> with CaSO<sub>4</sub> have approximately equal values for  $\Delta G_{\text{ex}}^{\circ}$ .

### Activity Coefficients at Constant Ionic Strength

Considering charge-symmetrical systems and mixing at a constant total ionic strength, the contribution of the Debye-Hückel term remains constant and variations of the activity coefficients will be caused only by specific ion-ion and ion-water interactions. If these interactions are dictated by  $\Delta G_{\text{ex}}^{\circ}$  of the corresponding exchange reaction, a plot of  $\ln \gamma_{\pm}$  against the ionic strength fraction of one salt component in the mixture should give the same pattern as shown in Fig. 1 for the molten salts.

Unfortunately, up to now no direct determinations of activity coefficients have been performed for charge-symmetrical reciprocal salt pairs at constant ionic strength, for instance by means of measurements with ion-selective electrodes. Even osmotic coefficients have been determined only for the systems Na<sup>+</sup>,K<sup>+</sup>//Cl<sup>-</sup>,Br<sup>-</sup>; Na<sup>+</sup>,K<sup>+</sup>//Cl<sup>-</sup>,NO<sub>3</sub><sup>-</sup>,<sup>26</sup> and Li<sup>+</sup>,K<sup>+</sup>//Cl<sup>-</sup>,NO<sub>3</sub><sup>-</sup>.<sup>32</sup> Under these circumstances the application of Pitzer's equations<sup>26</sup> seems to be the most reliable way of providing some information about the behaviour of the activity coefficients of a large number of reciprocal systems of constant ionic strength.

For a binary 1-1 electrolyte mixture of AX and BY the dependence of the activity coefficient of AX on the ionic strength fraction  $y_b$  of BY is given by Equations (6a-c),

$$\begin{aligned} \ln \gamma_{\pm}(\text{AX}) = & \ln \gamma_{\pm}^{\circ}(\text{AX}) + \\ & y_b m \{ B_{\text{MY}} + B_{\text{NX}} - 2B_{\text{MX}} + \theta_{\text{MN}} + \theta_{\text{XY}} + m [ B'_{\text{MY}} + \\ & B'_{\text{NX}} - 2B'_{\text{MX}} + 2(C_{\text{MY}} + C_{\text{NX}} - 2C_{\text{MX}}) + \psi_{\text{MNX}} + \psi_{\text{MXY}} ] \} \\ & + y_b^2 m^2 \{ B'_{\text{NY}} - B'_{\text{MY}} + B'_{\text{MX}} - B'_{\text{NX}} + \\ & C_{\text{NY}} - C_{\text{MY}} + C_{\text{MX}} - C_{\text{NX}} + (1/2) [\psi_{\text{MNX}} + \psi_{\text{NXY}}] - \\ & \psi_{\text{MNX}} - \psi_{\text{MXY}} \} \end{aligned} \quad (6a)$$

$$B_{ij} = \beta_{ij}^{(0)} + \frac{\beta_{ij}^{(1)}}{2m} [1 - (1 + 2\sqrt{m}) \exp(-2\sqrt{m})] \quad (6b)$$

$$B'_{ij} = \frac{\beta_{ij}^{(1)}}{2m^2} [(1 + 2\sqrt{m} + 2m) \exp(-2\sqrt{m}) - 1] \quad (6c)$$

wherein  $m$  represents the total molality,  $\gamma_{\pm}^{(0)}$  the activity coefficient of the pure binary solution,  $\beta_{ij}^{(0)}$ ,  $\beta_{ij}^{(1)}$ ,  $c_{ij}$  are constants characterizing the pure binary electrolyte solutions and  $\theta_{ij}$ ,  $\psi_{ijk}$  are the so-called mixing parameters, which have to be evaluated from the ternary systems with a common ion. Appropriate replacements of the indices in the Equations (6a-c) yield the activity coefficient of BY.

The advantage of the Pitzer equations compared to other treatments, based on the specific ionic interaction approach, is a smaller number of adjustable parameters and an enhanced predictive power. As has been pointed out,<sup>26</sup> in most cases of simple electrolyte mixtures the activity coefficients are described fairly well at moderate concentrations ( $m < 3$  mol/kgH<sub>2</sub>O), even if the mixing parameters are not included.

Using the coefficients tabulated by Pitzer,<sup>26</sup> we calculated the non-common ion trace activity coefficients of all components of 54 reciprocal systems. In order not to exceed the concentration range, within which Pitzer's parameter had been established, a total molality of one was chosen. All systems are listed in Table 5. Again, the stable pairs are arranged on the left-hand side. The last column contains the  $\Delta G_{\text{ex}}^{\circ}$  values of the conversion of the stable pair into the unstable under standard conditions. The systems are arranged according to falling values of  $\Delta G_{\text{ex}}^{\circ}$ . The arrow behind each component (e.g. AX) indicates, whether its trace activity coefficient in the solution of the other non-common ion component (BY) is larger ( $\uparrow$ ) or smaller ( $\downarrow$ ) than the activity coefficient of the component (AX) in its own, pure aqueous solution.

Thus, the change of the activity coefficients will agree with the sign of  $\Delta G_{\text{ex}}^{\circ}$ , if the arrows of the stable pair are both directed towards the top and those of the instable pair towards the bottom. As can be seen from Table 5, this is valid for the systems with the largest values of  $\Delta G_{\text{ex}}^{\circ}$ . Calculations of the full ionic strength dependence of these systems revealed for  $\ln \gamma_{\pm}$  the same pattern with crossed, nearly straight lines as shown in Fig. 1 for the molten salt mixtures. With decreasing values of  $\Delta G_{\text{ex}}^{\circ}$  the differences in the hydration ability becomes more and more impor-

Table 5. Direction of the variation of the activity coefficients of mixing at a total ionic strength of one molal as calculated from Pitzer's equation.  $\Delta G_{ex}^{\circ}$  represents the standard Gibbs energy of the exchange reaction converting AX+BY into AY+BX, values calculated from ref.<sup>12</sup>, arrow  $\uparrow$  ( $\downarrow$ ) behind component AX (BY, AY, BX) denotes a larger (smaller) value of the trace activity coefficient of AX (BY, AY, BX) in a solution of BY (AX, BX, AY) than in its own pure solution;  $\star$  – direction of the activity coefficient variation is opposite to predictions of Eq. (7a, 7b),  $\bullet$  – prediction of Eq. (7a, 7b) is uncertain.

| AX + BY                     |              | AY + BX                  |              | $\Delta G_{ex}^{\circ}$ kJ/mol |              |                           |              |       |
|-----------------------------|--------------|--------------------------|--------------|--------------------------------|--------------|---------------------------|--------------|-------|
| NaF                         | $\uparrow$   | CsI                      | $\uparrow$   | NaI                            | $\downarrow$ | CsF                       | $\downarrow$ | 91.5  |
| NaI                         | $\uparrow$   | LiOH                     | $\uparrow$   | NaOH                           | $\downarrow$ | LiI                       | $\downarrow$ | 82.3  |
| NaBr                        | $\uparrow$   | LiOH                     | $\uparrow$   | NaOH                           | $\downarrow$ | LiBr                      | $\downarrow$ | 74.3  |
| KNO <sub>3</sub>            | $\uparrow$   | LiOH                     | $\uparrow$   | KOH                            | $\downarrow$ | LiNO <sub>3</sub>         | $\downarrow$ | 73.5  |
| NaCl                        | $\uparrow$   | LiOH                     | $\uparrow$   | NaOH                           | $\downarrow$ | LiCl                      | $\downarrow$ | 67.6  |
| NaF                         | $\uparrow$   | CsNO <sub>3</sub>        | $\uparrow$   | NaNO <sub>3</sub>              | $\downarrow$ | CsF                       | $\downarrow$ | 67.2  |
| NaF                         | $\uparrow$   | CsCl                     | $\uparrow$   | NaCl                           | $\downarrow$ | CsF                       | $\downarrow$ | 61.2  |
| $\star$ LiNO <sub>3</sub>   | $\downarrow$ | $\star$ KI               | $\downarrow$ | LiI                            | $\downarrow$ | KNO <sub>3</sub>          | $\downarrow$ | 50.7  |
| NaF                         | $\downarrow$ | KI                       | $\downarrow$ | NaI                            | $\downarrow$ | KF                        | $\downarrow$ | 47.1  |
| LiCl                        | $\downarrow$ | $\bullet$ CsI            | $\downarrow$ | LiI                            | $\downarrow$ | CsCl                      | $\downarrow$ | 45.1  |
| KF                          | $\downarrow$ | CsI                      | $\downarrow$ | $\bullet$ KI                   | $\downarrow$ | CsF                       | $\downarrow$ | 44.4  |
| LiOH                        | $\downarrow$ | NaNO <sub>3</sub>        | $\downarrow$ | LiNO <sub>3</sub>              | $\downarrow$ | NaOH                      | $\downarrow$ | 43.5  |
| NaOH                        | $\downarrow$ | KI                       | $\downarrow$ | NaI                            | $\downarrow$ | KOH                       | $\downarrow$ | 41.9  |
| NaF                         | $\downarrow$ | KBr                      | $\downarrow$ | NaBr                           | $\downarrow$ | KF                        | $\downarrow$ | 40.1  |
| $\star$ LiNO <sub>3</sub>   | $\downarrow$ | $\star$ NaI              | $\downarrow$ | LiI                            | $\downarrow$ | NaNO <sub>3</sub>         | $\downarrow$ | 38.8  |
| KF                          | $\downarrow$ | CsBR                     | $\downarrow$ | KBr                            | $\downarrow$ | CsF                       | $\downarrow$ | 37.3  |
| $\star$ LiNO <sub>3</sub>   | $\downarrow$ | $\star$ KBr              | $\downarrow$ | LiBr                           | $\downarrow$ | KNO <sub>3</sub>          | $\downarrow$ | 35.7  |
| NaF                         | $\downarrow$ | KNO <sub>3</sub>         | $\downarrow$ | NaNO <sub>3</sub>              | $\downarrow$ | KF                        | $\downarrow$ | 35.2  |
| NaOH                        | $\downarrow$ | KBr                      | $\downarrow$ | $\bullet$ NaBr                 | $\downarrow$ | KOH                       | $\downarrow$ | 34.9  |
| NaF                         | $\downarrow$ | KCl                      | $\downarrow$ | NaCl                           | $\downarrow$ | KF                        | $\downarrow$ | 32.2  |
| $\star$ KF                  | $\downarrow$ | CsNO <sub>3</sub>        | $\downarrow$ | KNO <sub>3</sub>               | $\downarrow$ | CsF                       | $\downarrow$ | 32.0  |
| $\star$ LiNO <sub>3</sub>   | $\downarrow$ | $\star$ NaBr             | $\downarrow$ | LiBr                           | $\downarrow$ | NaNO <sub>3</sub>         | $\downarrow$ | 30.7  |
| $\star$ NaCl                | $\downarrow$ | CsI                      | $\downarrow$ | NaI                            | $\downarrow$ | CsCl                      | $\downarrow$ | 30.3  |
| NaOH                        | $\downarrow$ | KNO <sub>3</sub>         | $\downarrow$ | $\star$ NaNO <sub>3</sub>      | $\downarrow$ | KOH                       | $\downarrow$ | 29.9  |
| LiCl                        | $\downarrow$ | KI                       | $\downarrow$ | LiI                            | $\downarrow$ | KCl                       | $\downarrow$ | 29.7  |
| $\star$ NaNO <sub>2</sub>   | $\downarrow$ | KNO <sub>3</sub>         | $\downarrow$ | NaNO <sub>3</sub>              | $\downarrow$ | KNO <sub>2</sub>          | $\downarrow$ | 29.45 |
| KF                          | $\downarrow$ | CsCl                     | $\downarrow$ | $\star$ KCl                    | $\downarrow$ | CsF                       | $\downarrow$ | 29.0  |
| NaOH                        | $\downarrow$ | KCl                      | $\downarrow$ | $\star$ NaCl                   | $\downarrow$ | KOH                       | $\downarrow$ | 26.9  |
| $\star$ NaNO <sub>2</sub>   | $\downarrow$ | $\star$ KCl              | $\downarrow$ | NaCl                           | $\downarrow$ | $\star$ KNO <sub>2</sub>  | $\downarrow$ | 26.4  |
| $\star$ LiNO <sub>2</sub>   | $\downarrow$ | NaNO <sub>3</sub>        | $\downarrow$ | LiNO <sub>3</sub>              | $\downarrow$ | $\star$ NaNO <sub>2</sub> | $\downarrow$ | 24.8  |
| $\star$ NaNO <sub>3</sub>   | $\downarrow$ | CsI                      | $\downarrow$ | NaI                            | $\downarrow$ | CsNO <sub>3</sub>         | $\downarrow$ | 24.3  |
| $\star$ LiNO <sub>3</sub>   | $\downarrow$ | NaCl                     | $\downarrow$ | LiCl                           | $\downarrow$ | NaNO <sub>3</sub>         | $\downarrow$ | 24.0  |
| LiCl                        | $\downarrow$ | CsBr                     | $\downarrow$ | LiBr                           | $\downarrow$ | CsCl                      | $\downarrow$ | 22.9  |
| $\star$ LiNO <sub>3</sub>   | $\downarrow$ | $\star$ KCl              | $\downarrow$ | LiCl                           | $\downarrow$ | KNO <sub>3</sub>          | $\downarrow$ | 21.0  |
| LiBr                        | $\downarrow$ | CsI                      | $\downarrow$ | LiI                            | $\downarrow$ | CsBr                      | $\downarrow$ | 19.4  |
| NaCl                        | $\downarrow$ | CsBr                     | $\downarrow$ | NaBr                           | $\downarrow$ | CsCl                      | $\downarrow$ | 16.2  |
| KCl                         | $\downarrow$ | CsI                      | $\downarrow$ | KI                             | $\downarrow$ | $\star$ CsCl              | $\downarrow$ | 15.3  |
| $\bullet$ LiCl              | $\downarrow$ | NaI                      | $\downarrow$ | NaCl                           | $\downarrow$ | LiI                       | $\downarrow$ | 14.8  |
| LiCl                        | $\downarrow$ | KBr                      | $\downarrow$ | LiBr                           | $\downarrow$ | KCl                       | $\downarrow$ | 14.7  |
| NaCl                        | $\downarrow$ | KI                       | $\downarrow$ | NaI                            | $\downarrow$ | KCl                       | $\downarrow$ | 12.8  |
| KNO <sub>3</sub>            | $\downarrow$ | $\star$ CsI              | $\downarrow$ | KI                             | $\downarrow$ | CsNO <sub>3</sub>         | $\downarrow$ | 12.4  |
| NaNO <sub>3</sub>           | $\downarrow$ | $\star$ KI               | $\downarrow$ | NaI                            | $\downarrow$ | KNO <sub>3</sub>          | $\downarrow$ | 11.9  |
| KCl                         | $\downarrow$ | CsBr                     | $\downarrow$ | KBr                            | $\downarrow$ | CsCl                      | $\downarrow$ | 8.2   |
| LiBr                        | $\downarrow$ | NaI                      | $\downarrow$ | LiI                            | $\downarrow$ | NaBr                      | $\downarrow$ | 8.0   |
| KBr                         | $\downarrow$ | CsI                      | $\downarrow$ | KI                             | $\downarrow$ | $\bullet$ CsBr            | $\downarrow$ | 7.1   |
| LiCl                        | $\downarrow$ | NaBr                     | $\downarrow$ | LiBr                           | $\downarrow$ | NaCl                      | $\downarrow$ | 6.7   |
| $\bullet$ NaCl              | $\downarrow$ | KBr                      | $\downarrow$ | NaBr                           | $\downarrow$ | KCl                       | $\downarrow$ | 6.45  |
| NaCl                        | $\downarrow$ | CsNO <sub>3</sub>        | $\downarrow$ | NaNO <sub>3</sub>              | $\downarrow$ | CsCl                      | $\downarrow$ | 6.0   |
| NaF                         | $\downarrow$ | $\star$ KNO <sub>2</sub> | $\downarrow$ | $\star$ NaNO <sub>2</sub>      | $\downarrow$ | KF                        | $\downarrow$ | 5.75  |
| NaF                         | $\downarrow$ | KOH                      | $\downarrow$ | $\bullet$ NaOH                 | $\downarrow$ | KF                        | $\downarrow$ | 5.3   |
| $\bullet$ NaNO <sub>3</sub> | $\downarrow$ | $\bullet$ KBr            | $\downarrow$ | NaBr                           | $\downarrow$ | KNO <sub>3</sub>          | $\downarrow$ | 4.9   |
| NaCl                        | $\downarrow$ | KNO <sub>3</sub>         | $\downarrow$ | NaNO <sub>3</sub>              | $\downarrow$ | KCl                       | $\downarrow$ | 3.0   |
| KCl                         | $\downarrow$ | CsNO <sub>3</sub>        | $\downarrow$ | KNO <sub>3</sub>               | $\downarrow$ | CsCl                      | $\downarrow$ | 2.9   |

tant, so that  $\gamma_{\pm}$  decreases ( $\downarrow$ ) for the stronger hydrating salt and increases ( $\uparrow$ ) for the other.

Looking for a more quantitative representation of these tendencies we tried to find a correlation with the relationship (7a, 7b) written here for the case of a stable pair.

$$\ln\gamma_{\pm}(\text{AX}) \approx \Delta G_{\text{ex}}^{\circ} + (\Delta_s G_{\text{AX}}^{\circ} - \Delta_s G_{\text{BY}}^{\circ}) \quad (7a)$$

$$\ln\gamma_{\pm}(\text{BY}) \approx \Delta G_{\text{ex}}^{\circ} + (\Delta_s G_{\text{BY}}^{\circ} - \Delta_s G_{\text{AX}}^{\circ}) \quad (7a)$$

This relationship involves the difference of the standard Gibbs energies of solutions of the two salts to account for varying hydration abilities. For the corresponding unstable pair the negative value of  $\Delta G_{\text{ex}}^{\circ}$  has to be inserted and the indices must be substituted by AY and BX.

The direction of the activity coefficient change predicted by Equations (7a, 7b) agrees with the calculations using Pitzer's equation in 174 cases, however, for 30 salts it fails (marked with asterisks in Table 5). In eight cases (marked with black dots) the direction of change of  $\ln\gamma_{\pm}$  according to Equations (7a, 7b) is uncertain, because the value is zero within the limits of uncertainty of the standard values. It should be emphasized that almost all the salts, which are marked by asterisks, belong to nitrate-containing systems. Simple binary mixtures of nitrates with common ions, like KCl-KNO<sub>3</sub>,<sup>36</sup> exhibit already a peculiar behavior. Presently it is difficult to decide for which of these systems the calculations by means of the Pitzer equation may have failed. Only for three systems (Na<sup>+</sup>,K<sup>+</sup>//Cl<sup>-</sup>,Br<sup>-</sup>; Na<sup>+</sup>,K<sup>+</sup>//Cl<sup>-</sup>,NO<sub>3</sub><sup>-</sup>; Li<sup>+</sup>,Na<sup>+</sup>//Cl<sup>-</sup>,NO<sub>3</sub><sup>-</sup>) are all mixing parameters available and from detailed calculations of these systems it follows that the mixing parameters are of greater importance for the reciprocal mixtures than for the common ion mixtures. On the other hand the results calculated by us for the system Li<sup>+</sup>,K<sup>+</sup>//Cl<sup>-</sup>,NO<sub>3</sub><sup>-</sup> are close to those given by Scatchard<sup>33</sup> derived from a thorough analysis of freezing point measurements.

## Conclusion

Reliable thermodynamic data of reciprocal salt systems in aqueous solutions are scarce, especially in concentrated solutions. In spite of this, the data from very different origins and sources, which have been discussed here, show clearly that the thermodynamic behaviour of mixed

aqueous solutions of reciprocal salt pairs is related to the Gibbs energy of the corresponding exchange reactions  $\Delta G_{\text{ex}}^{\circ}$  referring to the pure components. In this respect a parallelism exists to the corresponding molten salt systems. But in aqueous solutions besides the exchange reaction also the differences in the hydration abilities of the ions of the two salts must be considered. As a measure of the latter the differences of the standard Gibbs energies of solution have been proved to be useful.

In applications of the Conformal Ionic Solution Theory to molten mixtures of reciprocal salt pairs, the complete second order expression is usually used, which means that besides the reaction term  $\Delta G_{\text{ex}}^{\circ}$  the mixing terms of the binary common ion subsystems are included. Similarly the addition of suitable binary mixing terms could be a way to account for the contribution of hydration within aqueous systems. However, in order to verify such an expression, more experimental data on aqueous reciprocal salt systems are required. To improve this situation, it is planned to perform solubility measurements in our next work.

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