Heats of melting of some alkali halide solid solutions*

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The heats of melting of some solid solutions were obtained in the following binary systems: KCl—RbCl, KCl—CsCl, and RbCl—CsCl. The results are correlated with the phase diagrams and known thermodynamic properties of the pure salts and of the mixtures.

Были найдены теплоты плавления некоторых твердых растворов в следующих двойных системах: KCl—RbCl, KCl—CsCl и RbCl—CsCl. Результаты сопоставляются с фазовыми диаграммами и известными термодинамическими свойствами отдельных солей и их смесей.

A systematical study [1—3] of the melting heats of binary salts mixtures, initiated in our laboratory, has been extended to alkali halide solid solutions, in order to obtain the experimental values and to study their relations with other thermodynamic properties.

The KCl—RbCl system forms in the solid state a continuous series of solutions without minimum on the phase diagram [4]. For the KCl—CsCl system [4, 5], the phase diagram shows a pronounced minimum at 0.36 mole % KCl and only a slight minimum is observed on the phase diagram of the RbCl—CsCl system at 0.115 mole % RbCl [6].

Experimental

A high-temperature differential calorimeter, calibrated by means of Sb and pure alkali halides using the method already reported [3] was applied. The *Dworkin* and *Bredig*'s values [7] for the heats of melting of alkali halides were used; they satisfy in the best way the sensitivity equation of the calorimeter.

The values chosen for calibration are (kJ mol⁻¹): 19.89 (Sb), 20.235 (CsCl) 23.575 (NaI) 24.00 (KI), 23.70 (RbCl), 25.50 (KBr), 26.08 (NaBr), 26.50 (KCl), 28.00 (NaCl).

The mixtures were prepared by melting together the pure salts, previously dried and melted in the respective acid atmosphere.

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Results and discussion

The experimental results are given in Table 1 and a plot of the heat of melting *vs.* composition is discussed. Every reported value is a result of at least five measurements (mean error $\pm 1.5\%$).

Table 1

Heats of melting of solid solutions

System	x_{KCl}	ΔH_m (exp) kJ mol^{-1}	$\Sigma x_i \, \Delta H_{m,i}$ kJ mol^{-1}
KCl—RbCl	0.25	24.46	24.40
	0.50	24.96	25.10
	0.75	25.08	25.80
KCl—CsCl	0.20	17.80	21.52
	0.36	16.72	22.40
	0.50	17.12	23.38
	0.75	19.23	24.95
	x_{RbCl}		
RbCl—CsCl	0.115	20.98	20.65
	0.25	20.60	21.12
	0.50	20.65	21.97
	0.75	22.47	22.83
	0.85	23.60	23.19

For the KCl—CsCl and RbCl—CsCl systems, the CsCl(II)/CsCl(I) solid transition is included in the heat of formation of the solid solutions; this transition (determined by us as 3.08 kJ mol^{-1}) does not appear before melting for composition with less than 88—89 mole % CsCl in both systems (for mixtures with more than 89 mole % CsCl the fluctuations of the experimental ΔH_m values are higher; the results are not reported here and an extended study of this region is necessary).

As seen from Fig. 1, there is a direct correlation between the shape of the phase diagram and the shape of the ΔH_m values *vs.* composition.

By means of a thermodynamic cycle, a relation can be obtained [3] by which the values of the heats of melting for binary solid solutions can be calculated, if the following thermodynamic properties of the pure salts and of the mixtures are known:

— the heats of melting of the pure components ΔH_A, ΔH_B,
— the heat of formation of the solid solutions ΔH_{ss},
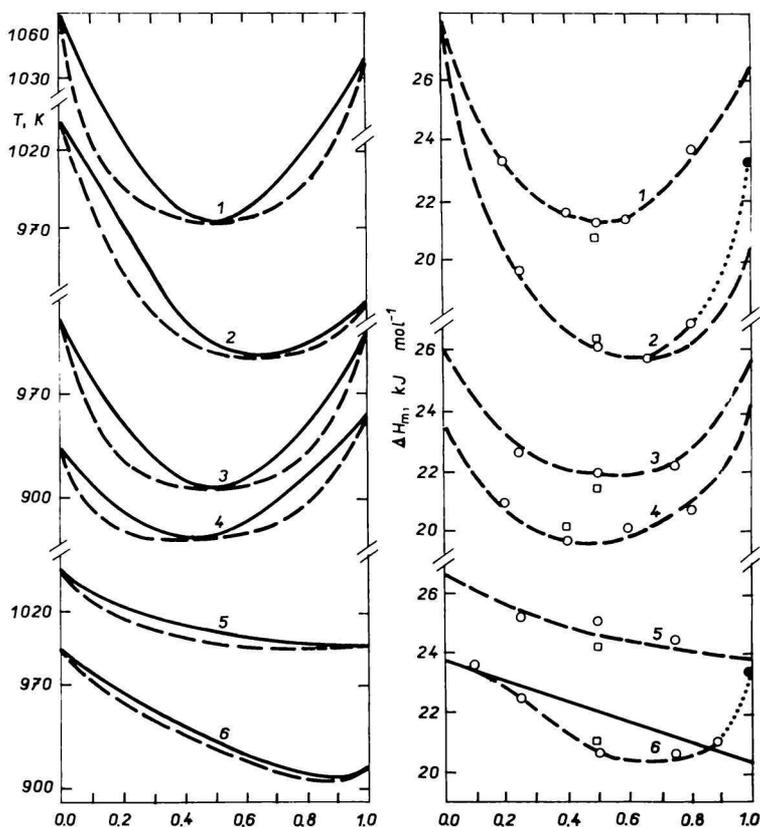— the heat of mixing in the liquid state ΔH_{mix} (*l*),

Fig. 1. Phase diagrams and heats of melting of the solid solutions.
1 NaCl—KCl; 2. KCl—CsCl; 3. NaBr—KBr; 4. NaI—KI; 5. KCl—RbCl; 6. RbCl—CsCl.
□ Calculated values; ○ experimental values; ● $\Delta H_m(CsCl)—\Delta H_{trans}(CsCl)$.

all these values being given at the melting temperature of the solid solution T_{AB}.

As these values are determined experimentally at other temperature, a correction $\Delta H(C_p)$ is necessary for the contribution of the heat capacities.

In this way, the following relation is obtained for the heat of melting, $\Delta H_m(AB)$, of the solid solution AB at T_{AB}

$$\Delta H_m(AB) = x_A \, \Delta H_A(T_A) + x_B \, \Delta H_B(T_B) + \Delta H_{mix} \, (l) \, (T) - \Delta H_{ss}(T_s) + \Delta H(C_P) \,, \tag{1}$$

where $T_s < T_A < T_B < T$; T_s usually 298 K.

In Table 2, the experimental values of $\Delta H_m(AB)$ for equimolar solid solutions are compared with the calculated ones. The ΔH_{ss} values have been determined experimentally [13] only for KCl—RbCl system (at 298 K). We have tried an

approximate evaluation of the heats of melting for KCl—CsCl and RbCl—CsCl equimolar mixtures (ΔH_m(calc)), using the experimental value of ΔH_{mix} (*l*) for KCl(RbCl)—CsCl(I) systems [14], the $\Delta H(C_P)$ calculated [15] for CsCl(I) and approximate values of ΔH_{ss} obtained by means of the plot [12, 13] of known experimental $\Delta H_{ss}^{0.5}$ for other systems of alkali halides *vs.* $(d_1 - d_2)^2/(d_1 + d_2)^3$, where d_1, d_2 are the interatomic distances for the two salts. Based on *Wasastjerna*'s theory [16] on heats of formation of solid solutions, a linear dependence of $\Delta H_{ss}^{0.5}$ (for equimolar mixtures) of the factor $(d_1 - d_2)^2/(d_1 + d_2)^3$ is obtained [13]. For the systems containing CsCl, the lattice parameters of KCl, RbCl [17], and CsCl [18] at 742 K (temperature of transition CsCl(II)/CsCl(I)) have been used; ΔH_{ss} from relation (*1*) for these systems refers to the process of mixing RbCl (or KCl) with CsCl(I). It is to be noticed that the interatomic distances increase with the temperature, but for alkali halides the rate is almost the same [17], so that the difference $d_1 - d_2$ is practically constant.

Table 2

Heats of melting for equimolar mixtures

System	$\Delta H(C_P)$ kJ mol^{-1}	$\Delta H_{ss}^{0.5}$ kJ mol$^-$	$\Delta H_{mix}^{0.5}$ kJ mol$^-$	$\Delta H_m^{0.5}$ (exp) kJ mol^{-1}	$\Delta H_m^{0.5}$ (calc) kJ mol$^-$
KCl—RbCl	−0.16 [8—11]	0.92 [13]	0.08 [15]	24.96	24.20
KCl—CsCl	−2.51 [8—12]	(4.42)* [13, 14]	0.79 [15]	17.12	17.24
RbCl—CsCl	−0.20 [9, 10, 12]	(2.09)* [13, 14]	0.33 [15]	20.65	20.01

* Estimated values.

The heat capacity contributions $\Delta H(C_P)$ were calculated [3] on the assumption

$$C_P^{ss}(AB) = x_A C_{P.A}^S + x_B C_{P.B}^S \quad \text{and} \quad C_P^l(AB) = x_A C_{P.A}^l + x_B C_{P.B}^l$$

i.e. for the heat capacities of the solid solutions and of the liquid mixtures, the values calculated additively from the heat capacities of components have been used. For a wide temperature range the errors in the calculated $\Delta H(C_P)$ are high, due to the different reported values of C_P for pure salts [8—12].

Conclusion

As seen from Fig. 1, where the heat of melting *vs.* composition plots for different systems (including the NaX—KX systems where X = Cl, Br, I) of alkali halide solid

solutions are given in connection with the phase diagrams, there is a direct correlation between the shapes of the two kind of plots.

In a theoretical explanation of the values of heats of melting two directions are to be searched: the temperature of melting and the entropy of melting. The alkali halides must have a simple mechanism of melting (it was well described as rigid sphere melting [19] or as the increase of configurational energy [20]).

The melting entropy for a mixture of alkali halides is very close to the additive value, *i.e.* the magnitude of the $\Delta H_m(AB)$ value is practically determined by the value of melting temperature. In fact, the rigid sphere description of a molten alkali halide [19] supports a $\Delta H_m \sim T_m$ relation.

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