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Heat Capacity of Solid Halide Eutectics and Their Enthalpy at Melting Point

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Abstract: The isobaric heat capacity of solid eutectic mixtures LiCl-KCl-CsCl, LiBr-CsBr and LiBr-KBr-CsBr was investigated from room temperature up to melting point. The molar heat capacity of all mixtures under study was found to be close to the additive sum of that of pure salts. The heat accumulated up to melting temperature is directly dependent on the melting point.

Keywords: alkali halides eutectics; heat capacity; enthalpy; melting temperature

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1. Introduction

Eutectic mixtures comprising halide salts are used as phase-change materials. The melting temperatures of eutectics are much lower than those of pure salts [1]. Low temperatures have certain advantages including a low vapour pressure in molten state and low corrosion activity.

It makes halide eutectics very attractive for use in solar energy production [2–6] or power sources [7]. Heat capacity is very important since it indicates the amount of energy that a given system can possess under certain conditions.

Heat capacity has been shown to be temperature independent in a molten state according to many studies [8–11], but in solids, the heat capacity rises with temperature. There are scarce data on the heat capacity of solid eutectic halide mixtures. FLINAK, a well-known eutectic mixture was measured in a solid state [12,13].

The aim of the present research was to investigate the heat capacity of the solid halide eutectic mixtures within temperature interval from room temperature up to melting point. The study was focused on the mixtures with melting temperatures below 600 K.

2. Materials and Methods

Alkali halide salts classified as "chemically pure" (99.5% of main substance) were used for mixture preparation. Lithium chloride was provided by FMC (UK), caesium salts were from Vekton, Russia. and lithium and potassium bromides were from Reachim, Russia. Chloride salts were purified by zone melting [14,15]. LiBr was purified from moisture and other admixtures through double recrystallization from anhydrous acetonitrile solution with additional treatment with molecular sieves. KBr and CsBr were purified from moisture by stepwise with vacuum drying. The detailed procedure was given in our previous work [1]. The mixtures prepared were subjected to thermal and gravimetric analysis in order to verify the melting temperature and sample mass stability. The samples were homogenous, and the melting temperature difference was within 5 degrees. The compositions of eutectic mixtures are given in Table 1.

Table 1. Compositions and melting points.

Molar Composition	Melting Point, K [1]	Molar Weight
0.575 LiCl–0.165 KCl–0.26 CsCl	541	78.6
0.62 LiBr–0.38 CsBr	556	134.7
0.561 LiBr–0.189 KBr–0.25 CsBr	510	124.45

The study of heat capacity was carried out on the samples of the prepared mixtures using the STA 449C Jupiter synchronous thermal analyser (NETZSCH). The experiments were carried out under the following conditions: heating rate 10K/min; argon atmosphere; and Pt–Rh crucibles with a perforated lid. The heat capacity was determined in three stages: first stage—measurement of the base curve when the crucibles were empty; second stage—measurement with a standard sample (sapphire); and final stage—measurement with test sample. The detailed description of the experimental procedure has been described elsewhere [1]. The uncertainty of heat capacity determination was 5%.

3. Results and Discussion

The heat capacity of solid eutectic mixtures under investigation is given in Table 2 according to temperature.

Table 2. Heat capacity of solid eutectics.

LiCl-KCl-CsCl		LiBr-CsBr		LiBr-KBr-CsBr	
T,K	Cp, J mole^{-1}	T,K	Cp, J mole^{-1}	T,K	Cp, J mole^{-1}
303	48.3	348	51.2	316	49.8
323	50.7	358	51.2	326	49.8
333	49.1	368	52.5	336	50.4
341	50.5	378	53.9	346	50.4
350	51.7	388	53.9	356	51.0
359	52.3	398	53.9	366	51.0
370	52.3	408	52.5	376	51.0
380	53.1	428	51.2	386	51.0
390	53.1	438	52.5	396	51.0
400	52.3	448	52.5	406	51.6
410	52.3	458	52.5	416	51.6
420	53.8	468	52.5	426	52.3
430	53.6	478	52.5	436	52.3
440	53.1	488	53.9	446	52.3
450	52.3	498	53.9	456	53.5
460	51.5	508	53.9	466	53.5
470	52.3	518	53.9	476	54.8
		528	55.2	481	54.8
		538	57.9		

The isobaric heat capacities of solid eutectic mixtures were measured up to melting temperature.

The results for LiCl-KCl-CsCl are shown in Figure 1. The calculation of molar heat capacity according to the Neumann–Kopp rule [16,17] is also presented as Cp mixture = ∑Cp component salt.

The usage of this rule for halide salt mixtures can be justified by the similarity of the halide salts' thermodynamic properties [18]. The experimental and calculated values were in good agreement. The pure salt data were taken from the available literature [8,19]. Experimental and calculated data were used for the calculation of the enthalpy accumulated by eutectic mixture up to the melting temperature. Calculation of the integral (by the standard trapezoid method [20]) from the LSQM-line produced a value of 21.9 kJ mole^{-1} for LiCl-KCl-CsCl. The accuracy of the calculations was approximately ±7.5%.

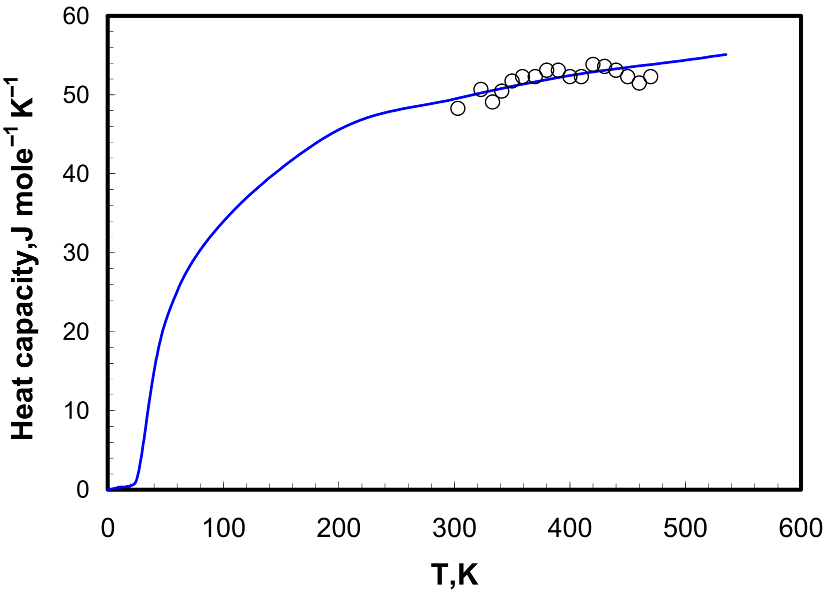

Figure 1. Heat capacity of LiCl-KCl-CsCl solid eutectic. ○—our data, line—values calculated according to the additive law based on the data available from the literature [8,19].

Molten bromide eutectics possess certain advantages in comparison with chloride systems, primarily, due to lower temperatures. For this reason, they were also interesting subjects for study. The isobaric heat capacities of solid eutectic mixtures LiBr-KBr and LiBr-KBr-CsBr were measured up to melting point.

The heat capacities of the bromide eutectics being investigated are shown in Figures 2 and 3. The enthalpy of samples was calculated for bromide eutectics for premelting temperature. Calculation of the integral gave the value of 21.4 kJ mole^{-1} for LiBr-KBr-CsBr and 23.95 kJ mole^{-1} for LiBr-CsBr. Comparison of enthalpy and melting temperature indicated their dependency. The data for eutectic mixtures can be considered as a derivative of pure salts and, thus, they have the same dependency as that of individual salts. The results for eutectic mixtures are given in Table 3 and Figure 4. The enthalpy and melting points of chloride, bromide, and iodide salts were taken from literature [21] and are shown in Table 4 and Figure 4.

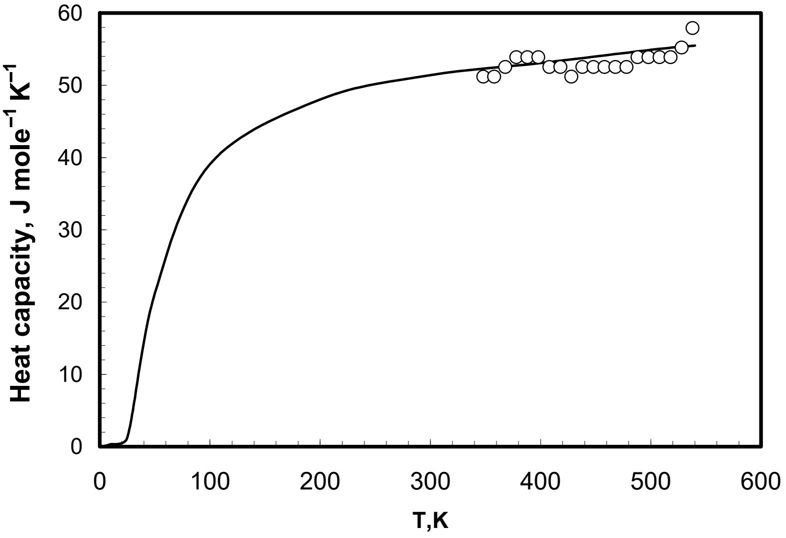

Figure 2. Heat capacity of the solid LiBr-CsBr eutectic mixture. ○—our data, line—values calculated according to additive law using literature data [8,19].

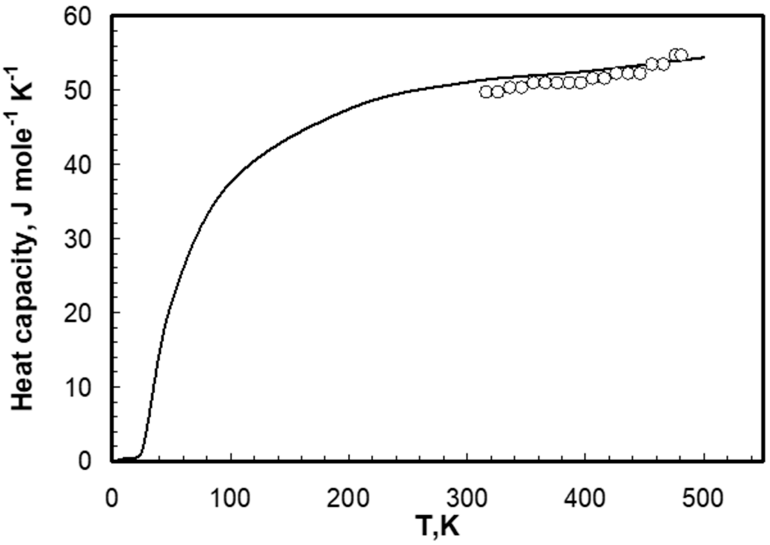

Figure 3. Heat capacity of solid the LiBr-KBr-CsBr eutectic mixture. ○—our data, line—values calculated according to additive law using literature data [8,19].

Table 3. Melting points and enthalpy before the melting of the eutectics.

Molar Composition	Melting Point, K [1]	Enthalpy at Melting Point kJ/mole
0.575 LiCl–0.165 KCl–0.26 CsCl	541	21.90
0.62 LiBr–0.38 CsBr	556	23.95
0.561 LiBr–0.189 KBr–0.25 CsBr	510	21.40

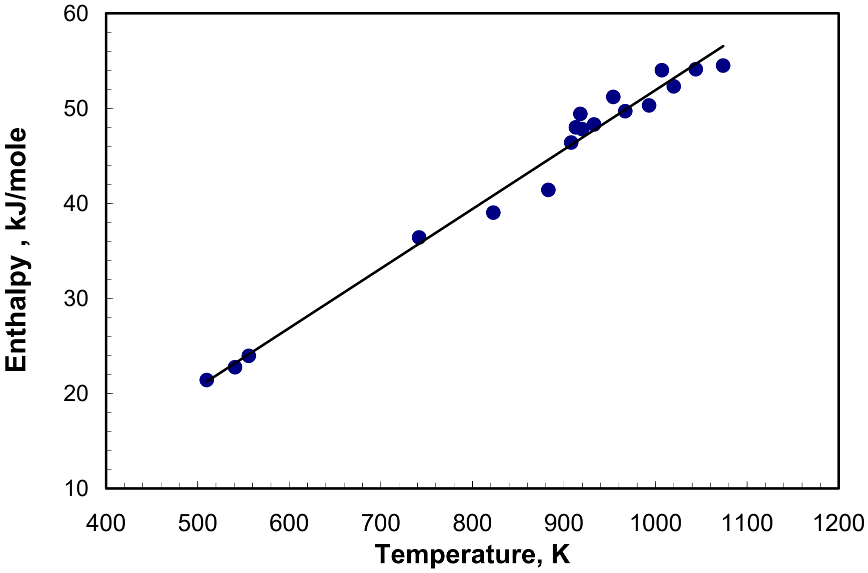

Figure 4. Enthalpy of salts and eutectics before melting versus melting point.

The fitting was carried out by two mathematical methods: LSQM and the interval method. LSQM is well known and provides reliable fitting parameters of data under treatment, but it gives only the maximal (by modulus) bounds $e_{\max}$ of measuring errors. Consequently, the parameters calculated by the standard least square method (LSQM) gives too broad an uncertainty interval. Under given conditions of uncertainty, interval analysis methods [22,23] give the guaranteed estimates of parameters (the information sets) which defines the area of possible values of property under investigation.

Table 4. Enthalpy (H) of solid halide salts before melting point (T_m) [17].

Salt	T_m, K	H, kJ mole^{-1}	Salt	T_m, K	H, kJ mole^{-1}
LiCl	883	41.4	KBr	1007	54.0
NaCl	1074	54.5	RbBr	967	49.7
KCl	1044	54.1	CsBr	908	46.4
RbCl	993	50.3	LiI	742	36.4
CsCl	918	49.4	NaI	933	48.3
LiBr	823	39.0	KI	954	51.2
NaBr	1020	52.3	RbI	920	47.8
			CsI	913	48.0

The fitting line was as follows: H (T) = A × T + B, where H is the enthalpy of the solid eutectic near melting point, T is the melting temperature, and A and B are the empirical coefficients.

The results of data treatment are shown in Figures 5 and 6. Figure 5 demonstrates the information set (the possible values of coefficients A and B). According to interval analysis, the minimal coefficient B is 5.48 × 10^{-2} kJ mole^{-1} K^{-1}, which relates to the maximal coefficient A equal to 23.9 KJ mole^{-1}. Maximal coefficient B is 6.95 × 10^{-2} kJ mole^{-1} K^{-1}, which relates to 18.3 kJ mole^{-1}. The optimal coefficients correspond to the central point (A_{cnt} = 6.22 × 10^{-2} kJ mole^{-1} K^{-1}, B_{cnt} = 21.169 kJ mole^{-1}). The results of LSQM are close (A = 6.26 × 10^{-2} kJ mole^{-1} K^{-1}, B = 21.208 kJ mole^{-1}).

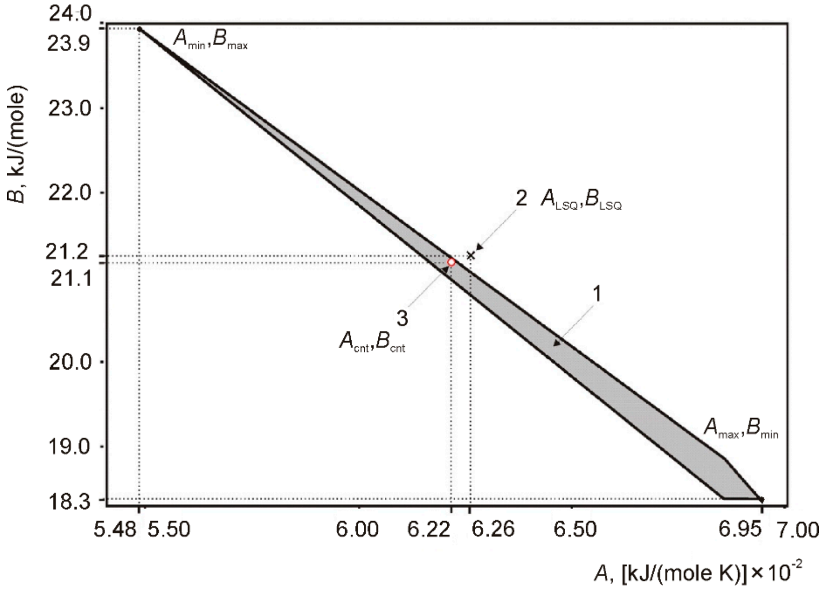

Figure 5. Results of estimation of admissible values of parameters for the approximation function H (T) = A × T + B. (1) Information set; (2) LSQM—estimate A_{LSQ}, B_{LSQ}; (3) central point A_{cnt} and B_{cnt} of the information set. Grey area is an area of possibleA and B coefficientsts according interval analysis, red circle is a point of fiiting coefficients related to to LSQM.

These results were related to the temperature interval 510–1074, and the constants were related to 510 K. At recalculating to zero point by temperature, the equation is as follows: LSQM results:

$$A_{\text{LSQ}} = 6.26 \times 10^{-2}\ \text{kJ mole}^{-1}\ \text{K}^{-1},\ B_{\text{LSQ}} = -10.655\ \text{kJ mole}^{-1}$$

The results of estimation on the basis of the interval approach are the following:

$$A_{\text{cnt}} = 6.22 \times 10^{-2}\ \text{kJ mole}^{-1}\ \text{K}^{-1},\ B_{\text{cnt}} = -10.718\ \text{J mole}^{-1}$$

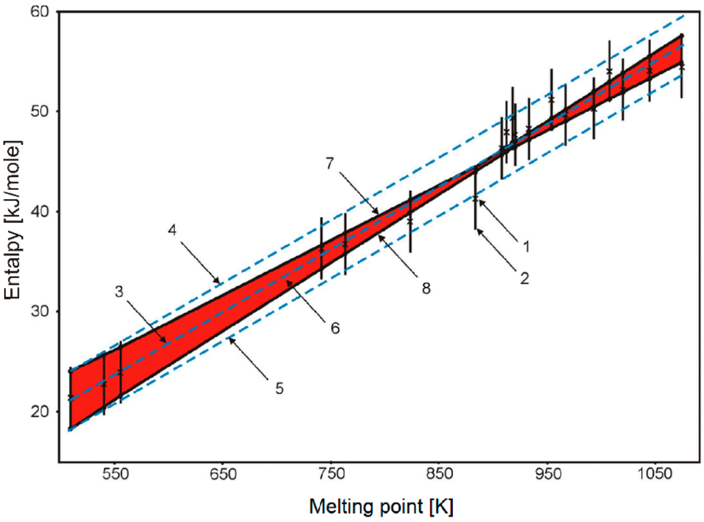

Figure 6. Input data and results of their processing.(1) measurements; (2) uncertainty interval H_n of each measurement; (3) line of the LSQM—approximation; (4,5) boundaries "+2σ" and "–2σ" of the LSQM—admissible curves of the process; (6) the tube of admissible curves according to the interval approach estimation; (7,8) the upper and lower boundaries of admissible curves according to interval approach estimation. Red area is an area of possible fitting lines according to interval analysis.

The results obtained demonstrated the independence of fitting results from the treatment method.

Thus, the amount of heat accumulated by solid halide eutectic mixtures up to melting point can be described by the following linear equation:

$$H = 62.2 \times T_m - 10.718 \text{ J mole}^{-1}$$

The enthalpy of the melting of halide eutectics is also dependent on the melting point [24] according to the following formula:

$$H = 38 \times T_\mathrm{m} - 11.220 \text{ J mole}^{-1},$$

where H is enthalpy of fusion, and T_m is melting point.

Thus, it is possible to calculate the amount of energy accumulated by salt or eutectic mixture before and just after melting as follows (Figure 7):

$$H = 98.6 \times T_\mathrm{m} - 21.855 \text{ J mole}^{-1}$$

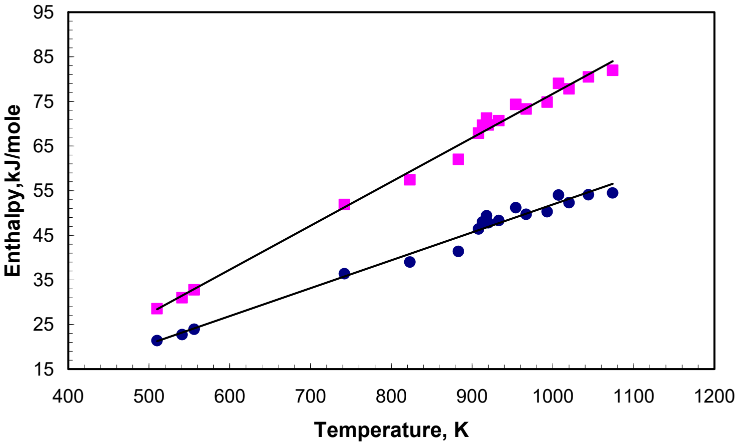

Figure 7. Enthalpy of salts and mixtures before (navy) and after melting (magenta).

This is the heat that the system possesses just after melting. This equation allows for the estimation of the amount of heat that the eutectic mixture can accumulate for heat storage.

4. Conclusions

1. The molar heat capacity of all mixtures under study was found to be close to the additive sum of that of pure salts.
2. The enthalpy of the solid eutectic mixtures closes to melting temperature was directly dependent on the melting point.
3. The results obtained allow for the estimation of the amount of energy that the eutectic mixture can accumulate for storage.

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Conflicts of Interest: The authors declare no conflict of interest.

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