Thermochimica Acta, 180 (1991) 225–239
Elsevier Science Publishers B.V., Amsterdam

ENTHALPY OF MIXING IN KCl–KBr MIXED CRYSTALS AT 25°C

K. PAPAZOVA-DENCHEVA

Sofia University, Anton Ivanov Ave. 1, Sofia 26 (Bulgaria)

V. PEKÁREK and J. NÝVLT *

Institute of Inorganic Chemistry, Czechoslovak Academy of Sciences, Majakovského 24,
160 00 Praha 6 (Czechoslovakia)

M. ŠÍPEK

Institute of Chemical Technology, Department of Physical Chemistry, Technická 5,
160 00 Praha 6 (Czechoslovakia)

(Received 21 August 1990)

ABSTRACT

The enthalpy of mixing in KCl–KBr mixed crystals (molar ratios of 1 : 0.33, 1 : 0.63 and 1 : 1.79) was calculated from calorimetric measurements of integral dissolution enthalpies at 25°C. The results are compared with experimental data reported in the literature and with values calculated by using different theories.

INTRODUCTION

The properties of alkali halide mixed crystals as model systems are of experimental and theoretical interest for the development of the thermodynamics of solid solutions. The data for KCl–KBr liquidus, mostly obtained from thermal analysis data, are listed in Refs. 1 and 2. The data for solidus were obtained by thermal analysis [1,2] and X-ray diffraction at room temperature [3,4] for samples prepared from quenched melts. The enthalpy of mixing of the solids has been measured calorimetrically at 25°C by a number of workers [5–13].

The phase diagrams of KCl–KBr systems were constructed from the published data [5,14–17] and different ideas were proposed for the miscibility of the KCl–KBr mixed crystals [5,14–16,18]; the results seem to be contradictory to some extent.

---

* Author to whom correspondence should be addressed.

0040-6031/91/$03.50

The linear variation in the mean lattice parameter with composition defined by Vegard's rule for the equilibrium interatomic distances was regarded as an important tool in various theories formulated to calculate the enthalpies of mixing in these systems. However, experimental measurements with the accuracy presently achievable show a definite deviation from Vegard's law for lattice parameters which was ascribed to the nonideality of the formed solid solutions in mixed crystals [19]. A simple mathematical relationship between the enthalpy of mixing and these deviations was introduced by Königsberger and Schrunner [20].

The theories proposed in order to try to explain the structure and interactions in the solid solution phase are mostly based on the energy of the crystal lattice and are usually applicable to alkali halide solid solutions [21–23]. The theory on point defects of ionic crystals [24,25] was developed and a good agreement between the experimentally determined enthalpies of solution and the theory was stated [26]. All the theories were usually adopted based on the presupposition that strictly ionic bonds exist in the compounds studied. However, a solution for species with covalent-type bonding was proposed by Hafner [27] for thallium halide systems.

As stated above, the solid solutions of KCl–KBr mixed crystals have been studied extensively; however, uncertainties in the defined structure of the prepared samples and the use of different experimental techniques and different data treatment make the results of the studies difficult to compare and actually complicated for various sample preparation methods.

In the present study the enthalpies of mixing of carefully prepared solid solutions of KCl–KBr mixed crystals were measured by means of precise calorimetric measurements of integral dissolution enthalpies of solid solutions with different KCl–KBr ratios and those of a mixture of pure KCl and KBr salts with the same overall composition as in the solid solution samples. We compare our findings with the results published previously by various authors.

EXPERIMENTAL

For the preparation of solid solutions, p.a. purity potassium chloride and potassium bromide (Lachema Brno, Czechoslovakia) were used. The following impurities exceeded the 0.001 wt% concentration limit. KBr: 0.2 wt% Cl^-; 0.005 wt% in H_2O insoluble substances, 0.002 wt% SO_4^{2-} and Ba^{2+}. KCl: 0.2 wt% Na^+; 0.005 wt% in H_2O insoluble substances; 0.003 wt% SO_4^{2-}, ClO_3^- and NO_3^-; and 0.002 wt% PO_4^{3-}. The mixed KCl–KBr crystals were prepared by slow crystallization from melts [8]. The recrystallized KCl and KBr were air dried, powdered and well mixed in different proportions, heated slowly to 800 °C and kept at 780 ° for 60 min. After this crystallization period, the temperature was slowly lowered to 20 °C over 12 h. After standing the preparations over silica gel for 3 h, the products were finely powdered and kept for a prolonged time over freshly dried $CaCO_3$.

The prepared samples were analysed by means of a modified potentiometric titration [28,29]. About 0.9 g of the powdered and dried sample was dissolved in 10 ml of water and 50 ml of 0.2-M HNO_3 and 5 ml of 5% $Ba(NO_3)_2$ were added, stirred. The solution was titrated against 0.1-M $AgNO_3$ using ion-selective electrodes and a calomel electrode as reference; the potential changes were measured using a precision pH meter.

The analytical method used for the Br^- and Cl^- determinations might be complicated by the precipitation of mixed halide crystals and by the adsorption of common ions on the silver halide precipitates and silver ion selective electrode. For these reasons $Ba(NO_3)_2$ [29] was added and a slightly acidic environment was maintained and a slow titration speed used in analysing the products. The accuracy of determinations was lower for samples with higher contents of Cl^- where the eliminating effect of barium nitrate was not fully satisfactory. However, the maximum uncertainty in the sample composition of 0.12% is about one order of magnitude lower than that expected for direct calorimetric measurements.

Dissolution enthalpy measurements were made using the heat conduction Calvet ms. 70 calorimeter (Setaram, France) for medium temperatures up to 200 °C with 10 ml experimental cells. The calorimeter was equipped with an RT 3000 temperature controller, an NV 724 nanovoltmeter, an integrating ITC unit and an ITC printer. The mixing was realized by rocking the body of the instrument within an angle of 160 °.

The calorimeter was calibrated using the dissolution enthalpy of KCl in water at 25 °C [30]. Suprapure KCl (Merck, Art. 4938) was used as the standard reference material.

All solutions were made up in water which had been redistilled in a quartz apparatus after oxidation of organic components by O_2 at the boiling temperature.

The pure KCl and KBr, their mixtures and the corresponding solid KCl–KBr solutions (0.292 to 0.296 g of the sample) were dissolved in 9.9–10.1 g of water with occasional stirring. The enthalpies of dissolution were calculated using previously reported polynomial functions [31]. The powder X-ray diffraction method was used to study the KCl–KBr mixed crystals (Geiger flax refractograph, Rigaku Denki, Japan, with Cu anode and Ni filter).

In the calculations based on the literature values, the conversion factor 1 cal = 4.184 J was used.

RESULTS AND DISCUSSION

Knowledge of the enthalpy of mixing (some authors use also the term enthalpy of formation) in solid solutions is of prime importance in learning about the nature of the forces acting between the ions over a wide range of interionic separation. Although theory and experiment have advanced uniformly for metallic alloys, there is a striking disproportion between knowledge of facts and their understanding for solid solutions of ionic crystals. Much of the available thermodynamic information pertaining to alkali halide solid solutions is based on experiments performed before 1940. These studies dealt mostly with determinations of the enthalpies of mixing and yielded results which are somewhat lacking in precision by present-day standards. The desirability of improving of the older work is readily apparent.

Solid solutions of the KCl–KBr binary systems in the previously reported studies were prepared by two methods: from quenched melts [5–9,22] or by crystallization from aqueous solutions [10,22]. The first method was used most often; however, serious problems arise with regard to the question of how much we can accept that the prepared solid phases of mixed halide crystals are in true thermodynamic equilibrium.

It was found that the enthalpies of mixing of equimolar KCl–KBr solid solutions which were more than 7 years old and those of solid solutions after 120 h annealing at 670 °C were different due to the ageing procedure [6]. Similarly, different values were found for equimolar solid solutions slowly crystallized from aqueous solutions at 20 °C [10] and for crystals rapidly cooled to 20 °C and then stored for 8 months [6], (928.9 to 953.9 J mol^{-1}, respectively). Hovi [22] also found differences between samples which were solidified by cooling at different rates down to room temperature. This shows that the properties of samples are dependent on the preparation conditions. Unusually high values were reported by Stryvalin et al. [32] who used the data of Hovi [33] and Wallace [34]. Similar conclusions can also be made for other systems. Hovi [33] found for TlCl–TlBr solid solutions that the enthalpies of mixing are higher for samples which are quenched at higher temperatures or over longer time periods. NaCl–KCl solid solutions annealed at 630 °C have enthalpies of mixing about 46–63 J mol^{-1} higher than samples treated at 500 °C [13]. These changes in thermodynamic quantities brought about by the use of different preparation methods and ageing procedures might be explained by shifting the systems in the direction of true thermodynamic equilibrium [21]. Whilst in the more recent papers the use of quenching or ageing procedures are usually reported as enhancing the value of the enthalpy of mixing, opposite statements are given in older papers. Tamman and Krings [35] found values for quenched preparations which were about 1.7–3.8 J g^{-1} lower than for samples prepared from solutions. Zemczuznyi and Rambach [36] stated that the enthalpy of mixing of the KCl–KBr equimolar solid solution freshly prepared from melts is -8.5 cal g^{-1}, but after 1–2 months ageing it is only -6.3 cal g^{-1}.

It is therefore clear that only results obtained for materials prepared by means of a defined procedure, which should ensure the equilibrium state of

TABLE 1

Composition of the KCl–KBr solid solutions

Cl^- (wt%)	Br^- (wt%)	Mean value and uncertainty limit (wt%)		mol%		Mole ratio KCl : KBr
		Cl^-	Br^-	KCl	KBr	
12.46	50.07	12.44 ± 0.05	50.12 ± 0.03	35.87	64.13	1 : 1.79
12.48	50.10					
12.40	50.16					
12.50	50.13					
12.36	50.14					
23.89	34.15	23.96 ± 0.05	34.17 ± 0.03	61.25	38.75	1 : 0.63
23.96	34.13					
24.03	34.16					
24.00	34.20					
23.92	34.21					
31.08	23.24	31.17 ± 0.06	23.17 ± 0.06	75.73	24.27	1 : 0.33
31.17	23.22					
31.26	23.14					
31.21	23.20					
31.13	23.06					

the solid phase, are of scientific importance. For these reasons we chose the method of very slow crystallization from melts and long-term ageing [5,8]. We prepared mixed KCl : KBr crystals of molar ratios 1 : 0.33, 1 : 0.63, and 1 : 1.79; the composition of these crystals is reported in Table 1. In order to check the equilibrium of the samples the KCl : KBr = 1 : 1.79 sample was aged for 6 and 15 months at room temperature over freshly dried $CaCO_3$ and its dissolution enthalpy in water measured under the same experimental conditions; values of 175.4 and 174.8 J g^{-1} respectively, were found. The difference in the values for the two samples of ca. 0.6 J g^{-1} lies within the limits of uncertainty of the dissolution measurements under the given conditions and so we can suppose that after 15-months of ageing our samples were virtually in equilibrium.

Another questionable feature of the studied mixed crystals is their solid solutions miscibility. Literature data on phase equilibria in the KCl–KBr–H_2O system have shown that there are two series of solid solutions. A discontinuity in the concentration dependence of the solubility data was confirmed. The phase equilibrium in this system at 25–35 °C was studied by Nikl and Nývlt [15] who concluded that there are two regions of solid solutions in the given system. The same problem was later stated by Bryan and Fitch [16] the results at 35 °C and illustrated as a phase diagram (see Fig. 1). The composition along the path B–D–E is the limiting composition for the formation of a mixture of two solid solutions. Furthermore, Fontell

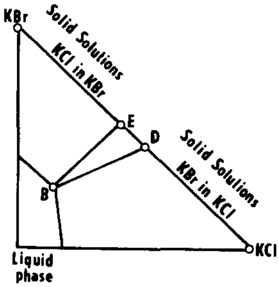

Fig. 1. Phase equilibria of the three-component KCl–KBr–H_2O system at 35 ° C.

[39] found that there is a miscibility gap in the temperature interval 25–120 ° C, and within the concentration region of 0.22–0.55 mole fractions of KCl no continuous solid solutions can be formed. However, the present exhaustive compilations done by Sangster and Pelton [14] and Königsberger [17] state that KCl–KBr solid solutions, prepared from quenched melts and examined by X-ray diffraction at room temperature [3,4], are completely miscible at room temperature. Studies of KCl–KBr melting points reported by Ruff and Plato [40] also showed complete miscibility of the two salts. Havighurst et al. [3] found KCl–KBr systems to be completely miscible and X-ray diffraction patterns recorded after 6-months ageing at room temperature showed the preparations to be unchanged at this time. If we take as our criterion of miscibility the percentage deviation between the lattice constants of the component salts of the solid solutions in question, considering the results of the exhausting systematic study of a large set of systems done by Tobolsky [41], then a value of 4.8% for the KCl–KBr system indicates complete miscibility of these salts at room temperature.

For these reasons we checked our samples by X-ray diffraction analysis to be sure that they did not contain admixed phases. The results are presented in Table 2, in which lattice constants calculated from pure components according to Tobolsky [41] are also given. It can be seen from these results

TABLE 2

Lattice constants of pure KCl and KBr salts and their solid solutions

Substance	Lattice constant ($\times 10^{10}$ m)		
	Exp.	Calc.	Exp. – Calc.
KCl	0.62905 ± 1	0.62905 ± 1	–
KCl–KBr solid solutions			
1 : 0.53 (wt)	0.63618 ± 4	0.63920	−0.00302
1 : 1.01 (wt)	0.64076 ± 5	0.64427	−0.00351
1 : 2.85 (wt)	0.64910 ± 2	0.64934	−0.00024
KBr	0.65949 ± 1	0.65949 ± 1	–

that the lattice parameters of all the solid solutions display a negative deviation from Vegard's law, the largest deviation being for the solid solution of 1 : 1.01 (wt) ratio composition. No superstructural lines are present in the diffractograms and so it can be assumed that there is no local order in the crystal lattices of the prepared mixed KCl–KBr crystals, i.e. the structure of the solid solutions is completely random.

For the equilibrium between a solid and a liquid phase in a common-ion binary alkali halide system with components A and B the integral excess Gibbs (G^{E}) energy can be written as

$$G^{\mathrm{E}} = H^{\mathrm{E}} - TS^{\mathrm{E}} \tag{1}$$

where H^{E} and S^{E} are the excess enthalpy and excess entropy, respectively. It is often supposed that the quantities H^{E} and S^{E} are temperature independent. The experience with alkali halide solutions has shown that the enthalpy term H^{E} is generally much larger than the entropy term TS^{E}. Hence, if available data are limited, it is reasonable to set $S^{\mathrm{E}} = 0$ and to assume that G^{E} is also temperature independent.

For phases of solid solutions with extended ranges of solubility, $H^{\mathrm{E}}(\mathrm{s})$ and $S^{\mathrm{E}}(\mathrm{s})$ may be expanded as polynomials in the mole fractions in the solid phase (s) as follows:

$$H^{\mathrm{E}}(\mathrm{s}) = x_{\mathrm{A}}x_{\mathrm{B}}\left(h_0 + h_1x_{\mathrm{B}} + h_2x_{\mathrm{B}}^2 + \ldots h_ix_{\mathrm{B}}^i\right) \tag{2a}$$

and

$$S^{\mathrm{E}}(\mathrm{s}) = x_{\mathrm{A}}x_{\mathrm{B}}\left(s_0 + s_1x_{\mathrm{B}} + s_2x_{\mathrm{B}}^2 + \ldots s_ix_{\mathrm{B}}^i\right) \tag{2b}$$

where h_i and s_i are empirical coefficients.

For alkali halide systems it is valid, as a general rule, that the larger the cations and the smaller the difference between the radii of the two anions in a common-cation binary system, the more closely the above approximations (one- or two-term polynomial expansions; $S^{\mathrm{E}}(\mathrm{s}) = 0$) are obeyed. If $G^{\mathrm{E}}(\mathrm{s})$ for the solid phase is positive, then there should be a zone of demixing in the solid, which means that a miscibility gap exists.

The partial molar excess Gibbs energies are defined by the following reaction:

$$G^{\mathrm{E}}(\mathrm{s}) = x_{\mathrm{A}}\bar{G}_{\mathrm{A}}^{\mathrm{E}}(\mathrm{s}) + x_{\mathrm{B}}\bar{G}_{\mathrm{B}}^{\mathrm{E}}(\mathrm{s}) \tag{3}$$

$$\bar{G}_{\mathrm{A}}^{\mathrm{E}}(\mathrm{s}) = \bar{H}_{\mathrm{A}}^{\mathrm{E}}(\mathrm{s}) - T\bar{S}_{\mathrm{A}}^{\mathrm{E}}(\mathrm{s}) = RT \ln \gamma_{\mathrm{A}}(\mathrm{s}) \tag{4a}$$

and

$$\bar{G}_{\mathrm{B}}^{\mathrm{E}}(\mathrm{s}) = \bar{H}_{\mathrm{B}}^{\mathrm{E}}(\mathrm{s}) - T\bar{S}_{\mathrm{B}}^{\mathrm{E}}(\mathrm{s}) = RT \ln \gamma_{\mathrm{B}}(\mathrm{s}) \tag{4b}$$

where $\bar{G}_{\mathrm{A}}^{\mathrm{E}}(\mathrm{s})$, $\bar{H}_{\mathrm{A}}^{\mathrm{E}}(\mathrm{s})$, $\bar{S}_{\mathrm{A}}^{\mathrm{E}}(\mathrm{s})$ and $\gamma_{\mathrm{A}}(\mathrm{s})$ are the partial molar excess Gibbs energies, enthalpies, entropies and activities of component A in the solidus, respectively. It is generally true that the activities in the solid phase are higher than those for the liquid equilibrium phase ($\gamma(\mathrm{s}) > \gamma(\mathrm{l})$).

The integral excess enthalpy, $H^{E}(s)$ and the integral excess entropy, $S^{E}(s)$, for the equilibrium state in solid solutions of binary alkali halide systems are equal to the enthalpy or entropy of mixing or formation in the given system. As mentioned in the Introduction, the enthalpy of mixing can be calculated either from lattice parameters or by means of direct calorimetric measurements. The main theories for calculating the enthalpy of mixing for KCl–KBr mixed crystals are Wasastjerna [21] and Hovi's [22] theory, the lattice theory with the Dick and Das model [24], and the Durham and Hawkins theory [38].

It has been proved experimentally that the actual equilibrium positions of the ions in the mixed KCl–KBr crystals do not coincide with the corresponding positions of the ideal crystal lattices. According to the first method, which was theoretically originated by Wasastjerna [21], the lattice of a mixed crystal can be characterized by geometrical long-range disturbances, which are responsible for the mean displacement of all ions in any direction, and by a superimposed local mean displacement which results from the asymmetry among the immediate neighbours of the ions. The author took into account these geometrical displacements and the lattice was assumed to be characterized by a certain degree of local order which maximizes the configurational partition function. His assumptions led to a very satisfactory agreement between theory and experiment for the KCl–KBr mixed crystals. Wasastjerna's theory [21] was simplified by Hovi [22] for the face centred lattice and he calculated the interatomic distances for the KCl–KBr mixed crystals by using Vegard's rule. Hovi used the Born–Mayer–Huggins repulsion energy function [34,38] to determine the positions of ions having minimum potential energy in terms of their displacement from the normal lattice; however, the calculated values often differ significantly from the measured values.

Hence, the theories do not always fit the experimental data perfectly and thus direct calorimetric measurements seem to be the best way to determine the enthalpies of mixing in solid solutions of halide mixed crystals. Such measurements were applied to KCl–KBr systems by Fontell and coworkers [5,10,41,42], Hovi [6], Lister and Meyers [12], Barrett and Wallace [13], Popoff et al. [8] and Ivankina [9] but the samples used in these studies were prepared in different ways and the results are thus scattered.

For these reasons we used the precise calorimetric method to determine the integral dissolution enthalpy of KCl–KBr solid solutions and mechanical mixtures of the corresponding salt components at the same compositions in water at 25 °C. The enthalpy of mixing was then calculated from the difference between these pairs of measurements.

The dissolution enthalpies of pure KCl and KBr salts in water at 25 °C are given in Table 3. The measured values and the values calculated from the recommended literature data are also given in Table 3 for comparison. The

TABLE 3

Experimental data of integral dissolution enthalpy measurements of KCl, KBr and KCl – KBr mixed crystals in water at 25 °C

Sample (mole ratio)	Molality (mol salt/kg H_2O)		Integral dissolution enthalpy, ΔH_m^{in} (J g^{-1})			ΔH_m^{in} (kJ mol^{-1})	$-\Delta H_{mix}$ (kJ mol^{-1})
	KCl	KBr	Results	Average	Calculated value		
KCl	0.3980		233.4	234.7	234.9	17.50	0
	0.3985		234.4				
	0.4006		234.3				
	0.3975		234.2				
	0.3976		235.6				
	0.3982		235.0				
	0.3977		236.2				
	0.3983		235.1				
	0.3992		234.2				
	0.3984		235.0				
Mixture KCl + KBr (1 : 0.33)	0.2631	0.0841	210.8	211.3	213.2	18.03	
	0.2625	0.0843	211.0				
	0.2634	0.0846	211.8				
	0.2632	0.0845	211.7				
	0.2626	0.0842	212.5				
	0.2634	0.0844	211.7				
	0.2634	0.0844	211.8				
	0.2632	0.0844	210.5				
	0.2630	0.0841	210.3				
	0.2643	0.0848	210.5				
KCl–KBr solid solution (1 : 0.33)	0.2591	0.0831	199.9	199.8	213.2	17.05	0.98
	0.2645	0.0848	199.8				
	0.2630	0.0843	199.4				
	0.2638	0.0846	200.2				
	0.2632	0.0844	200.6				
	0.2629	0.0843	199.9				
	0.2632	0.0844	199.3				
	0.2636	0.0845	199.8				
	0.2630	0.0843	199.5				
	0.2621	0.0840	200.0				
Mixture KCl + KBr (1 : 0.63)	0.1983	0.1255	199.0	200.1	202.4	18.37	
	0.1979	0.1252	199.2				
	0.1974	0.1250	200.3				
	0.1978	0.1252	200.3				
	0.1981	0.1253	200.4				
	0.1979	0.1254	200.2				
	0.1977	0.1250	200.1				
	0.1977	0.1251	200.4				
	0.1973	0.1255	199.7				
	0.1977	0.1250	201.0				
	0.1976	0.1252	200.5				

TABLE 3 (continued)

Sample (mole ratio)	Molality (mol salt/kg H_2O)		Integral dissolution enthalpy, ΔH_m^{in} (J g^{-1})			ΔH_m^{in} (kJ mol^{-1})	$-\Delta H_{mix}$ (kJ mol^{-1})
	KCl	KBr	Results	Average	Calculated value		
KCl–KBr solid solution (1:0.63)	0.1980	0.1253	185.5	186.9	202.4	17.15	1.22
	0.1983	0.1255	186.0				
	0.1986	0.1257	185.2				
	0.1983	0.1255	186.8				
	0.1981	0.1253	187.7				
	0.1984	0.1255	187.0				
	0.1985	0.1256	186.3				
	0.1981	0.1254	187.8				
	0.1977	0.1251	187.9				
	0.1979	0.1253	186.8				
	0.1979	0.1253	188.5				
Mixture KCl + KBr (1:1.79)	0.1028	0.1842	184.3	184.1	186.6	18.97	
	0.1033	0.1846	185.3				
	0.1033	0.1847	182.8				
	0.1031	0.1842	184.1				
	0.1034	0.1848	184.6				
	0.1032	0.1844	185.4				
	0.1033	0.1847	181.9				
	0.1032	0.1844	183.9				
	0.1033	0.1845	183.5				
	0.1034	0.1847	185.5				
KCl–KBr solid solution (1:1.79)	0.1035	0.1850	175.6	174.2	186.6	17.95	1.02
	0.1033	0.1846	174.1				
	0.1046	0.1850	174.4				
	0.1035	0.1849	173.6				
	0.1034	0.1849	174.8				
	0.1033	0.1846	173.5				
	0.1029	0.1839	173.4				
	0.1033	0.1846	173.0				
	0.1033	0.1847	174.8				
KBr		0.2489	168.8	168.8	169.0	20.09	0
		0.2505	168.9				
		0.2500	169.2				
		0.2492	168.7				
		0.2500	168.3				
		0.2494	168.7				
		0.2502	166.8				
		0.2487	172.9				
		0.2507	168.2				
		0.2500	167.6				

following equations were used for the calculations [31]:

$$\Delta H^{\text{in}}_{m(\text{KCl})} = 17.228 + 1.741m^{1/2} - 2.493m + 0.759m^{3/2} - 0.0775m^2 \qquad (5a)$$

$$\Delta H^{\text{in}}_{m(\text{KBr})} = 19.879 + 1.732m^{1/2} - 2.974m + 0.946m^{3/2} - 0.111m^2 \qquad (5b)$$

where ΔH^{in} is the integral enthalpy of dissolution.

The dissolution enthalpy of KCl in water was determined with the mean square deviation of ± 0.751 J g^{-1} and differs from the average value of the previously reported findings by about 0.09% only. The dissolution enthalpy of KBr in water was determined with the mean square deviation of ± 1.53 J g^{-1} and differs from the average of the previously reported findings by 0.12%. The very good agreement between the measured and calculated data is independent proof that the measurements made under the given experimental conditions were not affected by any systematic experimental error.

It is worth noting that the scatter of data for the KBr measurements is much higher (see Table 3) than that of the data for KCl. The same was found [43] for the NH_3Br system where a much higher uncertainty in dissolution enthalpies as compared with other salts was found without any satisfactory explanation of this behaviour. These phenomena might be explained to some extent by the lower chemical purity and probable homogeneity of the bromides prepared.

The integral dissolution enthalpies of mixtures of KCl and KBr salts are also presented in Table 3; the mixtures were made in the same molar ratios as the solid solutions of mixed crystals. The measured dissolution enthalpies of the mechanical salt mixtures are compared with the calculated values under the assumption that thermodynamic quantities are ideally additive; i.e. we summed the dissolution enthalpies of the two salts which were calculated for the resulting concentration, using eqns (5a) and (5b). However, the calculated values are all slightly higher than the measured dissolution enthalpies of mechanically mixed salts. The corresponding differences for KCl : KBr molar ratios of 1 : 0.33, 1 : 0.63 and 1 : 1.79 are 0.9, 1.2 and 1.4%, respectively. These deviations from ideal behaviour are small and lie within the limits of experimental uncertainty.

The concentration dependence of the dissolution enthalpies of the mechanical mixtures of KCl and KBr ($\Delta H^{\text{in}}_{\text{mixt.}}$) and the corresponding solid solutions of KCl–KBr mixed crystals ($\Delta H^{\text{in}}_{\text{cryst.}}$) at 25 °C can be expressed by the following cubic correlations

$$\Delta H^{\text{in}}_{\text{mixt.}}(\text{kJ mol}^{-1}) = 20.08944 - 3.693315x_A + 1.919569x_A^2 - 0.817175x_A^3 \qquad (6a)$$

$$\Delta H^{\text{in}}_{\text{cryst.}}(\text{kJ mol}^{-1}) = 20.09033 - 7.302045x_A + 3.138226x_A^2 + 1.574562x_A^3 \qquad (6b)$$

where x_A is the molar fraction of KCl in the salt mixture or solid solution.

TABLE 4

The dependence of the enthalpy of mixing on the molar composition of the KCl–KBr solid solutions

Mole fraction of KCl	Eqn. (6a) $\Delta H^{\text{in}}_{\text{mix}}$ (kJ mol^{-1})	Eqn. (6b) $\Delta H^{\text{in}}_{\text{cryst.}}$ (kJ mol^{-1})	Eqn. (7) $\Delta H^{\text{in}}_{\text{mix}}$ (kJ mol^{-1})	Eqn. (8) $\Delta H^{\text{in}}_{\text{mix}}$ (kJ mol^{-1})	Measured $\Delta H^{\text{in}}_{\text{mix}}$ (kJ mol^{-1})
0	20.09	20.09	0	0	0
0.1	19.74	19.39	0.35	0.35	–
0.2	19.42	18.77	0.65	0.65	–
0.3	19.13	18.23	0.90	0.91	–
0.3587	18.97	17.95	1.02	1.03	1.02
0.4	18.87	17.77	1.10	1.09	–
0.5	18.62	17.42	1.20	1.20	–
0.6	18.39	17.18	1.21	1.21	–
0.6125	18.36	17.16	1.20	1.20	1.22
0.7	18.16	17.06	1.10	1.11	–
0.7573	18.03	17.04	0.99	0.99	0.98
0.8	17.95	17.06	0.89	0.88	–
0.9	17.73	17.21	0.52	0.52	–
1	17.50	17.50	0	0	0

The enthalpies of dissolution of mechanical mixtures of alkali halide salts are higher than those of the corresponding solid solutions. The higher this difference, the larger the potential energy of the solid solution and the weaker the binding of ions in the solid solution lattice [9]. Using our experimental results we calculated the enthalpy of mixing ($\Delta H^{\text{in}}_{\text{mix}}$) as

$$\Delta H^{\text{in}}_{\text{mix}} = \Delta H^{\text{in}}_{\text{mixt.}} - \Delta H^{\text{in}}_{\text{cryst.}} \tag{7}$$

i.e. the difference between the measurements for the mechanically mixed KCl and KBr salts and the true solid solutions at the same molar KCl : KBr ratios. The calculated values of $\Delta H^{\text{in}}_{\text{mix}}$ are presented in Table 4 and in Fig. 2 are compared with the results of other authors.

The plot of the enthalpy of mixing vs. the molar ratio of KCl in the prepared solid KCl–KBr solutions can be described by the cubic function

$$\Delta H^{\text{in}}_{\text{mix}} = 3.605534x_{\text{A}} - 1.215371x_{\text{A}}^2 - 2.392675x_{\text{A}}^3 \tag{8}$$

Note that the enthalpy of mixing of these solid solutions is in general endothermic, i.e. heat is absorbed in their formation. This is in accordance with the fact that the solubility in the solid state of alkali halide mixed crystals usually increases with temperature. For alkali halide pairs which are isomorphous at room temperature, the average enthalpy of mixing for equimolar solid solutions of the family of halides is only about 1.05 kJ mol^{-1} compared with lattice energies of the order of magnitude of 670 kJ mol^{-1} [38].

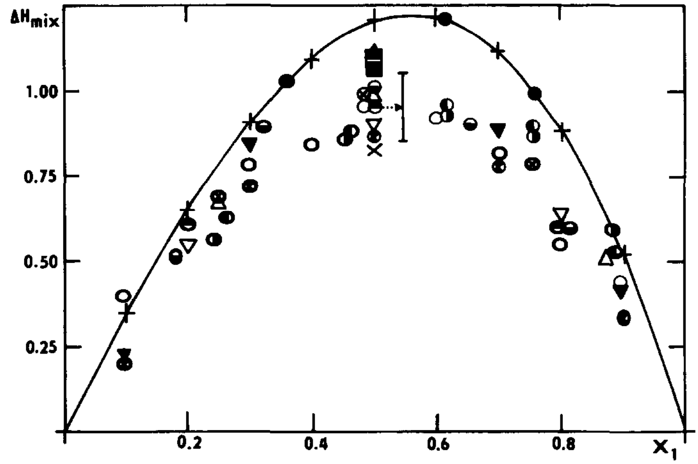

Fig. 2. Plot of the enthalpy of mixing (ΔH_{mix}) vs. the mole fraction of KCl (x_1) in KCl–KBr solid solutions. (+) Calculated values according to the eqns. (6a), (6b) and (7); (●) experimental values, eqn. (7); (×) Vlasov and Makarov [37]; (◑) Hovi [22], calculated values; (◐) Hovi [22], experimental data for samples prepared by crystallization at 20 °C; (⊖) Sangster and Pelton [14], recommended values with the literature experimental scatter I; (⊖) Königsberger and Schrunner [20]; (△) Fontell [5]; (▲) Fontell [5], preparation after 300 h annealing; (▽) Fancher and Barsch [26]; (■, □) Popoff and Jaworowskaya [7] sample after preparation and after 300 h annealing; (▼) Popoff et al. [8]; (○) Ivankina [9]; (⊕) Durham and Hawkins [38]; (⊗) Wallace [34].

According to the extensive literature survey presented by Sangster and Pelton [14], all the calorimetrically determined values of $\Delta H^{\text{in}}_{\text{mix}}$ at 25 °C for KCl–KBr mixed crystals published before 1985 can be represented by the simplified expression which presumes a symmetrical function of the $\Delta H^{\text{in}}_{\text{mix}}$ on the molar composition of the solid phase

$$\Delta H^{\text{in}}_{\text{mix}} = (3.78 \pm 0.40) x_A x_B \text{ kJ mol}^{-1} \qquad (9)$$

The maximum value for $x_A = 0.5$ makes, according to this equation, 0.95 ± 0.10 kJ mol^{-1} (see Fig. 2). Using our experimental results and the same correlation we obtained the equation

$$\Delta H^{\text{in}}_{\text{mix}} = (4.98 \pm 0.45) x_A x_B \text{ kJ mol}^{-1} \qquad (10)$$

If we consider the maximum positive and negative uncertainties for both equations, our findings for $x_A = 0.5$ are still about 0.1 kJ mol^{-1} higher than the published data. However, according to our findings and the results of other authors [8,12,22] the dependence of $\Delta H^{\text{in}}_{\text{mix}}$ on the molar composition of the solid phase is an unsymmetrical function with the maximum value shifted towards the KCl–KBr mixed crystals containing a higher fraction of KCl. A similar asymmetry was also found for the experimentally determined critical parameters of nucleation [18]. This asymmetry is probably due to the fact that small Cl$^-$ is incorporated in the KBr crystal lattice more easily than the larger Br^- anions are incorporated in the KCl crystal lattice. However, these deviations from ideal behaviour by mixing the two components in the KCl–KBr crystal lattice were not detected in the X-ray diffraction analysis.

The excess Gibbs energy of solid solutions of KCl–KBr mixed crystals at 25 °C was derived from the solubilities of the single and mixed salts in aqueous solution and the measured activity coefficients in saturated aqueous solutions [44]

$$G^E(s) = (3.3 \pm 0.2)x_A x_B \text{ kJ mol}^{-1} \tag{11}$$

The equation derived from Knudsen effusion mass spectrometry measurements by Miller and Skudlarski [45] offers a lower value of

$$G^E(s) = (1.9 \pm 0.2)x_A x_B \text{ kJ mol}^{-1} \tag{12}$$

Taking into account these values and our determined enthalpies of mixing we can, according to eqn. (1), calculate the entropic term of mixing. By using eqns. (8) and (11) for a molar fraction of 0.5, $S^E(s) \simeq 0.001$ e.u., which is in agreement with the theoretical assumptions discussed above, i.e. that for this system the entropic term can be neglected because it approaches zero.

Another value for the entropic term of mixing was determined by McCoy and Wallace [44] from the solubility and activity data at 25 °C. The maximum value of the entropy of mixing which includes the vibrational and configurational parts for a KCl mole ratio of 0.5 yielded a much higher value of 6.65 e.u. which is in a poor agreement with the predictions of Wasastjerna's theory [21].

The open question seems to be: Why are our results higher than those published previously? (see Fig. 2). From this picture and from the fact that the absolute value of the enthalpy of mixing increases as the solid phase approaches the equilibrium state, we can suppose that preparations treated by a long ageing procedure (in our case up to 15 months) in order to be as close as possible to the true equilibrium state will have significantly different enthalpy of mixing values. The wide scatter in literature data as seen from Fig. 2 might, therefore, be explained by these phenomena.

REFERENCES

1 A. Bellanca, Period. Mineral., 10 (1939) 9.
2 J.B. Wrzesnewsky, Z. Anorg. Chem., 74 (1912) 95.
3 R.J. Havighurst, E. Mack and F.C. Blake, J. Am. Chem. Soc., 47 (1925) 29.
4 H.L. Link and L.J. Wood, J. Am. Chem. Soc., 62 (1940) 766.
5 N. Fontell, Soc. Sci. Fenn. Comment. Physico-Math., 10 (1940) 1.
6 V. Hovi, Ann. Acad. Sci. Fenn. Ser. A1, 55 (1948) 1.
7 M.M. Popoff and S.F. Jaworowskaya, Z. Phys. Chem., 167A (1933) 180.
8 M.M. Popoff, A. Bundel and W. Choller, Z. Phys. Chem., 147A (1930) 302.

9 M.S. Ivankina, Izv. Tomsk. Politekh. Inst., 95 (1958) 192.
10 N. Fontell, V. Hovi and H. Mikkola, Ann. Acad. Sci. Fenn., Ser. A1, 54 (1948) 1.
11 K. Dencheva, Physico-chemical Properties of Systems Containing Alkali Halides, Thesis, Prague Institute of Chemical Technology, Department of Physical Chemistry, Prague, 1988.
12 M.W. Lister and N.F. Meyers, J. Phys. Chem., 62 (1958) 145.
13 W.T. Barrett and W.E. Wallace, J. Am. Chem. Soc., 76 (1954) 366.
14 J. Sangster and A.D. Pelton, J. Phys. Chem. Ref. Data, 16 (1987) 509.
15 S. Nikl and J. Nývlt, Collect. Czech. Chem. Commun., 41 (1976) 2657.
16 A.L. Bryan and K.M. Fitch, AICHE Symp. Ser., 153 (1978) 72.
17 E. Königsberger, Prediction of phase diagrams from simple mixing models: binary alkali halide systems, Z. Phys. Chem. (1990) in press.
18 K. Papazova-Dencheva, J. Nývlt, V. Pekárek and M. Šípek, Collect. Czech. Chem. Commun., 55 (1990) 1175.
19 S.N. Maity, D. Roy and S. Sengupta, Phys. State Sol. 99(b) (1980) 327.
20 E. Königsberger and H. Schrunner, Phys. State Sol., 151(b) (1989) 101.
21 J.A. Wasastjerna, Soc. Sci. Fenn. Comment. Physico-Math., XV (1949) 1.
22 V. Hovi, Soc. Sci. Fenn. Comment. Physico-Math., XV (1950) 1.
23 V.S. Urusov, Energeticheskaya Kristallokhimiya, (Energetic Crystallochemistry), Nauka, Moscow, 1975.
24 B.G. Dick and T.P. Das, J. Appl. Phys., 33 (1962) 2815.
25 T.B. Douglas, J. Chem. Phys., 45 (1966) 4571.
26 D.L. Fancher and G.R. Barsch, J. Phys. Chem. Solids, 30 (1969) 2503, 2517.
27 S. Hafner, J. Phys. Chem. Solids, 27 (1966) 1881.
28 V.J. Shiner and M.L. Smith, Anal. Chem., 28 (1956) 1043.
29 W. Clark, J. Am. Chem. Soc., 48 (1926) 749.
30 R. Rychlý and V. Pekárek, J. Chem. Thermodynam., 9 (1977) 391.
31 V. Vacek and V. Pekárek, Chem. Průmysl (Prague), 32 (1982) 178.
32 I.T. Stryvalin, O.A. Esin and V.G. Korpachev, Usp. Khim., 35 (1966) 1.
33 V. Hovi, Acta Metal., 4 (1956) 362.
34 W.E. Wallace, J. Chem. Phys., 17 (1949) 1095.
35 G. Tamman and W. Krings, Z. Anorg. Chem., 130 (1923) 229.
36 R. Zemczuznyi and R. Rambach, Z. Anorg. Chem., 65 (1909) 403.
37 J.G. Vlasov and L.L. Makarov, Zhur. Phys. Khim., 41 (1967) 806.
38 G.S. Durham and J.A. Hawkins, J. Chem. Phys., 19 (1957) 149.
39 N. Fontell, Soc. Sci. Fenn. Comment. Phys.-Math., 10 (1940) 1.
40 O. Ruff and W. Plato, Ber. Bunsenges Phys. Chem., 36 (1903) 2357.
41 A.V. Tobolsky, J. Chem. Phys., 10 (1942) 187.
42 N. Fontell, V. Hovi and L. Hyvonen, Ann. Acad. Sci. Fennica, AI(65) (1949) 1.
43 V. Pekárek, V. Vacek, G. Wolf and M. Unterricker, Thermochim. Acta, 113 (1987) 151.
44 W.H. McCoy and W.E. Wallace, J. Am. Chem. Soc., 78 (1956) 5995.
45 M. Miller and K. Skudlarski, Ber. Bunsenges Phys. Chem., 89 (1985) 916.