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Note

On the heat of formation of Rb(Br,I) and Cs(Br,I) solid solutions

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INTRODUCTION

Theoretical investigations on the heat of formation of binary alkali halide solid solutions cover a great range of mixed crystals[1-3]. On the other hand, although calorimetric measurements have been made for many of these[4-10], the experimental results for binary systems Rb(Br, I) and Cs(Br, I) are not found in literature. In this work a study has been made to determine the heat of formation for these two mixed crystals near the equimolar composition range.

EXPERIMENTAL

The simple dropping-type differential solution calorimeter used in the measurements is basically the same described earlier[11]. Modifications done in recording the temperature differences when dissolving the mixed crystal and reference salt are given elsewhere[12]. The reagents used for measurements are given in Table I. Solid solutions of Rb(Br, I) and Cs(Br, I) were prepared by melting suitable amounts of dried components in a platinum crucible and homogenizied at 400°C over night. The quenched samples were then ground at room temperature and specimens of 0.03 mole were stored at 110°C [Rb(Br, I)] and 400°C [Cs(Br, I)] in lightly sealed glass ampoules

TABLE I

REAGENTS MADE BY MERCK AG (DARMSTADT, GERMANY) WITH CATALOG NUMBERS

Rubidium bromide, Suprapur	7626
Rubidium iodide, Suprapur	7619
Cesium bromide, Suprapur	2860
Cesium iodide, Suprapur	2861
Potassium chloride, G.R.	4936[a]
Potassium iodide, neutral G.R.	5043[b]

[a]Used for calibration. [b]Used for calibration and as reference salt.

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in order to avoid the decomposition due to the humidity if cooled below the critical solution temperature[13,14]. Mixed crystals were held at room temperature in a desiccator for some hours before the dissolving. The Cs(Br, I) solid solutions were measured against the corresponding mixture, but for Rb(Br, I) measurements 0.03 mole of potassium iodide was used as reference salt. Calibration of the temperature differences obtained was done by dissolving 0.06 and 0.03 mole KI against the same amount of potassium chloride using heat of solution values taken from literature[11,15]. The experimental results for the enthalpy difference of the dissolving process of Rb(Br, I) solid solution with respect to potassium iodide and the heat of formation of Cs(Br, I) measured are given in Table II.

TABLE II

THE ENTHALPY DIFFERENCE OF SOLUTION $\delta\Delta H$ OF Rb(Br,I) MIXED CRYSTALS AND POTASSIUM IODIDE, AND THE HEAT OF FORMATION ΔU OF Cs(Br,I) SOLID SOLUTIONS (in cal mole^{-1}), AS A FUNCTION OF THE BROMIDE MOLE FRACTION $12x_{\text{Br}}$

$12x_{\text{Br}}$	$\delta\Delta H\,[Rb(Br,I)-KI]$	$\Delta U\,[Cs(Br,I)]$
0	1253	
4	737; 705	[illegible]; 396
5	607; 638	472; 480
6	544; 518; 500	[illegible]8; 528; 533
6.021		516
7	481; 504	575; 586
7.231	459	
8	420; 439	511; 500
12	481	

RESULTS AND DISCUSSION

The heat of formation $\Delta U(x)$ as a function of the mole fraction x for the Rb(Br, I) system is calculated simply

$$\Delta U(x) = x\delta\Delta H(1) + (1-x)\delta\Delta H(0) - \delta\Delta H(x). \tag{1}$$

The mean value for the equimolar heat of formation with the estimated errors is 330±35 and 525±25 cal mole^{-1} for mixed crystals Rb(Br, I) and Cs(Br, I), respectively. The indirectly measured, less accurate value of the rubidium halide system is in fair agreement[1,3] with calculated values from 380 to 465 cal mole^{-1}. The experimental method used in this work is not particularly suitable for Rb(Br, I), where the difference in the measured differential solution enthalpy, $1253-481 = 772$ cal mole^{-1}, of the pure substances versus the reference salt, is about twice the derived value for heat of formation 330 cal mole^{-1}. A more precise direct measurement of the differential heat of solution of the equimolar solid solution and the corresponding mixture is necessary; this is planned in future. The theoretically found result 469 cal mole^{-1} is about[13] 11±5% smaller than the experimentally measured one for Cs(Br, I) mixed crystal, which is of same order as earlier found relative deviation in another cesium chloride type binary system[2,7] Cs(Cl, Br). A possible explanation for this deviation is given by Hietala[2].

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