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Thermodynamic Properties of AgCl and AgBr

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Temperatures and enthalpies of fusion as well as the heat capacity of silver chloride and silver bromide were measured by differential scanning calorimetry. A polynomial heat capacity dependence on temperature was used to fit the experimental data. The thermodynamic functions of AgCl and AgBr were calculated by combining these heat capacity results with the entropy at 298.15 K, temperatures, and enthalpies of fusion.

Introduction

Ionic transport properties of silver halides have attracted special attention for a long time.[1–11] There were two main questions concerning the understanding of experimental results on these materials. The first, what is the mechanism of ion transport in each of these compounds, and the second, how does ionic conduction relate to other physical properties. The motivation for studying these compounds is their challenging physics and application potential in the areas of batteries, electrochemical sensors, fuel cells, and electrochemical devices.

It was found that an unusually high increase of ionic conductivity of AgCl and AgBr with temperature is the result of Frenkel-defects formation.[1–5] Some Ag^+ ions leave their lattice sites and occupy interstitial sites inside the crystal. Two disorder centers (vacancy and interstitial ion) are formed per misplaced lattice ion.[1] The experimental methods most commonly used for testing disorder models and for the quantitative determination of disorder data are conductivity, diffusion measurements, and heat capacity measurements. The increase in the intrinsic disorder in the crystal lattice with rising temperature means that more energy is required, and this in turn increases the heat content of the crystal. The heat capacity must therefore contain a component due to the change in disorder with temperature.

The only existing numerical heat capacity data on AgCl and AgBr, which could be helpful in disordering interpretation, are the data of Pankratz[12] and Kubaschewski.[13] However, they show big discrepancies. In addition, graphical data that were published[4,5] for AgBr differ significantly from those of Pankratz and Kubaschewski. Thus, precise heat capacity measurements for both the solid and liquid phase of AgCl and AgBr would be of considerable interest. Therefore, we have decided to undertake the investigation of thermodynamic properties of these compounds. The present work reports thermodynamic properties (temperatures and enthalpies of fusion as well as heat capacity $C^0_{p,\mathrm{m}}$) of silver chloride and bromide.

Table 1. Temperatures and Enthalpies of Fusion of AgCl and AgBr Compounds

compound	T_{fus}/K	$\Delta_{\mathrm{fus}}H_{\mathrm{m}}$/kJ·mol^{-1}	ref
AgCl	736	13.16 ± 0.32	this work
AgCl	730	12.3	12
AgCl	728	13.2	13
AgCl	728	−	19
AgBr	695	7.92 ± 0.27	this work
AgBr	700	8.5	12
AgBr	700	13.0	13
AgBr	695	−	5
AgBr	693	−	19

Experimental

Chemicals. Silver halides (AgCl and AgBr) were Merck Suprapur reagent grade (min. 99.9 %). Prior to use, they were progressively heated to fusion under a gaseous HX atmosphere (X = Cl or Br, respectively). HX in excess was then removed from the melt by argon bubbling.

All chemicals were handled in an argon glovebox with a measured volume fraction of water of about $2 \cdot 10^{-6}$ and continuous gas purification by forced recirculation through external molecular sieves. Due to the sensitivity of silver halides to UV-light, all preparation procedures were performed under red light.

Measurements. The temperatures and enthalpies of AgCl and AgBr fusion were measured with a Setaram DSC 121 differential scanning calorimeter. The apparatus and the measurement procedure were described previously.[14,15] Samples of (300 to 500) mg were contained in quartz ampoules (about 6 mm diameter, 15 mm length) sealed under reduced pressure of argon. The sidewalls of ampoules were grounded to fit the cells snugly into the heat flow detector. Experiments were conducted at heating and cooling rates of 5 K·min^{-1}. Temperatures and enthalpies of phase transitions were determined as mean values from two to three measurements performed on three different samples of each compound. The error on temperature determination did not exceed ± 1 K. The standard error on enthalpy determination is presented in Table 1 together with experimental results.

Heat capacity was measured with the same Setaram DSC 121 operated in a stepwise mode. This so-called "step method" has been described[16–18] previously. The same operating conditions (i.e., initial and final temperatures, temperature increment,

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isothermal delay, and heating rate) were used in all experimental series. Experimental monitoring, data acquisition, and processing were performed with the Setaram Setsys software.

As mentioned previously[18] the Setaram DSC 121 apparatus was calibrated by the Joule effect, and some test measurements were performed separately with NIST 720 α-Al_2O_3 Standard Reference material prior to investigation. These tests resulted in $C_{p,\mathrm{m}}$ values consistent with standard data for Al_2O_3 (difference less than 1.5 %), with the exception on the temperature range (300 to 370) K, in which measured values were significantly larger. The vaporization of moisture condensed from air on the external grounded sidewalls of ampoules used in measurements may be given as a tentative explanation of discrepancies in this temperature range. Accordingly, the results of measurements in the temperature range (300 to 370) K were not taken into account in the polynomial fitting of experimental data.

In the present heat capacity experiments, each 5 K heating step was followed by a 400 s isothermal delay. The heating rate was 1.5 $K\cdot min^{-1}$. Experiments were performed in the (300 to 920) K and (300 to 750) K temperature ranges for AgCl and AgBr, respectively. The mass difference of the quartz cells in any individual experiment did not exceed 1 mg (cell mass: (400 to 500) mg). To establish the repeatability and uncertainty of the results, three different samples of each compound were used in the measurements. All these results were used in calculation of coefficients in the equation describing the temperature dependence of heat capacity as well as the standard deviation on $C^0_{p,\mathrm{m}}$. The maximal deviations of individual series from mean values did not exceed ± 3 %.

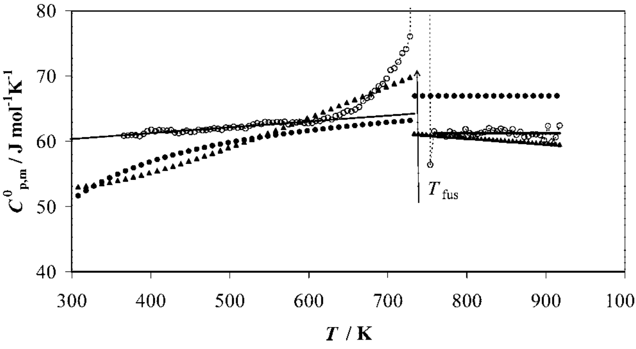

Figure 1. Molar heat capacity $C^0_{p,\mathrm{m}}$ of AgCl: open circles and broken line, mean values from experimental results; solid lines, linear fitting of experimental results; black triangles, literature data;[12] black circles, literature data.[13]

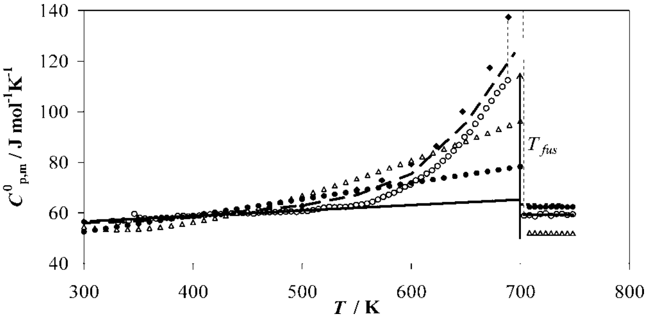

Figure 2. Molar heat capacity $C^0_{p,\mathrm{m}}$ of AgBr: open circles and thin broken line, mean values from experimental results; solid lines, linear fitting of experimental results; open triangles, literature data;[12] black circles, literature data;[13] black diamonds, literature data;[4] thick broken lines, literature data.[5]

Results and Discussion

Temperature and Enthalpy of Fusion. In all DSC curves, both for AgCl and AgBr, only one peak corresponding to compound fusion was observed. The experimental temperatures and enthalpies of fusion are presented in Table 1 together with literature data. Our fusion temperature 736 K for AgCl is slightly higher than that measured by Pankratz[12] and reported by Kubaschewski,[13] who did not however quote the origin of their data. The melting enthalpy of AgCl was found in excellent agreement with Kubachewski's reported value,[13] again with no details of its source, whereas Pankratz's[12] experimental result is smaller by about 6 %. Our fusion temperature of AgBr is about 5 K lower than the Pankratz[12] and Kubaschewski[13] data but agrees very well with other literature data[5,19] obtained by drop calorimetry and differential scanning calorimetry. Fusion enthalpy data given by Kubaschewski (13 $kJ\cdot mol^{-1}$) differs significantly from our and Pankratz's values [(7.9 and 8.5) $kJ\cdot mol^{-1}$, respectively].

Heat Capacity. Experimental heat capacity data (mean values from measurements performed on three different samples) on AgCl and AgBr are plotted against temperature in Figures 1 and 2 together with existing literature data. It should be noted that some literature data on AgBr included in Figure 2, inaccessible in the form of numerical values, were determined graphically from figures in the appropriate references.[4,5]

We found that the heat capacity of AgCl (Figure 1) varies linearly with temperature up to about 629 K with a standard deviation of 1.66 $J\cdot mol^{-1}\cdot K^{-1}$. From 629 K, a rapid rise in heat capacity with temperature starts to appear. A second-order polynomial was used to represent the heat capacity dependence on temperature (standard error of estimation 2.12 $J\cdot mol^{-1}\cdot K^{-1}$). A constant heat capacity value, $C^0_{p,\mathrm{m}} = (61.23 \pm 2.26)$ $J\cdot mol^{-1}\cdot K^{-1}$, was found for liquid AgCl. This value is smaller by 9 % than that given by Kubaschewski,[13] but it is in good agreement with the data of Pankratz.[12] However, it should be pointed out that we did not find any dependence of heat capacity on temperature for the liquid phase, as was found by Pankratz by drop calorimetry.

Similar results were obtained for AgBr (Figure 2). For this compound too, heat capacity varies linearly with temperature up to 500 K (standard error of estimation 1.15 $J\cdot mol^{-1}\cdot K^{-1}$), and subsequently, a rapid quasiexponential increase is observed up to the melting point. The dependence of heat capacity on temperature in the higher temperature range [(500 to 695) K] is described by a third-order polynomial, with a standard error of estimation of 2.37 $J\cdot mol^{-1}\cdot K^{-1}$. A constant heat capacity value $C^0_{p,\mathrm{m}} = (59.25 \pm 2.46)$ $J\cdot mol^{-1}\cdot K^{-1}$ was found for liquid AgBr. This time a better agreement was found with the data of Kubaschewski[13] and Jost and Kubaschewski[5] [(62.3 and 63.3) $J\cdot mol^{-1}\cdot K^{-1}$]. Values of heat capacity given by Pankratz[13] are significantly smaller (about 52.1 $J\cdot mol^{-1}\cdot K^{-1}$ at 728 K), and a decrease of heat capacity of the AgBr liquid phase was found as for AgCl.

The rapid rise in heat capacity of solid AgCl and AgBr is presumably associated with the energy absorbed in the creation of lattice defects. If temperature evolution of heat capacity in a perfect crystal lattice is taken as a reference to a "normal" behavior, $C^0_{p,\mathrm{m}}$ data are related to the heat of activation for both the formation of defects and their number at any temperature. The increase of the disorder in the crystal lattice with rising temperature means that more energy is required, and this in turn increases the heat content of the crystal. The heat capacity must therefore contain a component due to the change in disorder with temperature. Silver chloride and silver bromide are well-known examples of compounds with predominant

Table 2. Thermodynamic Functions of Silver Halides: Values of *A*, *B*, *C*, *D*, *E*, *F*, and *I* parameters in Equations 1, 3, 5, and 7

	temp. range	A	$B\cdot10^3$	$C\cdot10^4$	$D\cdot10^6$	E	F	I
compd	K	$J\cdot mol^{-1}\cdot K^{-1}$	$J\cdot mol^{-1}\cdot K^{-2}$	$J\cdot mol^{-1}\cdot K^{-3}$	$J\cdot mol^{-1}\cdot K^{-4}$	$J\cdot mol^{-1}$	$J\cdot mol^{-1}\cdot K^{-1}$	$J\cdot mol^{-1}\cdot K^{-1}$
$AgCl_{(s)}$	298 to 629	57.67 ± 0.22	8.933 ± 0.439	–	–	−17591 ± 85	−235.04 ± 1.38	−292.71 ± 1.60
$AgCl_{(s)}$	629 to 736	420.97 ± 21.15	−1166.23 ± 63.394	9.500 ± 0.474	–	−92440 ± 4556	−2024.94 ± 105.50	−2445.91 ± 126.66
$AgCl_{(l)}$	736 to 1000	61.23 ± 2.26	–	–	–	−4132 ± 282	−233.38 ± 5.93	−294.61 ± 6.93
$AgBr_{(s)}$	298 to 500	50.12 ± 0.53	21.577 ± 1.237	–	–	−15902 ± 213	−190.30 ± 3.39	−240.42 ± 3.92
$AgBr_{(s)}$	500 to 700	−535.0. ± 82.88	3732.65 ± 428.10	−78.098 ± 7.330	5.45637 ± 0.41610	−52936 ± 12214	2339.46 ± 376.33	2874.48 ± 459.28
$AgBr_{(l)}$	700 to 1000	59.25 ± 0.42	–	–	–	−6340 ± 174	−219.40 ± 1.84	−278.64 ± 2.28

Table 3. Thermodynamic Functions of AgCl at Selected Temperatures from (298.15 to 1000) K

T	$C^0_{p,m}(T)$	$S^0_{p,m}(T)$	$-(G^0_{p,m}(T) - H^0_m(298.15\ K))/T$	$H^0_m(T) - H^0_m(298.15\ K)$
K	$J\cdot mol^{-1}\cdot K^{-1}$	$J\cdot mol^{-1}\cdot K^{-1}$	$J\cdot mol^{-1}\cdot K^{-1}$	$kJ\cdot mol^{-1}$
298.15	60.33	96.20	96.20	0.00
300	60.35	96.57	96.20	0.11
400	61.24	114.06	98.58	6.19
500	62.14	127.82	103.10	12.36
600	63.03	139.23	108.20	18.62
629	63.29	142.21	109.70	20.45
629	63.29	142.21	109.70	20.45
700	70.11	149.25	113.35	25.13
736	77.23	152.93	115.20	27.77
736	61.23	170.81	115.20	40.93
800	61.23	175.92	119.85	44.85
900	61.23	183.13	126.49	50.97
1000	61.23	189.58	192.48	57.10

Table 4. Thermodynamic Functions of AgBr at Selected Temperatures from (298.15 to 800) K

T	$C^0_{p,m}(T)$	$S^0_{p,m}(T)$	$-(G^0_{p,m}(T) - H^0_m(298.15\ K))/T$	$H^0_m(T) - H^0_m(298.15\ K)$
K	$J\cdot mol^{-1}\cdot K^{-1}$	$J\cdot mol^{-1}\cdot K^{-1}$	$J\cdot mol^{-1}\cdot K^{-1}$	$kJ\cdot mol^{-1}$
298.15	56.55	101.70	101.70	0.00
300	56.59	102.05	101.70	0.10
400	58.75	118.63	103.95	5.87
500	60.91	131.97	108.26	11.86
500	60.91	131.97	108.26	11.86
600	71.62	143.66	113.19	18.28
695	118.57	156.94	118.21	26.92
695	59.25	168.33	118.21	34.84
700	59.25	168.75	118.57	35.13
800	59.25	176.66	125.34	41.06

Frenkel disorder of the cations in the crystal lattice.[1–9] A significant disorder in these compounds[4,5,9–11] appears at temperatures about (100 to 200) K lower than the melting temperatures, which is in excellent agreement with our heat capacity experimental results.

The comparison of these results with literature data (Figures 1 and 2) leads to the conclusion that both the Kubaschewski[13] and Pankratz[12] data are incorrect. Kubaschewski values for solid AgCl show an almost linear increase of heat capacity at high temperature [(500 to 728) K] and therefore do not suggest any excess heat capacity related to lattice defect formation. Kubaschewski[13] reported an extended linearity range for heat capacity of AgBr, also with no evidence of defect formation. On the other hand, the data of Pankratz[12] are incorrect too. These data suggest the possibility of disordering starting at ambient temperature, which has not been reported in the literature[4,5,9–11] nor found in the course of our experimental determinations. Also, heat capacity evolution when approaching the AgCl and AgBr melting temperature seems inconsistent with a widely accepted premelting disorder. In the case of silver bromide, our experimental results agree quite well with the data of Christy and Lawson[4] and Jost and Kubaschewski.[5] This agreement is excellent up to 450 K. Beyond, those values are larger by about 10 % and 6 %, respectively. The latter data were obtained by drop calorimetry, whereas the former ones by a pseudocalorimetric device (apparatus for obtaining comparative heating rates of various samples using identical power inputs). However, it should be pointed out that all three heat capacity vs temperature plots are almost the same, as could be expected from thermally activated defect formation.

Thermodynamic Functions. Due to a significant rise in heat capacity, a third-order polynomial heat capacity dependence on temperature

$$C^0_{p,m}/J\cdot mol^{-1}K^{-1} = A + B\cdot(T/K) + C\cdot(T/K)^2 + D\cdot(T/K)^3 \quad (1)$$

was used to fit the experimental data. The coefficients A, B, and C in eq 1 are collected in Table 2. The $C^0_{p,m} = f(T)$ equation was then used to calculate enthalpy increments $H^0_m(T) - H^0_m(298.15\ K)$ in $J\cdot mol^{-1}$, entropy $S^0_m(T)$, and Gibbs energy functions $-(G^0_m(T) - H^0_m(298.15))/T$ in $J\cdot mol^{-1}\cdot K^{-1}$ for both the solid and the liquid phase of the compounds under investigation

$$H^0_m(T) = H^0_m(298.15) + \int C^0{}_{p,m}dT \quad (2)$$

$$H^0_m(T) - H^0_m(298.15) = A\cdot T + 1/2\cdot B\cdot T^2 + 1/3\cdot C\cdot T^3 + 1/4\cdot D\cdot T^4 + E \quad (3)$$

$$S^0_m(T) = S^0_m(298.15) + \int \frac{C^0_{p,m}}{T}dT \quad (4)$$

$$S^0_m(T) = A\cdot \ln T + B\cdot T + 1/2\cdot C\cdot T^2 + 1/3\cdot D\cdot T^3 + F \quad (5)$$

$$-(G^0_m(T) - H^0_m(298.15))/T = A\cdot \ln T + 1/2\cdot B\cdot T + 1/6\cdot C\cdot T^2 + 1/12\cdot D\cdot T^3 - E\cdot T^{-1} + I \quad (6)$$

The parameters E, F, and I in the above equations were calculated by setting T = 298.15 K into eqs 3, 5, and 6. They are also presented in Table 2. Our experimental melting (transition) temperatures and enthalpies were used together with heat capacity data in this calculation. We determined heat capacity values $C^0_{p,m}$(s, 298.15 K) for both compounds by extrapolation of experimental results to 298.15 K (Tables 3 and 4). The values of entropy at 298.15 K also necessary in these calculations were taken from the literature.[13] These standard entropies were (96.2 and 101.7) $J\cdot mol^{-1}\cdot K^{-1}$ for AgCl and AgBr, respectively. The calculated values of thermodynamic functions are presented at selected temperatures in Tables 3 and 4.

Summary

The temperatures and enthalpies of fusion as well as heat capacities of solid and liquid AgCl and AgBr were determined. These data were used to calculate the whole set of thermodynamic functions for solid and liquid silver chloride and bromide. An unusual, quasiexponential rise in heat capacity was observed in both AgCl and AgBr when approaching the melting temperature. This rise results from disordering of the cationic sublattice (predominant Frenkel defect formation).

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