

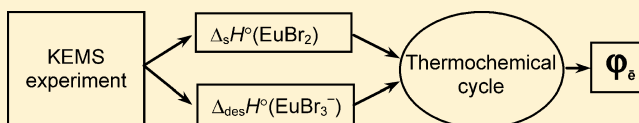
Determination of the Work Function for Europium Dibromide by Knudsen Effusion Mass Spectrometry

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ABSTRACT: The experimentally measured values of the EuBr_2 sublimation enthalpy and EuBr_3^- desorption enthalpy were used to construct a thermochemical cycle to determine the work function $\varphi_{\text{e}} = 405 \pm 39 \text{ kJ}\cdot\text{mol}^{-1}$ ($4.2 \pm 0.4 \text{ eV}$) for europium dibromide.



INTRODUCTION

Thermal electron emission is a well-known method for determining the work function φ_{e} for metals. For many ionic compounds, in particular metal halides, which do not emit electrons on heating, information on φ_{e} is usually obtained by threshold techniques, for example, photoemission.¹ However, these data are scanty and contradictory due to an ambiguity in the interpretation of experimental results. It has, however, been established that the thermal emission of positive and negative ions is observed for many ionic compounds.² This phenomenon also has a potential application for the determination of φ_{e} , which in ionic crystals is related to such characteristics as band gap and electron affinity,³ and in this way plays an important role in the fundamental description of their electronic properties. This technique has recently been proposed by the authors⁴ for congruently vaporizing ionic compounds. It is based on the mass spectrometric determination of the sublimation enthalpy of molecules and the desorption enthalpy of polyatomic ions with the subsequent calculation of φ_{e} from a thermochemical cycle. This technique was successfully used to determine the work functions of alkali halides³ and a number of lanthanide tribromides.⁴

This paper presents the results of determining the work function for EuBr_2 which is the only lanthanide dibromide stable at high temperatures.

EXPERIMENTAL SECTION

An MI1201 magnetic-sector-type (90° , curvature radius of 200 mm) mass spectrometer modified for high temperature studies was used. A special ion source allowed us to perform measurements under electron ionization (EI) and thermal ion emission (TE) regimes and to study both neutral and charged vapor components. The molecular composition of the equilibrium vapor over the condensed phase was analyzed in the EI regime. Mass spectra of a molecular beam from the Knudsen effusion cell were recorded at 70 eV energy of the ionizing electrons and an emission current of 1 mA from the cathode. A movable molecular beam shutter, placed between the effusion cell and the ionization chamber, made it possible to distinguish the species effusing from the cell from those of the

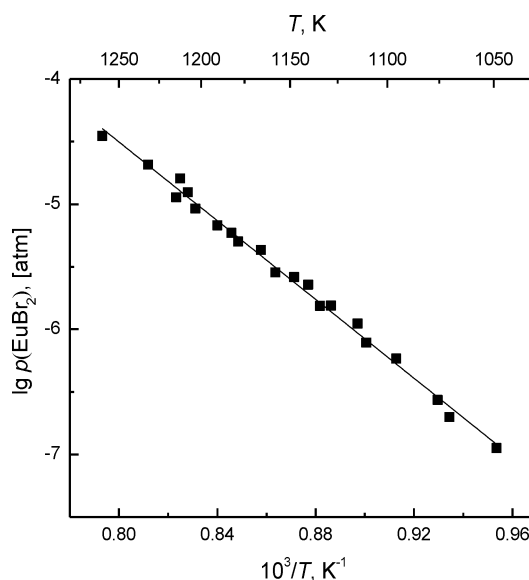


Figure 1. Temperature dependence of the EuBr_2 equilibrium vapor pressure.

background. The charged species were identified in the TE regime. In this case, the ions generated inside the effusion cell at high temperature are withdrawn from it by a weak ($10^4 \text{ V}\cdot\text{m}^{-1}$ to $10^5 \text{ V}\cdot\text{m}^{-1}$) electric field. The voltage applied to the cell was negative with respect to the ground to detect the emission of negative ions. The system for recording ion currents included a secondary electron multiplier combined with a Keithley picoammeter. The sensitivity of the registration system for direct current was 10^{-17} A . The sample under investigation was loaded into a graphite cell. The ratio of the cross section area of the cell to the area of the effusion orifice (0.16 mm^2) was about 300. The cell was heated by a resistance oven. The temperature of the cell was measured by a

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standard tungsten–rhenium thermocouple calibrated by the melting points of pure NaBr and Ag. The accuracy of the temperature measurement was estimated to be within ± 5 K. The instrument was calibrated according to the internal standard procedure using metallic silver as a reference. The measurement program⁵ automatically recorded the ion current, the temperature of the cell, and the energy of ionizing electrons. A more detailed description of the unit and the experimental procedure can be found in refs 4 and 6.

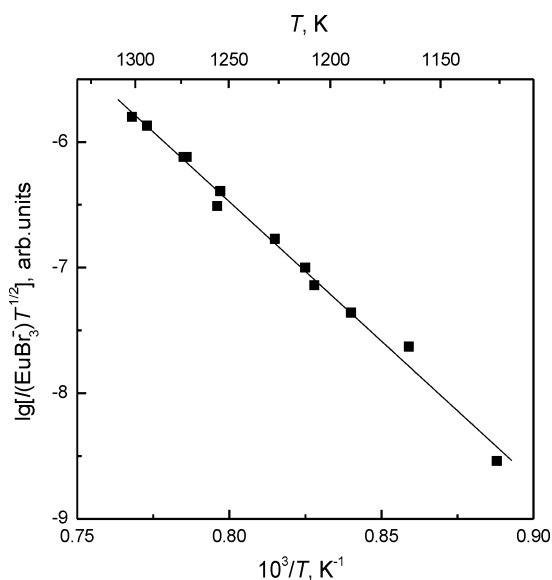


Figure 2. Temperature dependence of the EuBr_3^- ion current.

Table 1. Enthalpy and Energy Data Used for the Calculations^a

parameter	$T = 298.15$ K	$T = 1264$ K
$\Delta_{\text{des}}H^\circ(\text{EuBr}_3^-)$		425 ± 12
$\Delta_s H^\circ(\text{EuBr}_2)$	354 ± 5^9	304 ± 5
$\Delta_{\text{diss}}H^\circ(\text{EuBr}_3^-)$	293 ± 31	289 ± 31
$D_{\text{at}}(\text{EuBr}_2)$	751 ± 19	756 ± 19
$EA(\text{Br})$	330.9 ± 0.2^{12}	350.8 ± 0.2

^aParameter values are given in $\text{kJ}\cdot\text{mol}^{-1}$.

CHEMICALS

The EuBr_2 sample was synthesized from Eu_2O_3 by the NH_4Br procedure,^{7,8} which includes the following stages: Eu_2O_3 (Fluka, mole fraction of 0.999) was dissolved in HBr , NH_4Br was added in an $\text{Eu}/\text{NH}_4\text{Br}$ ratio of 1:3.5, and the solution was dried. The residue ($(\text{NH}_4)_3\text{EuBr}_6$ and NH_4Br) was ground in an agate mortar. The powder was heated to 453 K in an argon

gas flow and to 673 K under vacuum, yielding a mixture of EuBr_2 and EuBr_3 . By further annealing at 773 K in vacuum, the EuBr_3 decomposed completely into EuBr_2 and Br_2 . The obtained product was examined by powder X-ray diffraction and chemical analysis. A complexometric analysis resulted in the Eu mole fraction of 0.4874 ± 0.0013 (theoretical value of 0.4875), and a mercurimetric analysis yielded the Br mole fraction of 0.5126 ± 0.0012 (theoretical value of 0.5125).

RESULTS AND DISCUSSION

On heating EuBr_2 to temperatures of (1049 to 1301) K, the major identified vapor species in the EI and TE regimes were the molecule EuBr_2 and the negative ion EuBr_3^- . The EI mass spectra, their interpretation, and the determination of the EuBr_2 pressure have been reported by us elsewhere.⁹ Figure 1 shows the temperature dependence of the pressure $p(\text{EuBr}_2)$. From these data, the sublimation enthalpy $\Delta_s H^\circ(\text{EuBr}_2, 298.15 \text{ K}) = 354 \pm 5 \text{ kJ}\cdot\text{mol}^{-1}$ was obtained by the techniques of the second and third laws of thermodynamics. Details are given in ref 9. Figure 2 shows the temperature dependence of the product $I(\text{EuBr}_3^-)T^{1/2}$, where I is the ion current. This product is proportional to the pressure $p(\text{EuBr}_3^-)$ as follows from the fundamental relationship² $p = kIT^{1/2}M^{1/2}$, where k is the sensitivity constant in the TE regime and M the mass of ion. The slope of a linear fit $\lg[I(\text{EuBr}_3^-)T^{1/2}] = (-22.20 \pm 0.64)\cdot 10^3/T + (11.29 \pm 0.52)$ (1126 to 1301) K yields the enthalpy of desorption of EuBr_3^- ions from the EuBr_2 surface at the mean temperature of the experiment: $\Delta_{\text{des}}H^\circ(\text{EuBr}_3^-, 1264 \text{ K}) = 425 \pm 12 \text{ kJ}\cdot\text{mol}^{-1}$.

The work function ϕ_e for EuBr_2 crystals is calculated on the basis of the thermochemical cycle shown in Figure 3 according to the equation

$$\phi_e = \Delta_{\text{des}}H^\circ(\text{EuBr}_3^-) - 4/3\Delta_s H^\circ(\text{EuBr}_2) + \Delta_{\text{diss}}H^\circ(\text{EuBr}_3^-) + EA(\text{Br}) - 1/3D_{\text{at}}(\text{EuBr}_2)$$

where $EA(\text{Br})$ is the electron affinity of the Br atom, $\Delta_{\text{diss}}H^\circ(\text{EuBr}_3^-)$ is the enthalpy of the reaction $\text{EuBr}_3^- = \text{Br}^- + \text{EuBr}_2$, and $D_{\text{at}}(\text{EuBr}_2)$ is the atomization energy of EuBr_2 . The initial data used in the calculation of ϕ_e are given in Table 1. The values $\Delta_{\text{diss}}H^\circ(\text{EuBr}_3^-)$ and $D_{\text{at}}(\text{EuBr}_2)$ were calculated by Hess's law using the formation enthalpies of the reaction participants. The formation enthalpies $\Delta_f H^\circ(\text{EuBr}_2, 298.15 \text{ K}) = -349 \pm 19 \text{ kJ}\cdot\text{mol}^{-1}$ and $\Delta_f H^\circ(\text{EuBr}_3^-, 298.15 \text{ K}) = -861 \pm 24 \text{ kJ}\cdot\text{mol}^{-1}$ were obtained and are discussed in ref 10. Additionally, the following reference data for $\Delta_f H^\circ(298.15 \text{ K})$ in $\text{kJ}\cdot\text{mol}^{-1}$ were used: 178.2 ± 3.0 for Eu ,¹¹ 111.86 ± 0.12 for Br , and -219.04 ± 0.23 for Br^- .¹² The data were reduced to a temperature of 1264 K using the enthalpy increments of the reaction participants.^{9,10,12}

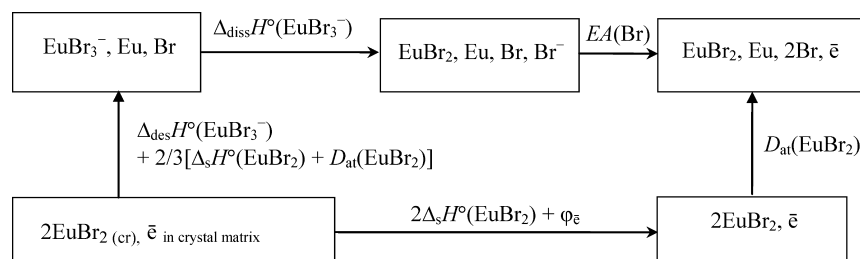


Figure 3. Thermochemical cycle for calculating the work function for EuBr_2 .

The work function $\varphi_{\bar{e}} = 405 \pm 39 \text{ kJ}\cdot\text{mol}^{-1}$ ($4.2 \pm 0.4 \text{ eV}$) for EuBr_2 is determined in this work for the first time. This value exceeds those for the lanthanide tribromides by about $100 \text{ kJ}\cdot\text{mol}^{-1}$.⁴

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