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Note

The thermodynamics of sublimation and vaporization of some volatile β-diketonates complexes with the elements of HTSC phases

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Abstract

The processes of sublimation and vaporization of six β-diketonate complex compounds of rare-earth metals, Ba and Cu with pivaloyltrifluoroacetone (Hpta) and hexafluoroacetylacetone (Hhfa) have been studied at different temperatures by the tensimetric flow method. The vapour pressure of the tetrakis chelate $Na[Y(pta)_4]$ was also determined by the static method with a silica-membrane zero gauge. These results are in agreement with the data obtained by the flow method.

The dependencies of vapour pressure on temperature, and the thermodynamic characteristics of vaporization and sublimation of the listed compounds are reported.

INTRODUCTION

In recent years, the increasing interest in the volatile β-diketonate complexes is due to their application in the chemical vapour deposition of high-temperature superconducting (HTSC) films. The fluorinated β-diketonates have high volatility and thermal stability at relatively low temperatures (350–550 K).

EXPERIMENTS AND RESULTS

Using the flow method, the following metal–organic compounds with fluorinated β-diketones were investigated: tetrakis chelates, containing an alkali metal ion, $Na[Ln(pta)_4]$ (where Ln is Y, Pr, Tb; Hpta is $(CH_3)_3CCOCH_2COCF_3$), $Cu(pta)_2$ ($T_m = 381$ K) and also the adducts with

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crown ethers $Cu(pta)_2 \cdot$ 15-crown-5 ($T_m = 358$ K) and $Ba(hfa)_2 \cdot$ 18-crown-6 (where Hhfa is $CF_3COCH_2COCF_3$). The synthesis and analysis of these compounds have been described [1, 2].

In the flow method, a certain volume of dry helium carrier gas was passed through the tube cell with the sample at constant temperature. The cell temperature gradient was 1 K, the temperature fluctuation was ±0.5 K, and the error of the flow measurements was ±2%. The amounts of the substances vaporized under quasi-equilibrium conditions were determined by weighing the cell. From the density of β-diketonate vapours, the values of their saturated vapour pressure were determined assuming that only monomolecular gas is formed under the conditions of the experiments. The initial substances and the condensates obtained in the cooler zone of the tube reactor had identical compositions and properties. The pressure values were independent of the flow rate, i.e. we had quasi-equilibrium conditions in our experiments.

The thermodynamic characteristics of vaporization and sublimation of the β-diketonates, calculated using the second law of thermodynamics, are listed in Table 1. The experimental data had good reproducibility in the indicated temperature ranges. The substances decomposed at higher temperatures.

The saturated vapour pressure of $Na[Y(pta)_4]$ was also studied by the static method with a silica-membrane gauge. The results obtained by both methods are in good agreement. This confirms that it was correct to assume that such compounds volatilize in the monomolecular form. The larger errors in the thermodynamic functions obtained using the static method can be explained by the more narrow temperature range employed and by some decomposition of the complex.

TABLE 1

Thermodynamic characteristics of vaporization and sublimation of the β-diketonate complexes

Compound	$\ln P/\mathrm{atm} = A/T + B$		$\Delta H^{\ominus}/$ kJ mol^{-1}	$\Delta S^{\ominus}/$ J K^{-1} mol^{-1}	T/K
	$-A$	B			
$Na[Pr(pta)_4](s)$	18600	31.93	155 ± 2	266 ± 5	423–483
$Na[Tb(pta)_4](s)$	19570	34.09	163 ± 3	283 ± 5	418–473
$Na[Y(pta)_4](s)$	15600	26.29	130 ± 3	219 ± 6	418–503
$Na[Y(pta)_4](s)$ [a]	17100	29.54	142 ± 12	246 ± 24	463–503
$Cu(pta)_2(s)$	12300	25.02	102 ± 3	208 ± 8	353–379
$Cu(pta)_2(l)$	9204	16.95	76.5 ± 2	141 ± 2	381–443
$Cu(pta)_2 \cdot$ 15-cr-5(l)	9650	16.93	80.2 ± 2	141 ± 3	368–443
$Ba(hfa)_2 \cdot$ 18-cr-6(s)	13800	20.93	115 ± 2	174 ± 5	428–473

[a] Using the static method.

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