

A SIMPLIFIED MODEL FOR CALCULATION OF THE GIBBS ENERGY OF MIXING IN CRYSTALS: THERMODYNAMIC THEORY, RESTRICTIONS AND APPLICABILITY

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A simplified model has been set up for calculation of the molar Gibbs energy of mixing $\Delta_{\text{mix}}G_{\text{m}}(\text{s})$ in crystals based on the assumption of a complete liquid–solid thermodynamic equilibrium in the water–salt systems. The procedure allows the $\Delta_{\text{mix}}G_{\text{m}}(\text{s})$ values to be calculated from the experimental solubility data for the saturated binary and ternary solutions. The $\Delta_{\text{mix}}G_{\text{m}}(\text{s})$ values and the excess Gibbs energy of mixing $\Delta_{\text{mix}}G_{\text{m}}^{\text{E}}(\text{s})$ were calculated for six alkali–halide systems (KCl–RbCl–H₂O, KBr–RbBr–H₂O, KI–RbI–H₂O, NH₄Cl–NH₄Br–H₂O, RbCl–RbBr–H₂O and CsCl–CsBr–H₂O). The results obtained were compared with experimental data taken from the literature and values calculated based on various theoretical approaches.

Key words: Mixing energy; Crystals; Binary ternary solutions.

Elucidation of the thermodynamics of mixed crystal formation is of both theoretical and practical importance. The determination of the most significant characteristics of this process, i.e. the molar Gibbs energy of mixing $\Delta_{\text{mix}}G_{\text{m}}(\text{s})$, the excess Gibbs energy of mixing $\Delta_{\text{mix}}G_{\text{m}}^{\text{E}}(\text{s})$, the excess enthalpy of mixing $\Delta_{\text{mix}}H_{\text{m}}^{\text{E}}(\text{s})$, and the excess entropy of mixing $\Delta_{\text{mix}}S_{\text{m}}^{\text{E}}(\text{s})$, is also of special interest for a further development of the thermodynamics of solid solutions.

The low values of these characteristics and the complexity of the experimental methods, such as the isopiestic method and direct calorimetric measurements on special mixed crystal samples, are sources of considerable differences, calling for the development of new theoretical models. A significant advance in this respect has been achieved after the development of the Pitzer ion-interaction model^{1,2}, which permits calculation of activity coefficients in unsaturated and saturated solutions of electrolytes with an accuracy of 2 to 6 per cent³.

As early as the fifties, McCoy and Wallace⁴ calculated the $\Delta_{\text{mix}}G_{\text{m}}(\text{s})$ values for K(Cl, Br) mixed crystals based on the equations:

$$\Delta_{\text{mix}}G_{\text{m}}(\text{s})/RT = x_1 \ln a_1(\text{s}) + x_2 \ln a_2(\text{s}) =$$

$$= x_1[\ln a_1(l) - \ln a_1(l_0)] + x_2[\ln a_2(l) - \ln a_2(l_0)] , \quad (1)$$

where the indices s , l and l_0 refer to mixed crystals and the saturated ternary and binary solutions, respectively.

Harvie, Møller and Weare⁵ and Filippov and Romyantsev⁶ applied Eqs (1) along with the Pitzer model to the determination of the thermodynamic characteristics of the process of mixing.

In our previous studies⁷⁻⁹ we proved the applicability of the equations to the determination of $\Delta_{\text{mix}}G_m(s)$ and $\Delta_{\text{mix}}G_m^E(s)$ for a series of systems which involved mixed crystals of both anhydrous salts and crystalline hydrates.

Königsberger¹⁰ determined the excess Gibbs energy of the solid phase based on Eq. (2), deduced from the subregular mixing model,

$$\Delta_{\text{mix}}G_m^E(s) = x(1-x)[G_1^E(s) + G_2^E(s)(1-2x)] , \quad (2)$$

where $G_1^E(s)$ and $G_2^E(s)$ are thermodynamic excess parameters. The parameters are obtained from fits to Lippmann diagrams¹¹, in which the total solubility constant ΣK is plotted vs mole fractions x of the solid phase and activity fractions x_{act} of the aqueous phase at thermodynamic equilibrium. Königsberger and Gamsjäger¹² determined the thermodynamic properties based on the thermodynamic equilibrium conditions for a system with a variable composition of the solid phase (equality of chemical potentials in the solid and liquid phases) and the stoichiometric saturation condition $dx = 0$. In response to that paper, Glynn and Reardon¹³ demonstrated that the regular solid-liquid model describes the properties of $K(\text{Cl}, \text{Br})$ mixed crystals with a reasonable accuracy. Königsberger proposed the method of recursive Bayesian estimation, which allows the thermodynamic excess parameters to be refined¹⁴.

References¹⁵⁻²⁰ give the $\Delta_{\text{mix}}G_m(s)$ values for mixed crystals of the $(\text{K}, \text{Rb})\text{X}$ ($\text{X} = \text{Cl}, \text{Br}$ or I) and $\text{M}(\text{Cl}, \text{Br})$ ($\text{M} = \text{NH}_4, \text{Rb}$ or Cs) types derived from solubility data of the simple salts and mixed crystals in aqueous solutions and from measurement of the activity coefficients in saturated ternary solutions by the isopiestic method. The authors calculated the Gibbs energy of mixing by using the following equation:

$$\Delta_{\text{mix}}G_m(s) = RT(x_1 \ln x_1 + x_2 \ln x_2 + x_1 \ln f_1 + x_2 \ln f_2) , \quad (3)$$

where f_i is the rational activity coefficient in the solid phase. In a detailed study, Sangster and Pelton²¹ summarized the data published before 1985 for 70 binary alkali halide systems. The authors proposed simplified expressions for the dependence of the excess

parameters $\Delta_{\text{mix}}H_m^E(s)$, $\Delta_{\text{mix}}S_m^E(s)$ and $\Delta_{\text{mix}}G_m^E(s)$ on the solid solution compositions given in terms of the mole fractions x_i . Where sufficient data were unavailable, they assumed that the excess entropy is equal to zero and $\Delta_{\text{mix}}G_m^E(s)$ is independent of temperature.

The present paper provides a theoretical basis for a simplified method of calculation of the thermodynamic characteristics [$\Delta_{\text{mix}}G_m(s)$, $\Delta_{\text{mix}}G_m^E(s)$] for the formation of mixed crystals in water–salt systems and discusses limitations to its applicability. The application of the method is demonstrated on six alkali–halide systems having (i) a common anion (KCl–RbCl–H₂O, KBr–RbBr–H₂O and KI–RbI–H₂O) or (ii) a common cation (NH₄Cl–NH₄Br–H₂O, RbCl–RbBr–H₂O and CsCl–CsBr–H₂O). The causes of differences between the values obtained in this study and those reported in the literature are also discussed. The $\Delta_{\text{mix}}G_m^E(s)$ values are calculated using the equation:

$$\Delta_{\text{mix}}G_m^E(s) = \Delta_{\text{mix}}G_m(s) - \Delta_{\text{mix}}G_m^{\text{id}}(s) = RT(x_1 \ln f_1 + x_2 \ln f_2) \quad (4)$$

The results obtained are presented by expressions illustrating the dependence of $\Delta_{\text{mix}}G_m^E(s)$ on the composition of the mixed crystals. The simplified expressions are deduced assuming that the entropy term $\Delta_{\text{mix}}S_m^E(s)$ is equal to zero and that in the polynomial expression

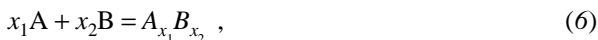
$$\Delta_{\text{mix}}H_m^E(s) = x_A x_B (h_0 + h_1 x_B + h_2 x_B^2 + \dots) \quad (5)$$

only the first empirical coefficient (h_0) is non-zero; hence, the “regular” solution model is adopted. Graphical presentation of the results [$\Delta_{\text{mix}}G_m^E(s)$ vs x_i] documents that this model is well suited to an accurate description of properties of mixed crystals formed in the alkali–halide systems under consideration.

THEORETICAL

Based on the scheme proposed by McCoy and Wallace⁴ and applied in papers^{6–9}, the Gibbs energy of mixing is determined from the difference between the partial molar Gibbs energies of each of the components in the liquid saturated ternary solution and in the saturated binary solutions, i.e. from the differences in the activities of the components in the solutions.

Let us write the reaction of mixed crystal formation as



where A and B are the components of the mixed crystals and x_1 and x_2 are the mole fractions of A and B in the solid phase, respectively. A and B can be anhydrous salts, crystalline hydrates, or double salts with a constant number of water molecules. If the water molecule content in the solid solution is not constant, then the chemical potential of water should be introduced. The $\Delta_{\text{mix}}G_m(s)$ value for reaction (6) is determined from the difference between the chemical potentials of the solid solution ($\mu(A_{x_1}B_{x_2})$) and the initial components (μ_A and μ_B) according to Eq. (7):

$$\Delta_{\text{mix}}G_m(s) = \mu(A_{x_1}B_{x_2}) - x_1\mu_A - x_2\mu_B \quad (7)$$

The chemical potential of the solid solution is given by the expression:

$$\mu(A_{x_1}B_{x_2}) = -RT[x_1 \ln a_A(s) + x_2 \ln a_B(s)] \quad (8)$$

where $a_A(s)$ and $a_B(s)$ are the activities of the components in the solid solution.

The chemical potentials of the starting components (μ_A and μ_B) are calculated from their activities in the saturated binary solutions ($a_A(s_0)$ and $a_B(s_0)$):

$$dG_i/dm = \mu_i = -RT \ln a_i(s_0) \quad (9)$$

The equality of the chemical potentials of the components in the liquid (l, l_0) and solid phases (s, s_0) is a prerequisite for the phase equilibrium:

$$\mu_i(s) = \mu_i(l), \quad \mu_i(s_0) = \mu_i(l_0), \quad \text{and hence,}$$

$$a_i(s) = a_i(l), \quad a_i(s_0) = a_i(l_0) \quad (10)$$

which leads to the widely applied Eqs (1).

Now, we propose a new approach to the calculation of the Gibbs energy of mixing, where the $\Delta_{\text{mix}}G_m(s)$ value is not determined based on the change in the chemical potential of each of the components during its transition from a saturated binary solution to a saturated ternary solution: instead, the transition from the eutectic solution to the saturated ternary solution is treated.

Thus, let us consider the RbCl–RbBr–H₂O ternary system where a continuous series of mixed crystals of the Rb(Cl, Br) type is formed (Fig. 1). The curve 1 corresponds to the saturated ternary solutions¹⁹. Assuming that no isomorphous co-crystallization of the

components occurs and the system is a simple eutectic type, i.e. no mixed crystals but only the simple substances which are components of the system (or their crystalline hydrates) crystallize from the saturated solutions, the solubility isotherm in Fig. 1 will transform into the curve 2. Point E corresponds to the so-called hypothetical eutectic. This approximation has been used by Fanghänel and Emons²² to predict the solubility isotherm of the KCl–MgCl₂–H₂O system at high temperatures, and by Christov et al.²³ to predict the solubility isotherms of carnallite type quaternary systems.

According to the conditions of chemical and phase equilibrium in solutions saturated with respect to a given salt of the composition $\alpha_1 A_1 \cdot \alpha_2 A_2 \cdot \alpha_3 A_3$, the value of the logarithm of activity of this salt will be constant and equal to the logarithm of activity in the saturated binary solution $\ln a(l_0)$, [$\ln a(l_0) = \ln K_{sp}^0$]:

$$\ln a(\alpha_1, \alpha_2, \alpha_3) = \alpha_1 \ln a_1 + \alpha_2 \ln a_2 + \alpha_3 \ln a_3 = \ln K_{sp}^0(\alpha_1, \alpha_2, \alpha_3) = \text{const} \quad (11)$$

where a_1 , a_2 and a_3 are the activities of the components A_1 , A_2 and H_2O in the saturated solution, respectively, and α_1 , α_2 and α_3 denote the stoichiometric coefficients in the salt.

The eutectic in the ternary systems is a point which satisfies simultaneously two equations describing the solubility isotherms of two solid phases and representing the solution of the systems, viz.

$$\ln a(\alpha_1, \alpha_2, \alpha_3; m_1, m_2) = \ln K_{sp}^0(\alpha_1, \alpha_2, \alpha_3) = \text{const}'$$

$$\ln a(\alpha_1, \alpha_2, \alpha_3; m_1, m_2) = \ln K_{sp}^0(\alpha_1, \alpha_2, \alpha_3) = \text{const}'' \quad (12)$$

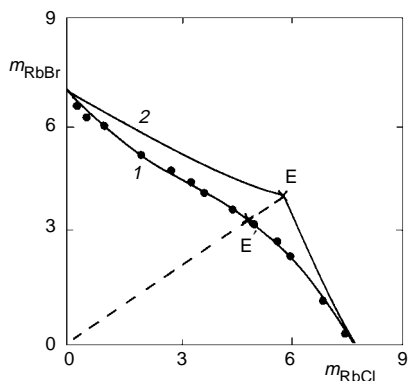


FIG. 1

Solubility isotherm of the RbCl–RbBr–H₂O system at $T = 296.15$ K: 1 experimental data by Makarov et al., ref.¹⁹; 2 calculated values

i.e. in the eutectic point the activities of the components in the ternary solution (a_1^{eut} , a_2^{eut}) are equal to the activities of the components in the corresponding binary solutions:

$$a_1^{\text{eut}} = a_1(l_0) \text{ and } a_2^{\text{eut}} = a_2(l_0) . \quad (13)$$

It will be clear from the above considerations that if the theoretical solubility isotherm is plotted in agreement with the conditions for thermodynamic equilibrium (conditions (12)), then the maximum absolute value of the Gibbs energy of mixing can be determined based on the change in the chemical potential of each component during its transition from the hypothetical eutectic solution (point E) to the corresponding saturated ternary solution of the experimental solubility isotherm (point E' in Fig. 1). The use of the fundamental Pitzer equations allows determining the composition of the eutectic solution (m_1^{eut} , m_2^{eut}) and the activities of the ternary solutions ($a_1(l)$, $a_2(l)$). The aim is to establish the composition (m_1 , m_2) of the saturated ternary solution corresponding to the eutectic.

The task can be simplified significantly by assuming that the system under consideration satisfies reasonably the additivity rule. In this case there are two prerequisites:

1. With respect to the liquid phase. The system should obey the Zdanovskii rule²⁴, which means that the isoactivities of water should lie on straight lines over the whole concentration region of the solutions.

2. With respect to the solid phase. The rational activity coefficients (f_1 and f_2) of the components should be equal to each other, i.e. $f_1/f_2 = 1$ over the entire mixed crystal composition region.

The case of ideal mixed crystal formation ($f_1 = f_2 = 1$) belongs here. The two conditions are actually the conditions of the so-called stoichiometric saturation ($dx = 0$) (refs^{12,13,25,26}) combined with the two subconditions concerning the liquid phase ($x_{\text{aq}} = x_{\text{act}}$) and the solid phase ($x_{\text{act}} = x$) (ref.¹²). The problem of the fulfilment of the conditions 1 and 2 by the alkali-halide systems will be discussed in the following section.

Many water-salt systems in which solid solutions are formed obey the Zdanovskii rule, and the numerical values for a series of properties of the mixed ternary solutions of electrolytes are additive with respect to the properties of the binary solutions mixed. If this rule is met, the subintegral function in the McKay-Perring equation becomes zero and the equations for the activity coefficients γ_1 and γ_2 of the components in the ternary solution can be written⁶ as

$$\gamma_1 = \frac{a_1(l_0)}{m_1 + m_2} ; \quad \gamma_2 = \frac{a_2(l_0)}{m_1 + m_2} . \quad (14)$$

The index l_0 refers to the binary solution which is isopiestic with respect to the ternary solution (m_1, m_2).

Equations (14) can be rearranged by simple transformations to:

$$\frac{a_1(l)}{a_1(l_0)} = \frac{m_1}{m_1 + m_2} ; \quad \frac{a_2(l)}{a_2(l_0)} = \frac{m_2}{m_1 + m_2} . \quad (15)$$

From the latter equation it is evident that if the systems follow the Zdanovskii rule, the activity ratio is constant for a constant mole fraction in the liquid phase. Then, in the corresponding saturated ternary solution, the mole fraction x_{aq} of each component should be the same as in the eutectic solution ($x_{\text{aq}}^{\text{eut}}$):

$$\frac{m_1}{m_1 + m_2} = \frac{m_1^{\text{eut}}}{m_1^{\text{eut}} + m_2^{\text{eut}}} ; \quad \frac{m_2}{m_1 + m_2} = \frac{m_2^{\text{eut}}}{m_1^{\text{eut}} + m_2^{\text{eut}}} . \quad (16)$$

The composition (m_1, m_2) can also be determined graphically. It corresponds to the point of intersection of the solubility isotherm with the beam connecting the hypothetical eutectic and the water angle (point E' in Fig. 1). If the model regular solution describes the system under consideration with a sufficient accuracy and the conditions 1 and 2 are met, then the maximum $\Delta_{\text{mix}} G_{\text{m}}(s)$ value can be calculated by using the equation:

$$\Delta_{\text{mix}} G_{\text{m}}(s) = 0.5RT \ln \frac{a_1(l)a_2(l)}{a_1(l_0)a_2(l_0)} , \quad (17)$$

where $a_1(l)$ and $a_2(l)$ are the activities of components in the saturated ternary solution in which the mole fraction of each component is equal to that in the hypothetical eutectic. The method suggested allows the mixing energy of crystals to be calculated based on the solubility in the saturated binary and ternary solutions alone, using the approximation that the corresponding system obeys the additivity rule.

Equation (17) was deduced directly from conditions (7)–(10) and represents a variant of Eq. (1) for $x_1 = x_2 = 0.5$.

CALCULATION OF THE GIBBS ENERGY OF MIXING

The method proposed in this paper was combined with the fundamental Pitzer equations for determination of the thermodynamic characteristics [$\Delta_{\text{mix}} G_{\text{m}}(s)$, $\Delta_{\text{mix}} G_{\text{m}}^{\text{E}}(s)$] of mixed crystals of the (K, Rb)X and M(Cl, Br) types formed in the KCl–RbCl–H₂O, KBr–RbBr–H₂O, KI–RbI–H₂O, NH₄Cl–NH₄Br–H₂O, RbCl–RbBr–H₂O and CsCl–CsBr–H₂O water–salt systems.

All of the Pitzer binary parameters of interionic interaction ($\beta^{(0)}$, $\beta^{(1)}$ and c^ϕ) needed for the simulation were taken from the literature^{5,7,9,23,27-32}, and parameters applicable to the widest concentration ranges (including saturation of the binary solutions) at the lowest possible standard deviations (σ) were used. Their applicability was proved by simulating ternary systems of the MX-M'X₂-H₂O type (M' = Mg, Mn, Ni, Co, Cu; X = Cl, Br) (refs²⁷⁻³²) and carnallite type quaternary systems²³, as well as by calculation of $\Delta_{\text{mix}}G_m(s)$ based on Eq. (2) (refs^{7,9}).

The values of the logarithm of the thermodynamic solubility product, $\ln K_{\text{sp}}^0$, were calculated on the basis of the binary parameters (Table I) and the saturated binary solution concentrations (m^s). The small differences between the $\ln K_{\text{sp}}^0$ values calculated in this paper (Table II) and reported in refs^{7,27,30-32} are due to the different m^s values used in the calculation.

The ternary interionic interaction parameters θ_{MN} and ψ_{MNX} for the KCl-RbCl-H₂O and RbCl-RbBr-H₂O systems were taken from ref.²³. For the remaining four systems, the θ_{MN} and ψ_{MNX} values were calculated assuming that the systems obey the Zdanovskii rule, i.e. based on data of the binary subsystems alone. This approach has been proposed by Filippov and Fedorov³³ for water-salt systems in which mixed crystals are formed, and has been applied with success in refs⁶⁻⁹. The values obtained (Table III) are very low.

Using isopiestic data for the ternary solutions, Pitzer and Kim³ have calculated the ternary parameters of interionic interaction for more than 50 water-salt systems. The results presented by them show that the θ_{MN} and ψ_{MNX} values are very low and their use

TABLE I
The Pitzer binary parameters for the MX-H₂O systems at $T = 298.15$ K

System	$\beta(0)$	$\beta(1)$	c^ϕ	m_{max}
NH ₄ Cl-H ₂ O	0.0521	0.1916	-0.0030	7.06
NH ₄ Br-H ₂ O	0.0618	0.1635	-0.0042	7.63
KCl-H ₂ O	0.0483	0.2122	-0.0008	4.88
KBr-H ₂ O	0.0559	0.2296	-0.0017	5.67
KI-H ₂ O	0.0658	0.3064	-0.0022	8.56
RbCl-H ₂ O	0.0409	0.1919	-0.0007	7.51
RbBr-H ₂ O	0.0370	0.1520	-0.0007	6.40
RbI-H ₂ O	0.0427	0.1107	-0.0016	7.72
CsCl-H ₂ O	0.0390	-0.0374	-0.0012	11.30
CsBr-H ₂ O	0.0301	0.0029	-0.0005	5.67

(rather than the assumption of $\theta_{MN} = \psi_{MNX} = 0$) does not always lead to better results concerning the properties of the ternary solutions ($\ln \gamma$ or ϕ). In this paper, θ_{MN} and ψ_{MNX} were calculated by using the Zdanovskii rule, and the values obtained are very low as well. A similar situation has also been established for other systems where mixed crystals are formed⁶⁻¹⁰. From this it can be deduced that the solutions investigated follow reasonably the Zdanovskii rule. Moreover, the very small values of θ_{MN} and ψ_{MNX} also determine the very weak ionic interactions of the M-N and M-N-X type in ternary solutions of the MX-NX-H₂O type, so that for the liquid phase it can be assumed that the active mole fraction is equal to the mole fraction ($x_{\text{aq}} = x_{\text{act}}$). To prove condition 1, we simulated the KCl-RbCl-H₂O system and plotted the theoretical solubility isotherms using the θ_{MN} and ψ_{MNX} values given in Table III and assuming that $\theta_{MN} = \psi_{MNX} = 0$. The results obtained indicate that the molalities in the hypothetical eutectic change only negligibly (Table IV). This allowed simulation while neglecting

TABLE II

Calculated values of the logarithm of the thermodynamic solubility product $\ln K_{\text{sp}}^0$ where m^s is the molality of the saturated binary solutions

Composition salt	$\ln K_{\text{sp}}^0$	m^s	Composition salt	$\ln K_{\text{sp}}^0$	m^s
NH ₄ Cl	2.860	7.45	NH ₄ Br	3.066	8.02
KCl	2.089	4.83	KBr	2.600	5.75
RbCl	3.023	7.78	RbBr	2.526	6.74
CsCl	3.485	11.33	CsBr	1.905	5.79
KI	3.999	8.90	RbI	2.780	7.63

TABLE III

The Pitzer ternary parameters for MX-M'X'-H₂O systems at $T = 298.15$ K

System	θ_{MN}	ψ_{MNX}
KCl-RbCl-H ₂ O	-0.00007	-0.00001
KBr-RbBr-H ₂ O	-0.00076	-0.00005
KI-RbI-H ₂ O	-0.00100	-0.00005
NH ₄ Cl-NH ₄ Br-H ₂ O	-0.00006	0.00002
RbCl-RbBr-H ₂ O	-0.00001	-0.00001
CsCl-CsBr-H ₂ O	-0.00010	0.00001

the ternary interactions in the ternary alkali-halide systems under investigation. The same approach has been adopted in refs⁷⁻¹⁰.

In order to check how the condition 2 concerning the solid phase is met, the activity coefficients of the components in the mixed crystal phase (f_i) were determined for all the systems investigated. The f_i values were evaluated from the values of activity of the ternary liquid ($a_i(l)$) and binary liquid ($a_i(l_0)$) solutions calculated based on the Pitzer equation (ref.⁷) and from the experimental data on the composition of the mixed crystals¹⁵⁻²⁰. The results are presented in Fig. 2 as a dependence of f_i on the solid phase composition (x_i). In accordance with the positive deviations from the ideal mixed crystals [$\Delta_{\text{mix}}G_m^E(s) > 0$], the f_i values are larger than one. The curves for all the systems under consideration are almost symmetric, the f_i values decreasing with increasing mole fraction. Of particular importance is the fact that the point of intersection of the curves (where $f_1 = f_2$) lies at $x_i \approx 0.5$, i.e. at the composition for which $\Delta_{\text{mix}}G_m(s)$ takes its maximum value. This implies that for the mixed crystal composition of interest, i.e. $x_i = 0.5$, condition 2 is met and Eq. (17) can be applied to determine the Gibbs energy of mixing. The results are given in Table V and Fig. 3. When calculating the excess Gibbs energy, we proceeded from the assumption that the regular model of mixing describes adequately the properties of the alkali-halide systems investigated, neglecting the excess parameter $G_2^E(s)$ in Eq. (2). The same approach has also been used in refs^{7-9,13,21,34-36}.

The results obtained in the present paper are in a very good agreement with the values calculated based on Eq. (2) (ref.⁷). The deviation never exceeds 5 per cent. The small differences in the values of the excess parameters $G_1^E(s)$ are due to the slight shift

TABLE IV
Composition of the hypothetical eutectic in molalities

Mixed crystals	m_1^{eut}	m_2^{eut}
(K, Rb)Cl ^a	$m_{\text{KCl}} = 2.20$	$m_{\text{RbCl}} = 6.45$
(K, Rb)Cl ^b	$m_{\text{KCl}} = 2.21$	$m_{\text{RbCl}} = 6.45$
(K, Rb)Cl ^c	$m_{\text{KCl}} = 2.19$	$m_{\text{RbCl}} = 6.53$
(K, Rb)Br ^a	$m_{\text{KBr}} = 3.65$	$m_{\text{RbBr}} = 4.70$
(K, Rb)I ^a	$m_{\text{KI}} = 7.08$	$m_{\text{RbI}} = 3.92$
NH ₄ (Cl, Br) ^a	$m_{\text{NH}_4\text{Cl}} = 5.51$	$m_{\text{NH}_4\text{Br}} = 6.50$
Rb(Cl, Br) ^a	$m_{\text{RbCl}} = 5.73$	$m_{\text{RbBr}} = 3.94$
Cs(Cl, Br) ^a	$m_{\text{CsCl}} = 10.14$	$m_{\text{CsBr}} = 2.24$

^a Based on the $\ln K_{\text{sp}}^0$ values from Table II, assuming that $\theta_{\text{MN}} = \psi_{\text{MNX}} = 0$. ^b Based on the $\ln K_{\text{sp}}^0$ values from Table II, assuming that $\theta_{\text{MN}} = -0.00007$, $\psi_{\text{MNX}} = -0.00001$. ^c Calculated using D'Ans and Busch³⁸ experimental data on the solubility, [$\ln K_{\text{sp}}^0(\text{KCl}) = 2.094$ and $\ln K_{\text{sp}}^0(\text{RbCl}) = 3.045$] and $\theta_{\text{MN}} = \psi_{\text{MNX}} = 0$.

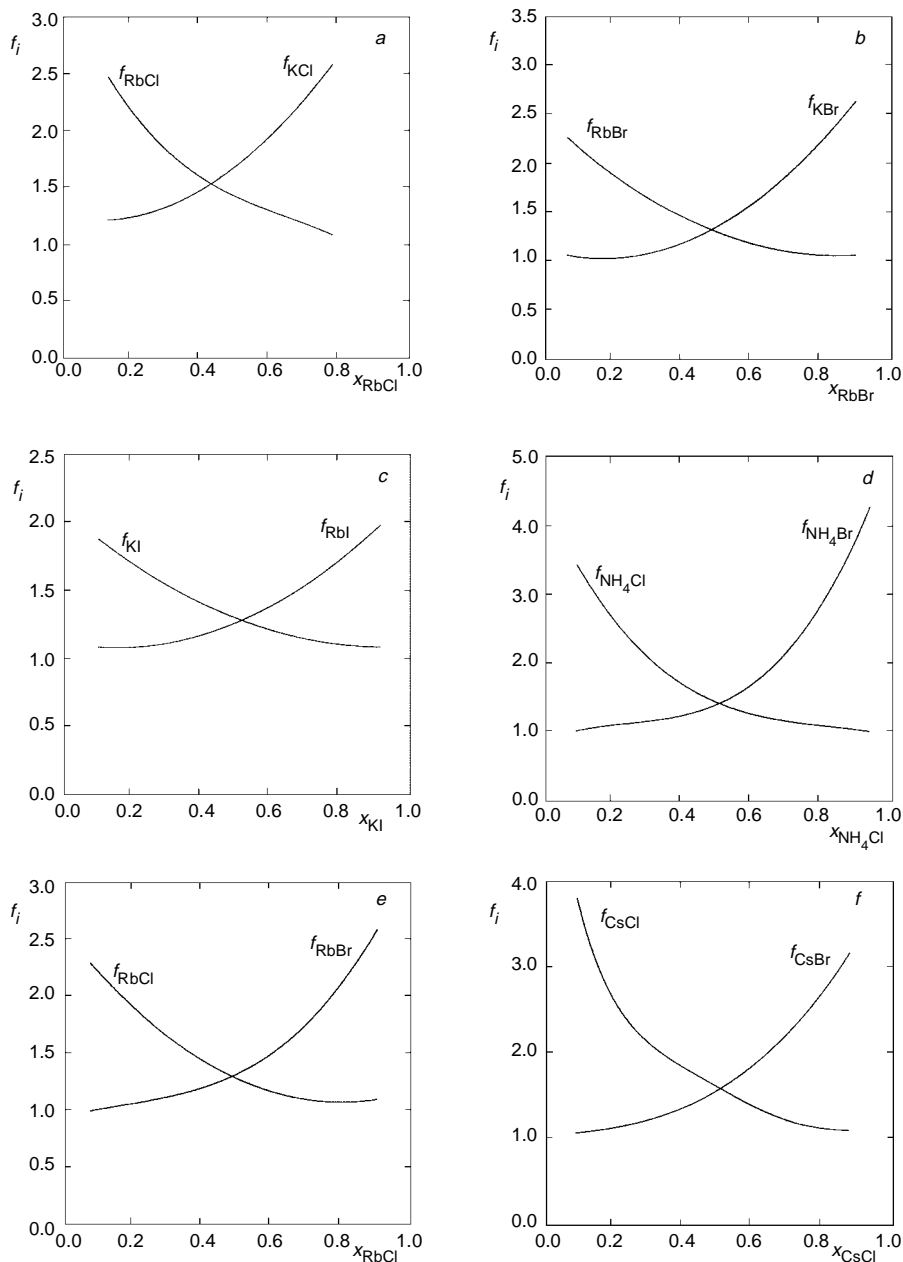


FIG. 2

Rational activity coefficients f_i vs composition (x_i) for *a* (K, Rb)Cl, *b* (K, Rb)Br, *c* (K, Rb)I, *d* $\text{NH}_4(\text{Cl}, \text{Br})$, *e* Rb(Cl, Br) and *f* Cs(Cl, Br) mixed crystals at $T = 298.15 \text{ K}$

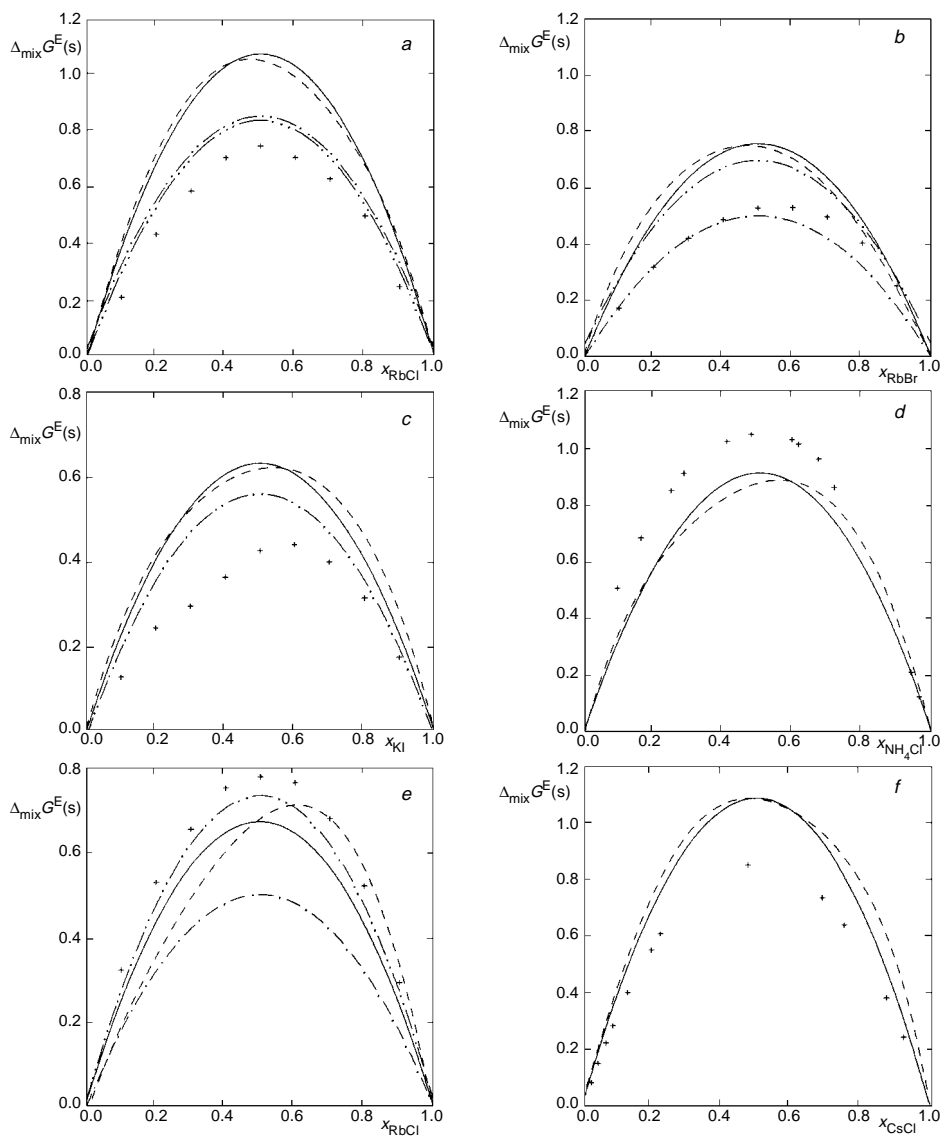


FIG. 3

Plot of the excess Gibbs energy $\Delta_{\text{mix}}G_m^E(\text{s})$ (kJ mol^{-1}) vs composition (x_i) for *a* (K, Rb)Cl, *b* (K, Rb)Br, *c* (K, Rb)I, *d* $\text{NH}_4(\text{Cl}, \text{Br})$, *e* Rb(Cl, Br) and *f* Cs(Cl, Br) mixed crystals at $T = 298.15$ K. *a* Theoretical results: —, . . . — . . . present model, data ref.¹⁵ and ref.³⁸, respectively; --- ref.⁷; - · - · - ref.¹⁰. Experimental results: + ref.¹⁵. *b* Theoretical results: — present model; --- ref.⁷; · - · - · ref.¹⁰. Experimental results: +, ref.¹⁶. *c* Theoretical results: — present model; --- ref.⁷; · - · - · ref.¹⁰. Experimental results: +, ref.¹⁷. *d* Theoretical results: — present model; --- ref.⁷. Experimental results: + ref.¹⁸. *e* Theoretical results: — present model; --- ref.⁷; · - · - · ref.¹⁰; - · - · - ref.²¹. Experimental results: + ref.¹⁹. *f* Theoretical results: — present model; --- ref.⁷. Experimental results: + ref.²⁰

of the maximum of $\Delta_{\text{mix}}G_{\text{m}}^{\text{E}}(\text{s})$ towards higher mole fractions of the component with the smaller ionic radius of the exchanging ion (for the common-anion systems the shift is towards higher mole fractions of KX, while for common-cation systems, it is towards higher mole fractions of MCl). It is interesting that the composition for which the maximum $\Delta_{\text{mix}}G_{\text{m}}^{\text{E}}(\text{s})$ is established (calculated by Eq. (2)) corresponds precisely to the point of intersection of the curves expressing the dependence of f_i on x_i (Fig. 2). For the alkali-halide systems, this deviation from symmetry, i.e. from the model of the regular solution, has also been discussed by others authors^{7,10,34,37}. As a general rule, the larger the cations and/or anions and the smaller the difference between the radii of the two cations in the common-anion binary system (or between the two anions in the common-cation binary system), the more closely the approximation of a one- or two-term polynomial expansion for $\Delta_{\text{mix}}H_{\text{m}}^{\text{E}}(\text{s})$ (Eq. (5)) and $\Delta_{\text{mix}}S_{\text{m}}^{\text{E}}(\text{s}) = 0$ is obeyed²¹. This is in agreement with our results: with the (K, Rb)Cl, (K, Rb)Br, $\text{NH}_4(\text{Cl}, \text{Br})$ and $\text{Rb}(\text{Cl}, \text{Br})$ mixed crystals, a deviation from symmetry is observed, as well as differences between the $G_{\text{I}}^{\text{E}}(\text{s})$ values calculated by Eq. (2) (column c in Table V) and those determined by the method proposed herein (column b, Table V), while for the systems having the largest common ion ((K, Rb)I and Cs(Cl, Br)) such deviations are minimal. This implies that the latter two systems approach most closely the regular solution model, i.e. the entropy term plays the least significant role in them.

TABLE V

Excess parameters at $T = 298.15 \text{ K}$

Mixed crystals	$G_{\text{I}}^{\text{E}}(\text{s}), \text{kJ mol}^{-1}$				
	a ^a	b ^b	c ^c	d ^d	e ^e
(K, Rb)Cl	3.0 ± 0.5	4.264 (3.335)	4.1 ± 0.5	3.345 ± 0.175	1.5
(K, Rb)Br	2.2 ± 0.6	3.021	3.0 ± 0.4	2.705 ± 0.035	2.0
(K, Rb)I	1.7 ± 0.0	2.517	2.5 ± 0.5	2.375 ± 0.018	1.7
$\text{NH}_4(\text{Cl}, \text{Br})$	4.2 ± 0.7	3.688	3.5 ± 0.5	–	–
$\text{Rb}(\text{Cl}, \text{Br})$	3.1 ± 0.4	2.690	2.8 ± 0.7	2.915 ± 0.075	2.0
$\text{Cs}(\text{Cl}, \text{Br})$	3.5 ± 0.3	4.340	4.3 ± 0.7	–	–

^a Experimental data, system KCl–RbCl–H₂O, ref.¹⁵; KBr–RbBr–H₂O, ref.¹⁶; KI–RbI–H₂O, ref.¹⁷; NH_4Cl – NH_4Br –H₂O, ref.¹⁸; RbCl–RbBr–H₂O, ref.¹⁹; CsCl–CsBr–H₂O, ref.²⁰. The data results are summarized in ref.⁷. ^b Calculated according to Eq. (17) and experimental data^{15–20} (data from ref.³⁸ in parentheses). ^c Calculated according to Eq. (1) and presented in ref.⁷. ^d From fits to Lippmann diagrams¹⁰ (for the mixed crystals (K, Rb)I, calculated according to equation $G_{\text{I}}^{\text{E}}(\text{s}) = H_{\text{I}}^{\text{E}}(\text{s})(1 - T/T_0)$, where $H_{\text{I}}^{\text{E}}(\text{s}) = 2.685 \pm 20$, $T_0 = 2\ 590$). ^e Generalized parameters of Sangster and Pelton²¹.

Relatively larger are the differences between the values obtained in this paper and those obtained from fits to the Lippmann diagrams¹⁰. Since we used binary parameters which are very close to those used by Königsberger¹⁰ and ternary interactions in the solutions were neglected ($\theta_{MN} = \psi_{MNX} = 0$) in both papers, it is reasonable to assume that the deviations are largely due to the different solubility data employed in the calculations. In the present paper, the data were taken from papers in which not only the compositions of the liquid and solid phases but also the thermodynamic characteristics of the mixing process are given¹⁵⁻²⁰. However, in order to check the prediction, we simulated thermodynamically the KCl-RbCl-H₂O system and determined the composition of the hypothetical eutectic point (Table IV) and the $G_1^E(s)$ value (Table V) using the solubility data obtained by D'Ans and Busch³⁸, which have also been utilized by Königsberger¹⁰. The results are in a very good agreement (Fig. 3a and Table V).

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