

THERMODYNAMICS OF THE SUBLIMATION OF LANTHANOID TRIIODIDES

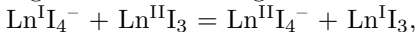
Kudin L.S., Motalov V.B., Dunaev A.M.*

ISUCT, Ivanovo, Russia

**lkudin@yandex.ru*

The sublimation of the lanthanide triiodides LnI_3 ($\text{Ln} = \text{La}, \text{Ce}, \text{Pr}, \text{Gd}, \text{Tb}, \text{Tm}, \text{Lu}$) has been studied by high temperature mass spectrometry. The of LnI_3 samples were loaded into the molybdenum effusion cells with the evaporation to effusion area ratio ≥ 400 . A single-focusing magnetic sector mass spectrometer MI1201 was used in this investigation.

The ions LnI_n^+ ($n = 0-3$), Ln_2I_n^+ ($n = 3-5$), Ln_3I_8^+ and the doubly charged ions LnI_n^{++} ($n = 0-2$) were registered in electron ionization mass spectra of saturated vapor over all lanthanide triiodides in the temperature range of 800–1000 K and the energy of ionizing electrons of 40 eV. In thermionic emission mass spectra the $\text{I}(\text{LnI}_3)_n^-$ negative ions with $n = 0-4$ were observed in the same temperature range. The mass spectra were found to be time-independent thereby indicating the thermal stability of the triiodides in the temperature range studied. Analysis of the ionization energy curves and the temperature dependences of ion currents allowed us to conclude that the ions with one atom of lanthanide are formed by ionization of monomer molecules and the ions Ln_2I_n^+ and Ln_3I_8^+ are the products of dissociative ionization of dimer and trimer molecules, respectively. The partial vapor pressures of the molecular constituents were determined by the standard mass spectrometric procedure. For individual compounds and systems based on them, the equilibrium constants of the homogeneous and heterogeneous ion-molecular reactions



were measured. Here Ln^{I} and Ln^{II} are two different lanthanides. In the framework of techniques of the second and third laws of thermodynamics, the sublimation enthalpies in the form of monomer and polymer molecules and the enthalpies of ion-molecular reactions were determined. On the basis of the obtained results and the available literature data the formation enthalpies of the observed molecules and ions were calculated.

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