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# Thermodynamic Functions of Definite Compounds Formed in $EuBr_2-MBr$ Binary Systems ($M = K, Rb$)

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Several compounds are formed in the $EuBr_2-KBr$ and $EuBr_2-RbBr$ binary systems. Their enthalpies of phase transitions and heat capacity were measured by differential scanning calorimetry. A polynomial heat capacity dependence on temperature was used to fit the experimental data. Through combination of these results with the entropy at 298.15 K, and enthalpies of phase transitions, the thermodynamic functions were calculated up to $T = 1100$ K.

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## Introduction

Due to their specific electronic configurations ($4f^n6s^2$ or $4f^{n-1}5d^16s^2$), lanthanide atoms tend to lose three electrons, usually one from 4f and two from 6s or one from 5d (if exists) and two from 6s, to attain their most stable oxidation state as trivalent ions. Thus, both in solution and in the solid state, the lanthanides adopt predominantly the +3 oxidation state. However, there are some exceptions when lanthanides form stable compounds with the oxidation state +4 or +2. Generally, the existence of these oxidation states is connected with not-filled ($Ce^{4+}$), half-filled ($Tb^{4+}$, $Eu^{2+}$), or full-filled ($Yb^{2+}$) 4f subshell. When filling a subshell, the electrons will half-fill with their spins parallel before pairing two electrons in the same orbital. This gives rise to a lower energy. Since electrons have the same charge, they will repel one another and will tend to occupy different orbitals to get far away from one another. Therefore, half-filling before pairing is to be expected. One of the conclusions of quantum mechanics is that as an electron occupies larger regions in space (is less confined) its kinetic energy decreases. An electron with the same spin can exchange places and thus occupy larger regions in space. This phenomenon is called spin exchange. The greater the number of spin exchanges possible, the lower the energy. Therefore, the electrons will tend to have their spins oriented parallel to one another. This is the reason for the stability of half-filled subshells, and such a situation takes place in the case of europium(II) compounds (half-filled 4f subshell). Accordingly, +2 is the predominant oxidation state of europium. Indeed, the compounds of Eu(II) are more stable than those of Eu(III) ($4f^6$ electronic structure).

**Table 1. Temperatures and Molar Enthalpies of Phase Transitions of Definite Compounds Existing in the $EuBr_2-MBr$ Binary Systems ($M = K, Rb$)**

| compound | $\frac{T_{form}}{K}$ | $\frac{\Delta_{trs}H_m}{kJ\cdot mol^{-1}}$ | $\frac{T_{trs}}{K}$ | $\frac{\Delta_{trs}H_m}{kJ\cdot mol^{-1}}$ | $\frac{T_{fus}}{K}$ | $\frac{\Delta_{fus}H_m}{kJ\cdot mol^{-1}}$ |
|---|---|---|---|---|---|---|
| $K_2EuBr_4$ | – | – | – | – | 834 | 30.3 ± 0.7 |
| $KEu_2Br_5$ | – | – | – | – | 880 | 60.2 ± 0.9 |
| $Rb_2EuBr_4$ | – | – | – | – | 776[a] | 40.9 ± 0.8 |
| $RbEu_2Br_5$ | – | – | – | – | 888 | 70.6 ± 1.2 |
| $RbEuBr_3$ | 633 | | 732 | 12.6 ± 0.3 | 852[b] | – |

[a] Decomposes peritectically. [b] Melts incongruently.

A substantial amount of thermochemical data have been reported on europium dichloride, but as with the trihalides, only few values were available for europium dibromide.[1–6] Available thermodynamic data on europium(II) bromide, i.e., temperature and enthalpy of fusion,[1,2,4] entropy at 298 K, and enthalpy of formation of solid $EuBr_2$ at 298 K,[5,6] were estimated values. A heat capacity of solid and liquid europium(II) bromide[6] was derived from vaporization experiments. As estimations are sometimes misleading, direct measurements of thermodynamic properties were thought to be of considerable interest. No information on $EuBr_2-MBr$ ($M =$ alkali metal) binary systems, which are interesting due to their luminescence properties, was found in the literature. Therefore, we decided to undertake the investigation of thermodynamic and transport properties of both pure $EuBr_2$ as well as $EuBr_2-MBr$ binary mixtures. Previously,[7] we have determined experimentally the temperature and enthalpy of fusion and the heat capacity of solid and liquid $EuBr_2$. These data were further used in thermodynamic functions calculation. The phase diagrams of $EuBr_2-LiBr$, $EuBr_2-NaBr$, $EuBr_2-KBr$, and $EuBr_2-RbBr$ binary systems and the electrical conductivity of the same liquid mixtures were also reported.[8–11] Following these previous investigations, the present work is focused on the thermodynamic properties of definite compounds that are formed in the europium(II) bromide−potassium bromide and europium(II) bromide−rubidium bromide binary systems. Temperatures and enthalpies of phase transitions as well as heat capacity ($C^0_{p,m}$) of these compounds are reported.

## Experimental

***Chemicals.*** Europium(II) bromide was synthesized from the oxide $Eu_2O_3$ (Aldrich 99.9 %) by a modified Haschke and Eick method.[12] Its chemical analysis was performed by mercurimetric (bromine) and complexometric (europium) methods. The results

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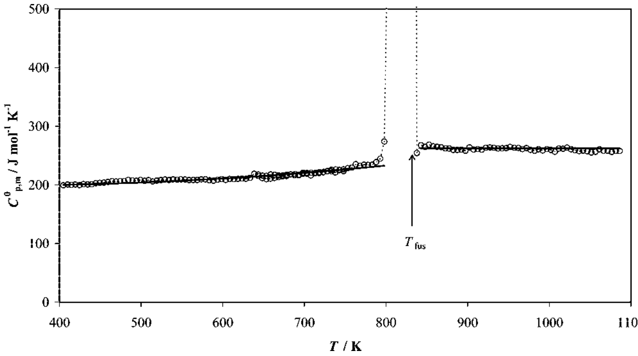

**Figure 1.** Molar heat capacity $C^0_{p,m}$ of $K_2EuBr_4$: open circles and broken line, mean value from experimental results; solid lines, polynomial fitting of experimental results.

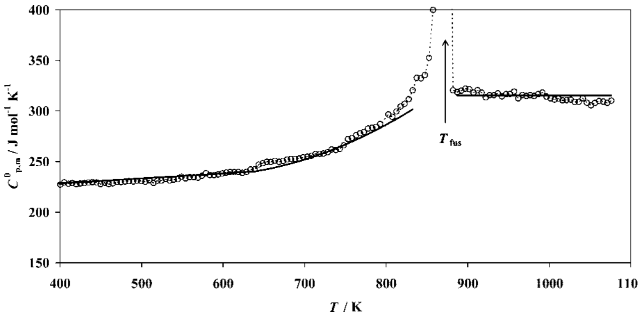

**Figure 2.** Molar heat capacity $C^0_{p,m}$ of $KEu_2Br_5$: open circles and broken line, mean value from experimental results; solid lines, polynomial fitting of experimental results.

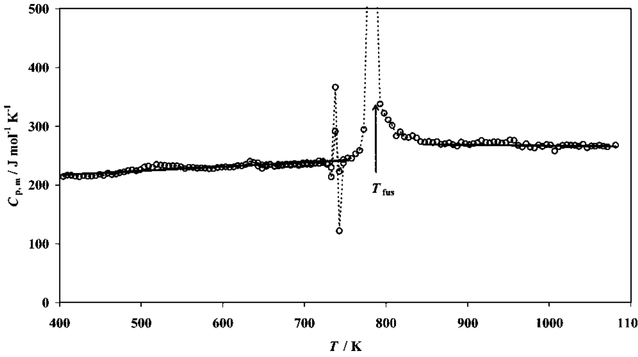

**Figure 3.** Molar heat capacity $C^0_{p,m}$ of $Rb_2EuBr_4$: open circles and broken line, mean values from experimental results; solid lines, polynomial fitting of experimental results.

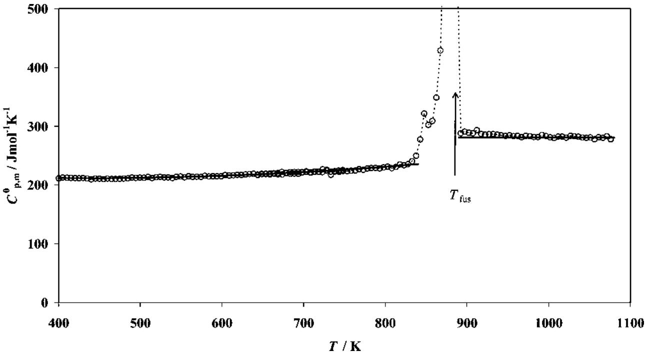

**Figure 4.** Molar heat capacity $C^0_{p,m}$ of $RbEu_2Br_5$: open circles and broken line, mean values from experimental results; solid lines, polynomial fitting of experimental results.

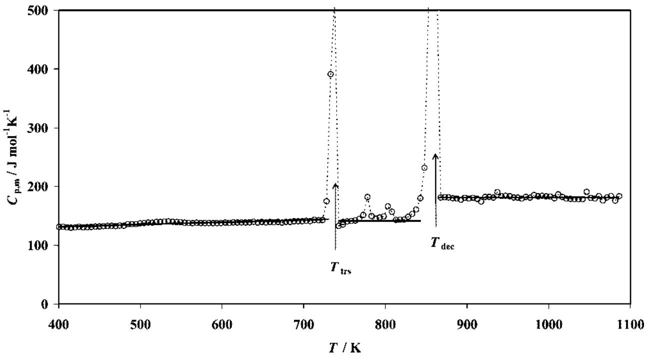

**Figure 5.** Molar heat capacity $C^0_{p,m}$ of $RbEuBr_3$: open circles and broken line, mean values from experimental results; solid lines, polynomial fitting of experimental results.

are as follows: Eu, 48.74 % found, 48.75 % calcd; Br, 51.26 % found, 51.25 % calcd.

Potassium and rubidium bromides were Merck Suprapur reagents (min. 99.9 %). Before use, they were progressively heated to fusion under a gaseous HBr atmosphere. An excess of HBr was then removed from the melt by argon bubbling.

The five stoichiometric compounds formed in the $EuBr_2-KBr$ and $EuBr_2-RbBr$ binary systems were prepared from $EuBr_2$ and MBr (M = K or Rb), which were weighed in appropriate molar ratio. All the mixtures were prepared in a glovebox filled with purified and water-free argon. Although only a small amount of samples were used for the differential scanning calorimetry (DSC) experiments (300 to 500) mg several grams of each compound were synthesized to avoid deviation from stoichiometry. Stoichiometric mixtures of bromides were melted in vacuum-sealed quartz ampoules in an electric furnace. Melts were homogenized by shaking and solidified. These samples were ground in an agate mortar in a glovebox. 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. The purity of the compounds prepared in this way is defined from that of the starting compounds $EuBr_2$ (Eu, 48.74 % found, 48.75 % calcd; Br, 51.26 % found, 51.25 % calcd) and MBr (Merck Suprapur reagents, min. 99.9 %). Their stoichiometry was controlled by DSC measurements. Only thermal effects related to phase transitions were observed in the corresponding DSC thermograms, and no other thermal effects which could have resulted from nonstoichiometry were observed, which confirmed the suitability of the method for compound preparation.

***Measurements.*** The temperatures and enthalpies of the phase transitions of definite compounds existing in the $EuBr_2-MBr$ (M = K, Rb) systems, namely, $K_2EuBr_4$, $KEu_2Br_5$, $Rb_2EuBr_4$, $RbEuBr_3$, and $RbEu_2Br_5$, were measured with a Setaram DSC 121 differential scanning calorimeter. The apparatus and the measurement procedure have been described in detail previously.[13,14] Samples of (300 to 500) mg were contained in quartz ampoules (about 6 mm diameter, 15 mm length) sealed under a reduced pressure of argon. The sidewalls of the ampoules were grounded to fit the cells snugly into the heat flow detector. Experiments were conducted at 5 $K \cdot min^{-1}$ heating and cooling rates. Temperatures and enthalpies of phase transitions were determined as mean values from 2 to 3 sets of measurements performed on at least three different samples of each compound (prepared from different batches). The error on temperature determination was within ± 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

**Table 2. Thermodynamic Functions of Definite Compounds from the $EuBr_2$−MBr Binary Systems (M = K, Rb): Values of *A*, *B*, *C*, *D*, *E*, and *F* parameters in Equations 1, 3, 5, and 7**

| | temp. range | $A$ | $B \cdot 10^2$ | $C \cdot 10^4$ | SE of $C^0_{p,\mathrm{m}}$ | $D$ | $E$ | $F$ |
|---|---|---|---|---|---|---|---|---|
| compound | K | $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$ | $\mathrm{J \cdot mol^{-1} \cdot K^{-2}}$ | $\mathrm{J \cdot mol^{-1} \cdot K^{-3}}$ | $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$ | $\mathrm{J \cdot mol^{-1}}$ | $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$ | $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$ |
| $K_2EuBr_{4(s)}$ | 298 to 834 | 211.37 ± 8.13 | −8.449 ± 2.889 | 1.3921 ± 0.2486 | 5.98 | −60494 ± 1359 | −853.50 ± 38.81 | −1064.87 ± 46.94 |
| $K_2EuBr_{4(l)}$ | 834 to 1100 | 262.28 ± 13.00 | – | – | 13.00 | −75090 ± 9930 | −1181.62 ± 86.14 | −1443.90 ± 99.14 |
| $KEu_2Br_{5(s)}$ | 298 to 638 | 208.66 ± 1.34 | 4.925 ± 0.263 | – | 4.83 | −64400 ± 520 | −813.25 ± 8.41 | −1021.90 ± 9.77 |
| $KEu_2Br_{5(s)}$ | 638 to 880 | 537.09 ± 56.87 | −106.470 ± 16.487 | 9.3913 ± 1.1880 | 11.47 | −128520 ± 12150 | −2414.80 ± 232.27 | −2951.88 ± 341.23 |
| $KEu_2Br_{5(l)}$ | 880 to 1100 | 317.10 ± 15.42 | – | – | 15.42 | −73620 ± 14270 | −1428.14 ± 89.76 | −1745.23 ± 140.53 |
| $Rb_2EuBr_{4(s)}$ | 298 to 776 | 188.38 ± 7.26 | 7.129 ± 1.249 | – | 6.31 | −59330 ± 2720 | −737.17 ± 45.09 | −925.54 ± 52.34 |
| $Rb_2EuBr_{4(l)}$ | 776 to 1100 | 269.42 ± 11.90 | – | – | 11.90 | −59870 ± 1730 | −1168.42 ± 65.20 | −1437.82 ± 77.10 |
| $RbEu_2Br_{5(s)}$ | 298 to 888 | 238.15 ± 9.56 | −12.229 ± 3.297 | 1.4190 ± 0.2749 | 7.56 | −66820 ± 1630 | −923.63 ± 45.86 | −1161.77 ± 55.43 |
| $RbEu_2Br_{5(l)}$ | 888 to 1100 | 280.75 ± 4.53 | – | – | 4.43 | −49100 ± 3750 | −1185.94 ± 22.81 | −1466.67 ± 34.70 |
| $RbEuBr_{3(s)}$ | 298 to 732 | 116.04 ± 1.29 | 3.866 ± 0.224 | – | 5.63 | −36320 ± 480 | −428.97 ± 8.00 | −545.02 ± 2.93 |
| $RbEuBr_{3(s)}$ | 732 to 852 | 141.52 ± 6.27 | – | – | 6.27 | −32050 ± 3200 | −551.57 ± 38.78 | −693.11 ± 37.80 |

been described[15–17] earlier. Experimental monitoring, data acquisition, and processing were performed with the Setaram Setsys software.

The 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 an exception in the temperature range (300 to 400) K, in which the measured values were significantly larger. The vaporization of the air moisture, condensed on the external grounded sidewalls of ampoules used in the measurements, can be given as a tentative explanation of this phenomenon. Results of measurements in this temperature range were not taken into account in the polynomial fitting of experimental results.

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·min$^{-1}$. All experiments were performed in the (300 to 1100) K temperature range. 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, prepared from different batches, were used in measurements.

## Results and Discussion

***Enthalpy of Phase Transitions.*** It was found previously[10] that two congruently melting compounds, namely, $K_2EuBr_4$, and $KEu_2Br_5$, exist in the $EuBr_2$−KBr binary system. They melt at the temperatures (834 and 880) K, respectively. The existence of another compound, $KEuBr_3$, which forms at higher temperatures and decomposes peritectically, was also postulated,[10] but it must be confirmed by high-temperature X-ray measurements. Three compounds, $Rb_2EuBr_4$, $RbEuBr_3$, and $RbEu_2Br_5$, were found to exist in the $EuBr_2$−RbBr binary system.[11] The first one melts peritectically at 776 K, whereas the third one melts congruently at 888 K. The $RbEuBr_3$ compound forms at high temperature (633 K) from $Rb_2EuBr_4$ and $RbEu_2Br_5$, undergoes a solid–solid phase transition at 732 K, and melts incongruently at 852 K. However, during cooling, its decomposition was not observed (probably due to kinetic reason), and a metastable phase of $RbEuBr_3$ was maintained at ambient temperature instead. A similar phenomenon was observed by Fink and Seifert[18] for the $RbEuCl_3$ compound that exists in the chloride system. The temperatures and enthalpies of phase transitions occurring in all compounds under investigation are collected in Table 1.

***Heat Capacity.*** All the heat capacity data were obtained for the first time in this work. They were used to calculate the coefficients in eq 1 describing the dependence of heat capacity $C^0_{p,\mathrm{m}}$ on temperature as well as their standard deviation. All the results (not mean values) for three different samples of each compound, prepared from different batches, were used in this calculation.

The polynomial heat capacity dependence on temperature

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

was fitted to experimental data for all the compounds under investigation. However, because of the strong $C_p$ increase when approaching phase transition or melting, only those data corresponding to a smooth heat capacity dependence on temperature were used.

These experimental heat capacity values (mean values from measurements performed on three different samples) for $K_2EuBr_4$, $KEu_2Br_5$, $Rb_2EuBr_4$, $RbEu_2Br_5$, and $RbEuBr_3$ are plotted against temperature in Figures 1, 2, 3, 4, and 5, respectively. Our conclusion about the proper stoichiometry of compounds from DSC tests (lack of additional thermal effects resulting from nonstoichiometry) was generally confirmed by heat capacity measurements. However, a small deviation from stoichiometry (not noticeable on DSC curves) was evidenced for $Rb_2EuBr_4$. Accordingly, a change in heat capacity was observed at about 740 K for this compound (Figure 3). The coefficients in eq 1 and the standard deviations of the fitting are presented in Table 2 for all the compounds. Once again, it should be pointed out that all experimental results (not mean

**Table 3. Thermodynamic Functions of $K_2EuBr_4$ at Selected Temperatures from (298.15 to 1100) K**

| $T$ | $C^0_{p,\mathrm{m}}(T)$ | $S^0_{\mathrm{m}}(T)$ | $-(G^0_{\mathrm{m}}(T) - H^0_{\mathrm{m}}(298.15\ \mathrm{K}))/T$ | $H^0_{\mathrm{m}}(T) - H^0_{\mathrm{m}}(298.15\ \mathrm{K})$ |
|---|---|---|---|---|
| K | $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$ | $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$ | $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$ | $\mathrm{kJ \cdot mol^{-1}}$ |
| 298.150 | 198.55 | 331.80 | 331.80 | 0.00 |
| 300 | 198.55 | 333.02 | 331.80 | 0.37 |
| 400 | 199.85 | 390.25 | 339.59 | 20.26 |
| 500 | 203.92 | 435.24 | 354.38 | 40.43 |
| 600 | 210.79 | 472.98 | 371.08 | 61.14 |
| 700 | 220.43 | 506.16 | 388.05 | 82.68 |
| 800 | 232.87 | 536.38 | 404.73 | 105.32 |
| 834 | 237.73 | 546.17 | 410.29 | 113.32 |
| 834 | 262.28 | 582.54 | 410.29 | 143.65 |
| 900 | 262.28 | 602.51 | 423.67 | 160.96 |
| 1000 | 262.28 | 630.15 | 442.96 | 187.19 |
| 1100 | 262.28 | 655.14 | 461.13 | 213.42 |

**Table 4. Thermodynamic Functions of $KEu_2Br_5$ at Selected Temperatures from (298.15 to 1100) K**

| $T$ | $C^0_{p,\mathrm{m}}(T)$ | $S^0_{\mathrm{m}}(T)$ | $-(G^0_{\mathrm{m}}(T) - H^0_{\mathrm{m}}$ (298.15 K))/$T$ | $H^0_{\mathrm{m}}(T) - H^0_{\mathrm{m}}$ (298.15 K) |
|---|---|---|---|---|
| K | $\mathrm{J\cdot mol^{-1}\cdot K^{-1}}$ | $\mathrm{J\cdot mol^{-1}\cdot K^{-1}}$ | $\mathrm{J\cdot mol^{-1}\cdot K^{-1}}$ | $\mathrm{kJ\cdot mol^{-1}}$ |
| 298.150 | 223.34 | 390.30 | 390.30 | 0.00 |
| 300 | 223.44 | 391.68 | 390.31 | 0.41 |
| 400 | 228.36 | 456.63 | 399.13 | 23.00 |
| 500 | 233.29 | 508.12 | 415.95 | 46.09 |
| 600 | 238.21 | 551.09 | 434.99 | 69.66 |
| 638 | 240.08 | 565.77 | 442.35 | 78.75 |
| 638 | 240.08 | 565.77 | 442.35 | 78.75 |
| 700 | 251.98 | 588.52 | 454.30 | 93.97 |
| 800 | 286.37 | 624.21 | 473.31 | 120.73 |
| 880 | 327.42 | 653.33 | 488.34 | 145.20 |
| 880 | 317.10 | 721.77 | 488.34 | 205.43 |
| 900 | 317.10 | 728.90 | 493.61 | 211.77 |
| 1000 | 317.10 | 762.31 | 518.84 | 243.48 |
| 1100 | 317.10 | 792.53 | 542.37 | 275.19 |

values) were used in this calculation for three different samples of each compound, prepared from different batches.

In the case of $RbEuBr_3$, due to incongruent melting, only the heat capacity of solid phases could be determined. The heat capacity measurements performed on $RbEuBr_3$ confirmed our conclusion about the formation of a metastable phase at ambient temperature. Indeed, no thermal accident was observed on the heat capacity vs temperature curve at the temperature corresponding to the compound formation (633 K).

***Thermodynamic Functions.*** Equation 1 was then used to calculate enthalpy increments $H^0_{\mathrm{m}}(T) - H^0_{\mathrm{m}}(298.15\ \mathrm{K})$ in $\mathrm{J\cdot mol^{-1}}$, entropy $S^0_{\mathrm{m}}(T)$, and Gibbs energy functions $(G^0_{\mathrm{m}}(T) - H^0_{\mathrm{m}}(298.15))/T$ in $\mathrm{J\cdot mol^{-1}\cdot K^{-1}}$ for both the solid and the liquid phase of the compounds under investigation

$$H = H_{298} + \int C_p \mathrm{d}T \tag{2}$$

$$H - H_{298} = A\cdot T + 1/2\cdot B\cdot T^2 + 1/3\cdot C\cdot T^3 + D \tag{3}$$

$$S = S_{298} + \int \frac{C_p}{T}\mathrm{d}T \tag{4}$$

$$S = A\cdot \ln T + B\cdot T + 1/2\cdot C\cdot T^2 + E \tag{5}$$

$$-(G - H_{298})/T = A\cdot \ln T + 1/2\cdot B\cdot T + 1/6\cdot C\cdot T^2 - E\cdot T^{-1} + F \tag{6}$$

The parameters $D$, $E$, and $F$ in the above equations were calculated by setting $T = 298.15$ K into eqs 3, 5, and 6. They are presented in Table 2. Our experimental melting (transition) temperatures and enthalpies together with heat capacity data were used in this calculation. We determined heat capacity values $C^0_{p,\mathrm{m}}(\mathrm{s}, 298.15\ \mathrm{K})$ for all compounds by extrapolation of experimental results to 298.15 K (Tables 3 to 7). The values of entropy at 298.15 K also necessary in these calculations were obtained by Latimer's method from anion and cation contributions.[19] The standard entropies $S^0_{\mathrm{m}}(\mathrm{s}, 298.15\ \mathrm{K})$ obtained in this way were (331.80, 390.30, 357.40, 403.10, and 243.70) $\mathrm{J\cdot mol^{-1}\cdot K^{-1}}$ for $K_2EuBr_4$, $KEu_2Br_5$, $Rb_2EuBr_4$, $RbEu_2Br_5$, and $RbEuBr_3$ respectively. The calculated values of thermodynamic functions are presented in Tables 3 to 7 at selected temperatures.

**Table 5. Thermodynamic Functions of $Rb_2EuBr_4$ at Selected Temperatures from (298.15 to1100) K**

| $T$ | $C^0_{p,\mathrm{m}}(T)$ | $S^0_{\mathrm{m}}(T)$ | $-(G^0_{\mathrm{m}}(T) - H^0_{\mathrm{m}}$ (298.15 K))/$T$ | $H^0_{\mathrm{m}}(T) - H^0_{\mathrm{m}}$ (298.15 K) |
|---|---|---|---|---|
| K | $\mathrm{J\cdot mol^{-1}\cdot K^{-1}}$ | $\mathrm{J\cdot mol^{-1}\cdot K^{-1}}$ | $\mathrm{J\cdot mol^{-1}\cdot K^{-1}}$ | $\mathrm{kJ\cdot mol^{-1}}$ |
| 298.150 | 209.63 | 357.40 | 357.40 | 0.00 |
| 300 | 209.77 | 358.69 | 357.41 | 0.39 |
| 400 | 216.90 | 420.02 | 365.72 | 21.73 |
| 500 | 224.02 | 469.18 | 381.66 | 43.77 |
| 600 | 231.15 | 510.66 | 399.79 | 66.53 |
| 700 | 238.28 | 546.82 | 418.27 | 90.00 |
| 776 | 243.70 | 571.66 | 432.10 | 108.32 |
| 776 | 269.42 | 624.34 | 432.10 | 149.20 |
| 800 | 269.42 | 632.55 | 438.00 | 155.67 |
| 900 | 269.42 | 664.28 | 461.41 | 182.61 |
| 1000 | 269.42 | 692.67 | 483.15 | 209.55 |
| 1100 | 269.42 | 718.35 | 503.38 | 236.49 |

**Table 6. Thermodynamic Functions of $RbEu_2Br_5$ at Selected Temperatures from (298.15 to 1100) K**

| $T$ | $C^0_{p,\mathrm{m}}(T)$ | $S^0_{\mathrm{m}}(T)$ | $-(G^0_{\mathrm{m}}(T) - H^0_{\mathrm{m}}$ (298.15 K))/$T$ | $H^0_{\mathrm{m}}(T) - H^0_{\mathrm{m}}$ (298.15 K) |
|---|---|---|---|---|
| K | $\mathrm{J\cdot mol^{-1}\cdot K^{-1}}$ | $\mathrm{J\cdot mol^{-1}\cdot K^{-1}}$ | $\mathrm{J\cdot mol^{-1}\cdot K^{-1}}$ | $\mathrm{kJ\cdot mol^{-1}}$ |
| 298.150 | 214.30 | 403.10 | 403.10 | 0.00 |
| 300 | 214.23 | 404.42 | 403.10 | 0.40 |
| 400 | 211.94 | 465.67 | 411.47 | 21.68 |
| 500 | 212.48 | 512.97 | 427.22 | 42.88 |
| 600 | 215.86 | 551.96 | 444.85 | 64.27 |
| 700 | 222.08 | 585.67 | 462.61 | 86.15 |
| 800 | 231.13 | 615.88 | 479.91 | 108.78 |
| 888 | 241.45 | 640.51 | 494.62 | 129.56 |
| 888 | 280.75 | 720.06 | 494.62 | 200.21 |
| 900 | 280.75 | 723.83 | 497.65 | 203.58 |
| 1000 | 280.75 | 753.41 | 521.77 | 231.65 |
| 1100 | 280.75 | 780.17 | 544.07 | 259.73 |

**Table 7. Thermodynamic Functions of $RbEuBr_3$ at Selected Temperatures from (298.15 to 852) K**

| $T$ | $C^0_{p,\mathrm{m}}(T)$ | $S^0_{\mathrm{m}}(T)$ | $-(G^0_{\mathrm{m}}(T) - H^0_{\mathrm{m}}$ (298.15 K))/$T$ | $H^0_{\mathrm{m}}(T) - H^0_{\mathrm{m}}$ (298.15 K) |
|---|---|---|---|---|
| K | $\mathrm{J\cdot mol^{-1}\cdot K^{-1}}$ | $\mathrm{J\cdot mol^{-1}\cdot K^{-1}}$ | $\mathrm{J\cdot mol^{-1}\cdot K^{-1}}$ | $\mathrm{kJ\cdot mol^{-1}}$ |
| 298.15 | 127.57 | 243.70 | 243.70 | 0.00 |
| 300 | 127.64 | 244.49 | 243.70 | 0.23 |
| 400 | 131.51 | 281.74 | 248.75 | 13.19 |
| 500 | 135.37 | 311.50 | 258.41 | 26.53 |
| 600 | 139.24 | 336.52 | 269.40 | 40.26 |
| 700 | 143.11 | 358.28 | 280.57 | 54.38 |
| 732 | 144.34 | 364.70 | 284.11 | 58.98 |
| 732 | 141.52 | 381.86 | 284.11 | 71.54 |
| 800 | 141.52 | 394.44 | 292.96 | 81.17 |
| 852 | 141.52 | 403.35 | 299.43 | 88.53 |

## Summary

The temperatures and enthalpies of phase transitions as well as heat capacity dependence on temperature were determined for both solid and liquid $K_2EuBr_4$, $KEu_2Br_5$, $Rb_2EuBr_4$, $RbEu_2Br_5$, and solid $RbEuBr_3$ compounds. These data were used to calculate the whole set of thermodynamic functions up to 1100 K for solid and liquid compounds under investigation.

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