

PHYSICAL METHODS  
OF INVESTIGATION

## Synthesis and Thermodynamic Properties of Cadmium Oxopivalate $\text{CdPiv}_2 \cdot \text{Cd}_4\text{OPiv}_6$

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**Abstract**—The cadmium oxopivalate complex  $\text{CdPiv}_2 \cdot \text{Cd}_4\text{OPiv}_6$  has been synthesized and its thermodynamic characteristics have been studied using the Knudsen effusion technique with the mass spectral analysis of the gas phase. It has been found that vaporization of this complex proceeds congruently and the saturated vapor above it consists of molecules  $\text{Cd}_2\text{Piv}_4$ ,  $\text{Cd}_4\text{Piv}_8$ , and  $\text{Cd}_4\text{OPiv}_6$ . The standard enthalpies of sublimation of these molecules have been determined; the standard enthalpy of vaporization of complex  $\text{CdPiv}_2 \cdot \text{Cd}_4\text{OPiv}_6$  and standard enthalpy of dissociation of the  $\text{Cd}_4\text{Piv}_8$  molecule according to the second and third laws of the thermodynamics have been found to be  $\Delta_S H_{298}^\circ = 297.0 \pm 12.1$  kJ/mol and  $\Delta_D H_{298}^\circ = 133.2 \pm 16.8$  kJ/mol, respectively. It is shown that the oxopivalate cadmium complex can be used as a precursor in the MO CVD method for the preparation of thin oxide films and coatings.

**Keywords:** thermodynamics, mass spectrometry, vaporization, pivalates

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### INTRODUCTION

Recently, interest has grown in multicomponent electrically conductive systems containing cadmium oxide [1, 2], which in terms of electrical [3, 4], optical [5–7], and catalytic [8] properties can compete with the most popular transparent conductive oxide (TCO) material ITO (indium tin oxide). To obtain functional film materials based on the aforementioned multicomponent oxide systems, one can use chemical vapor deposition (CVD) [9], in which volatile complex compounds of trimethylacetic acid are used as precursors [10].

In the study of cadmium pivalate with a polymer structure, it was shown that its vaporization is accompanied by complete thermal decomposition forming cadmium atoms, carbon dioxide, carbonyl, carboxyl, and other gaseous products of ligand decomposition and oxidation [11]. In order to exclude the polymerization of the condensed phase and thereby increase the volatility of the complex, was used a technique which is related to saturation of the coordination sphere of the complexing agent with an additional ligand. It was demonstrated [12] that the cadmium pivalate complex with additional *o*-phenanthroline  $\text{CdPiv}_2 \cdot \text{Phen}$  ligand is characterized by high volatility and congruent vaporization process, and the gas phase over it consists only of  $\text{CdPiv}_2 \cdot \text{Phen}$  molecules. Similar results were obtained when studying silver pivalate with tributylphosphine [13]. It should be noted that

the thermodynamic characteristics of these complexes remained constant for several months, which is very important for their practical use in CVD methods [14]. However, there is also a simpler way of transforming a hardly volatile complex into a volatile compound. It was shown earlier that pivalates of *p*- and *d*-transition metals are easily hydrolyzed to form thermally stable oxopivalates, which are characterized by high volatility [15–18]. In this regard, the aim of this work is to synthesize and study the thermodynamics of the processes of vaporization of oxo complexes based on cadmium pivalate.

### EXPERIMENTAL

#### *Synthesis of Cadmium Oxocomplexes*

**Procedure I.** A weighed portion of  $\text{CdPiv}_2 \cdot 2\text{H}_2\text{O}$  (1 g) synthesized by the known method [19] was placed in a quartz tube in a VUP-5 vacuum unit and heated to 573 K at residual pressure  $p = 1.3 \times 10^{-3}$  Pa. After 10 h of heating, ~0.31 g of a volatile white substance (**I**, sublimate) was condensed at the cold end of the tube; the mass of the nonvolatile residue was 0.2 g, which was determined by X-ray powder diffraction to be cadmium oxide.

Molecular analysis of sublimate **I** was performed on a Thermo Finnigan DSQ II serial quadrupole mass spectrometer with a direct input system. Figure 1

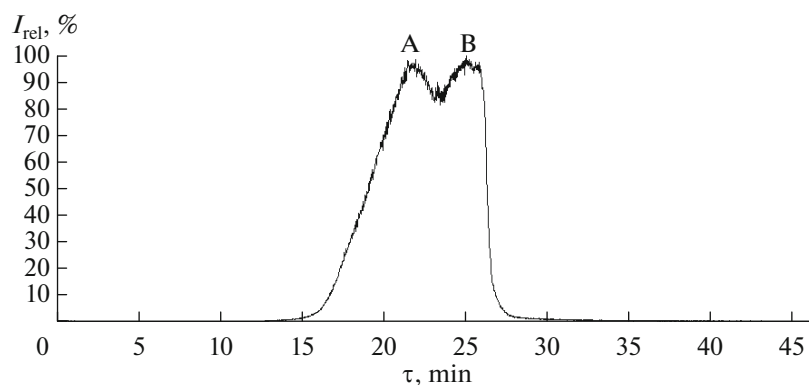
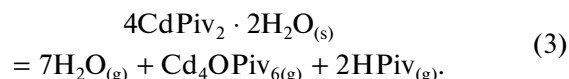
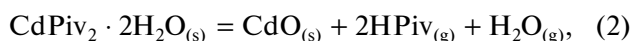
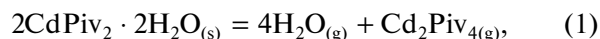


Fig. 1. Polytherm of sublimation of complex I.

shows the sublimation polytherm of the volatile synthesis product constructed from the total ion current of the gas phase mass spectrum. Its noticeable asymmetry and analysis of the mass spectrum of the gas phase (Table 1) allow us to conclude that the vaporization of sublimate I can be described by the transition of two substances into the gas phase with markedly different volatilities. According to mass spectral analysis, the initial stage (A) of vaporization corresponds to the sublimation of the substance mainly in the form of  $\text{Cd}_4\text{OPiv}_6$  molecules, while the second stage (B) reflects the sublimation of the substance mainly in the form of  $\text{Cd}_4\text{OPiv}_6$  and  $\text{Cd}_2\text{Piv}_4$  molecules.

The results obtained allow us to conclude that the process of vaporization of  $\text{CdPiv}_2 \cdot 2\text{H}_2\text{O}$  in vacuum in the temperature range of 298–550 K is accompanied

by dehydration, partial hydrolysis, and transition of molecules  $\text{Cd}_2\text{Piv}_4$  and  $\text{Cd}_4\text{OPiv}_6$  into the gas phase:



The data of mass-spectral analysis correlate with the data of the CHN analysis of the volatile product (sublimate I) of high-temperature hydrolysis performed at the Centre of Collective Use of the Kurnakov Institute, Russian Academy of Sciences, on an Eurovector 300 CHN analyzer, which correspond to a mixture of two complexes,  $\text{Cd}_4\text{OPiv}_6$  and  $\text{CdPiv}_2$ .

For  $\text{Cd}_4\text{C}_{30}\text{H}_{54}\text{O}_{13}$  anal. calcd. (%): C, 33.59; H, 5.04.

For  $\text{CdC}_{10}\text{H}_{18}\text{O}_4$  anal. calcd. (%): C, 38.17; H, 5.73.

Found (%): C, 34.06; H, 6.24.

**Procedure II.** Metallic cadmium (KD1-99.3 wt %) was dissolved in hydrochloric acid (Sigma Tech, special purity grade, Russian State Standard). An alkali solution obtained by dissolving a weighed portion of KOH (analytical grade) in double-distilled water was slowly added to the solution obtained with stirring until the precipitation ceased. Precipitated cadmium(II) hydroxide of a white color was washed with double-distilled water by centrifugation. Then a portion of pivalic acid (Aldrich) in the form of an aqueous suspension was mixed with the precipitate of cadmium hydroxide. The resulting viscous white substance was filtered off and washed on a Büchner funnel with bidistilled water. The dried sample was sublimated on a VUP-5 vacuum unit at residual pressure  $p = 1.3 \times 10^{-3}$  Pa and  $T = 420$ –500 K. The product purified by sublimation was identified similarly as in the first case. The type of evaporation polytherm (Fig. 2) reflects the sublimation of an individual compound, and the mass spectrum corresponds to vaporization of a substance

Table 1. Mass spectrum\* of the gas phase of compound I ( $T = 508$  K,  $U_{\text{ioniz}} = 70$  V,  $I_{\text{ioniz}} = 1.5$  mA)

$m/z$	Ion	Relative intensity, %	
		stage A	stage B
114	$\text{Cd}^+$	3.3	8.9
215	$[\text{CdPiv}]^+$	1.1	36
327	$[\text{Cd}_2(\text{Piv})]^+$	—	1.8
556	$[\text{Cd}_3\text{O}(\text{Piv})_2]^+$	3	3
529	$[\text{Cd}_2(\text{Piv})_3]^+$	1.3	32
657	$[\text{Cd}_3\text{O}(\text{Piv})_3]^+$	12	9.1
843	$[\text{Cd}_3(\text{Piv})_5]^+$	—	2.5
813	$[\text{Cd}_4\text{O}(\text{Piv})_4-57]^+$	42	30
972	$[\text{Cd}_4\text{O}(\text{Piv})_5]^+$	100	100
1042	$[\text{Cd}_4\text{O}(\text{Piv})_6]^+ - 30$	10	10

\* Hereinafter, the mass spectra are given taking into account the isotopic composition of cadmium.

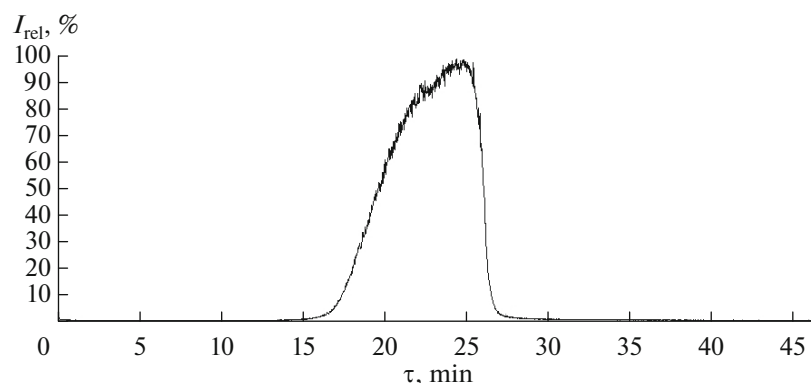


Fig. 2. Polytherm of sublimation of complex II.

in the form of two molecules, namely  $\text{Cd}_4\text{OPiv}_6$  and  $\text{Cd}_2\text{Piv}_4$ . The results of the CHN analysis correlate with the mass spectral analysis data. Thus, the second method apparently leads to the synthesis of individual compound II.

## RESULTS AND DISCUSSION

The thermodynamic characteristics of product II were studied using the Knudsen effusion method with mass spectral analysis of the gas phase on an MS 1301 instrument designed for thermodynamic studies. A standard molybdenum effusion cell with a ratio of the evaporation area to effusion area being  $\geq 600$  was used in the experiments. The temperature was measured with a Pt–Pt/Rh thermocouple and kept constant with an accuracy of  $\pm 2$  deg.

The intensities of the main ions recorded in the mass spectrum of saturated vapor in the temperature range 470–530 K are given in Table 2.

Analysis of experimental data shown in Table 2 and our study of the dependence of the mass spectrum on the energy of ionizing electrons made it possible to conclude that mainly molecules  $\text{Cd}_4\text{O}(\text{Piv})_6$  and  $\text{Cd}_2(\text{Piv})_4$  are present in the saturated vapor over cadmium compound II. Knowing the individual mass spectrum of the  $\text{Cd}_4\text{O}(\text{Piv})_6$  molecule (Table 1) made it possible to find the mass spectrum of the  $\text{Cd}_2(\text{Piv})_4$  molecule by simple subtraction and determine the saturated vapor mass spectrum over compound II (Table 3). The relatively small range of mass numbers of the MS-1301 device did not allow us to assign unambiguously  $\text{Cd}_3\text{Piv}_5^+$  and  $[\text{Cd}_3\text{Piv}_3 + \text{OH}]^+$  ion currents to a specific kind of molecules based only on mass spectral data. Therefore, to determine the composition of the gas phase, we used the literature data [20] on mass spectral studies of pivalate complexes of divalent *d*-transition metals. This approach allowed us to conclude that the molecular precursors of these ions are the  $\text{Cd}_4(\text{Piv})_8$  molecules.

To determine the nature of the vaporization of the complex and calculate the absolute values of the partial pressures, experiments were performed on the complete isothermal sublimation of a weighed portion of compound II. The results of one of several experiments are shown in Fig. 3.

The results of the experiment show that the vaporization of complex II is characterized by the constancy of the intensities of all ion currents (the partial pressure values of molecules) up to the complete burnout of the sample. This fact and the absence of a non-volatile residue in the effusion cell after completion of the experiment indicate the congruent nature of the vaporization of the complex in the form of  $\text{Cd}_4\text{OPiv}_6$ ,  $\text{Cd}_2(\text{Piv})_4$ , and  $\text{Cd}_4(\text{Piv})_8$  molecules.

The congruent character of vaporization of cadmium complex II and the knowledge of the mass spectra of the molecules present in the saturated vapor made it possible to write the Hertz–Knudsen equation

Table 2. Mass spectrum of the gas phase of compound II ( $T = 508$  K,  $U_{\text{ioniz}} = 70$  V,  $I_{\text{ioniz}} = 1.5$  mA)

$m/z$	Ion	$I, \%$	
		MC-1301	DSQII
114	$\text{Cd}^+$	17	5
215	$[\text{CdPiv}]^+$	19	8
327	$[\text{Cd}_2\text{Piv}]^+$	15	5
428	$[\text{Cd}_2\text{Piv}_2]^+$	3	1
529	$[\text{Cd}_2\text{Piv}_3]^+$	53	19
657	$[\text{Cd}_3\text{Piv}_3 + \text{OH}]^+$	11	11
815	$[\text{Cd}_4\text{O}(\text{Piv})_4-57]^+$	–	28
843	$[\text{Cd}_3\text{Piv}_5]^+$	2	9
871	$[\text{Cd}_4\text{O}(\text{Piv})_4]^+$	23	18
972	$[\text{Cd}_4\text{O}(\text{Piv})_5]^+$	100	100

**Table 3.** Individual mass spectra of gas-phase molecules over compound **II**

Cd <sub>4</sub> O(Piv) <sub>6</sub>		Cd <sub>2</sub> Piv <sub>4</sub>		Cd <sub>4</sub> (Piv) <sub>8</sub> (assessment)	
ion	<i>I</i> , %	ion	<i>I</i> , %	ion	<i>I</i> , %
Cd <sup>+</sup>	8	Cd <sup>+</sup>	16	Cd <sup>+</sup>	10
[Cd <sub>4</sub> O(Piv) <sub>4</sub> ] <sup>+</sup>	11	[CdPiv] <sup>+</sup>	37	[CdPiv] <sup>+</sup>	10
[Cd <sub>4</sub> O(Piv) <sub>5</sub> ] <sup>+</sup>	100	[Cd <sub>2</sub> Piv] <sup>+</sup>	6	[Cd <sub>3</sub> Piv <sub>4</sub> + 18] <sup>+</sup>	15
[Cd <sub>4</sub> O(Piv) <sub>6</sub> ] <sup>+</sup>	10	[Cd <sub>2</sub> Piv <sub>2</sub> ] <sup>+</sup>	23	[Cd <sub>3</sub> Piv <sub>5</sub> ] <sup>+</sup>	20
		[Cd <sub>2</sub> Piv <sub>3</sub> ] <sup>+</sup>	100	[Cd <sub>4</sub> Piv <sub>7</sub> ] <sup>+</sup>	100

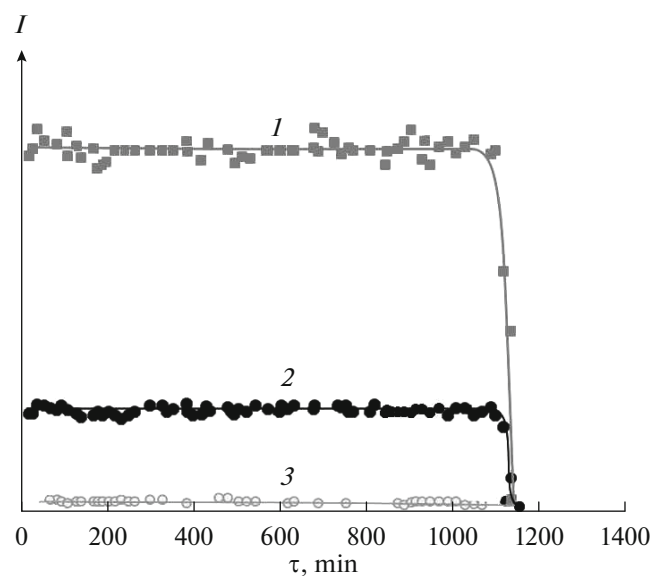
**Table 4.** Absolute values of partial pressures of saturated vapor components over complex **II**, Pa

Sublimation conditions	Cd <sub>4</sub> O(Piv) <sub>6</sub>	Cd <sub>2</sub> (Piv) <sub>4</sub>	Cd <sub>4</sub> Piv <sub>8</sub>	Total pressure
Effusion cell	$6.04 \times 10^{-2}$	$2.53 \times 10^{-2}$	$3.35 \times 10^{-4}$	$8.58 \times 10^{-2}$
Closed volume	$3.90 \times 10^{-2}$	$3.90 \times 10^{-2}$	$2.05 \times 10^{-4}$	$7.8 \times 10^{-2}$

for the complex composition of the gas phase and calculate the absolute values of the partial pressures of saturated vapor components:

$$q_{\text{II}} = S_{\text{ef}} \frac{k}{\sigma_{\text{Cd}_2\text{Piv}_4}} t B \left( M_{\text{Cd}_2\text{Piv}_4}^{1/2} I_{\text{Cd}_2\text{Piv}_4} + \frac{\sigma_{\text{Cd}_2\text{Piv}_4}}{\sigma_{\text{Cd}_2\text{Piv}_8}} \times M_{\text{Cd}_2\text{Piv}_8}^{1/2} I_{\text{Cd}_4\text{Piv}_8} + \frac{\sigma_{\text{Cd}_2\text{Piv}_4}}{\sigma_{\text{Cd}_2\text{OPiv}_6}} M_{\text{Cd}_2\text{Piv}_6}^{1/2} I_{\text{Cd}_4\text{OPiv}_6} \right), \quad (4)$$

$$p_i = k/\sigma_i I_i T,$$



**Fig. 3.** Isotherms of complete sublimation of a weighed sample of complex **II** ( $T = 508$  K): (1)  $[\text{Cd}_4\text{OPiv}_5]^+$ , (2)  $[\text{Cd}_2\text{Piv}_3]^+$ , and (3)  $[\text{Cd}_3\text{Piv}_5]^+$ . Intensity of  $[\text{Cd}_3\text{Piv}_5]^+$  is increased by five times.

where  $S_{\text{ef}}$  is the effective effusion area,  $M_i$  is the molar mass of the  $i$ th component of the gas phase,  $I_i$  is the total ion current of the  $i$ th component of the gas phase,  $t$  is the sublimation time of the complex sample,  $B = (T/2\pi R)^{1/2}$ ,  $q_{\text{II}}$  is the sample of compound **II**,  $\sigma_i$  is the total ionization cross section of the  $i$ th component of the gas phase, and  $k$  is the sensitivity coefficient of the device.

The total ionization cross sections were calculated according to the additivity rule [21] based on the data reported [22]. The partial pressure values found by this procedure at  $T = 508$  K are given in Table 4. The values of the partial pressures of the components of the gas phase corresponding to the minimum of total pressure, which are set in a closed volume in the absence of vapor effusion, are also given in Table 1.

The congruent character of vaporization of complex **II** and the absolute values of the partial pressures make it possible to calculate the composition of this complex, which should be equal to the composition of the molecular flow leaving the effusion cell. If we consider this complex in the framework of the two-component system  $\text{CdPiv}_2\text{--Cd}_4\text{O(Piv)}_6$ , then the ratio

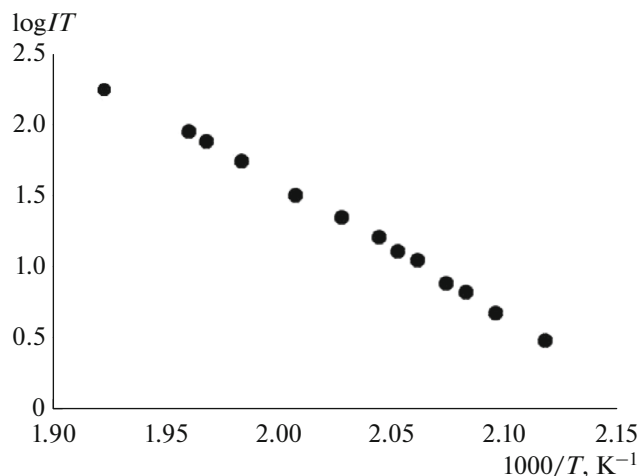
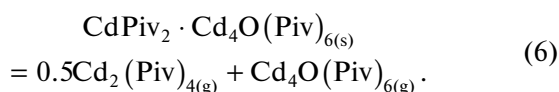
$$\frac{n}{m} = \frac{\left( \frac{2p_{\text{Cd}_2\text{Piv}_4}}{\sqrt{M_{\text{Cd}_2\text{Piv}_4}}} + \frac{4p_{\text{Cd}_4\text{Piv}_8}}{\sqrt{M_{\text{Cd}_4\text{Piv}_8}}} \right)}{\frac{p_{\text{Cd}_4\text{OPiv}_6}}{\sqrt{M_{\text{Cd}_4\text{OPiv}_6}}}} \quad (5)$$

corresponds to the composition of the molecular stream and, therefore, to the composition of congruently sublimated compound **II**. The calculation performed showed that the ratio  $n/m = 1.1$ . Taking into account the accuracy of the experimental data, the composition of the complex can be expressed by the

**Table 5.** Enthalpies of transition of  $\text{Cd}_2(\text{Piv})_4$ ,  $\text{Cd}_4\text{O}(\text{Piv})_6$ , and  $\text{Cd}_4(\text{Piv})_8$  molecules from condensed phase to gas phase ( $T = 470\text{--}530\text{ K}$ ), kJ/mol

$\text{Cd}_2(\text{Piv})_4$	$\text{Cd}_4\text{O}(\text{Piv})_6$	$\text{Cd}_4(\text{Piv})_8$	
$\text{Cd}_2(\text{Piv})_3^+$	$\text{Cd}_4\text{O}(\text{Piv})_4^+$	$\text{Cd}_3(\text{Piv})_5^+$	$\text{Cd}_3\text{O}(\text{Piv})_3^+$
$207.2 \pm 8.6$	$195.8 \pm 8.1$	$277.7 \pm 13.1$	$249.7 \pm 3.3$
$203.7 \pm 5.1$	$189.2 \pm 4.3$	$266.9 \pm 3.8$	$269.6 \pm 4.2$
$196.4 \pm 4.0$	$198.7 \pm 2.8$	$269.1 \pm 3.1$	$275.5 \pm 5.0$
$202.7 \pm 4.3$	$180.9 \pm 5.8$	$241.3 \pm 7.3$	$263.8 \pm 5.1$
$189.0 \pm 5.5$	$190.1 \pm 3.5$	$268.3 \pm 4.8$	$244.7 \pm 4.7$
$205.1 \pm 4.3$	$212.2 \pm 8.3$	$254.1 \pm 6.6$	$270.6 \pm 2.5$
$200.1 \pm 5.6$	$205.7 \pm 5.4$	$263.6 \pm 6.8$	$264.2 \pm 3.7$
$199.4 \pm 3.2$	$212.0 \pm 4.1$	$272.2 \pm 4.9$	$243.0 \pm 3.6$
$197.3 \pm 1.4$	$191.6 \pm 2.1$	$272.4 \pm 2.6$	$255.3 \pm 10.3$
$206.2 \pm 4.1$	$211.4 \pm 7.3$	$281.2 \pm 5.3$	$250.2 \pm 9.7$
$194.9 \pm 8.7$	$198.3 \pm 2.8$	$243.0 \pm 9.9$	$242.4 \pm 7.2$
$207.6 \pm 6.2$	$186.6 \pm 11.0$	—	—
$202.8 \pm 8.7$	$191.5 \pm 2.0$	—	—
$195.2 \pm 5.2$	—	—	—
$196.8 \pm 6.1$	—	—	—
$189.7 \pm 2.4$	—	—	—
Average			
$199.5 \pm 7.3$	$197.2 \pm 11.9$	$264.5 \pm 13.1$	$254.1 \pm 13.3$

formula  $\text{CdPiv}_2 \cdot \text{Cd}_4\text{O}(\text{Piv})_6$ , and its vaporization can be expressed by the reaction:

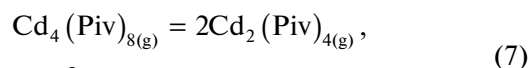


**Fig. 4.** Temperature dependence of  $[\text{Cd}_2\text{Piv}_3]^+$  ion current intensity.

When studying the temperature dependences of the  $I_{[\text{Cd}_2(\text{Piv})_3]^+}$ ,  $I_{[\text{Cd}_4\text{O}(\text{Piv})_4]^+}$ ,  $I_{[\text{Cd}_3(\text{Piv})_5]^+}$ , and  $I_{[\text{Cd}_4(\text{Piv})_4+18]^+}$  ion current intensities (partial pressure of molecules) in the temperature range 470–530 K using the Clausius–Clapeyron and van't Hoff equations, the standard enthalpies of the transition of  $\text{Cd}_2(\text{Piv})_4$ ,  $\text{Cd}_4\text{O}(\text{Piv})_6$ , and  $\text{Cd}_4(\text{Piv})_8$  molecules from the condensed phase of complex **II** to the gas phase were calculated (Table 5). Figure 4 shows the results of one of the experiments for the  $[\text{Cd}_2\text{Piv}_3]^+$  ion as an example.

Given the low temperatures of the experiment, it was assumed that the obtained values correspond to a temperature of 298.15 K; the given errors represent the mean square error of a single measurement. It should be noted that the equality of the vaporization enthalpies of molecules  $\text{Cd}_2(\text{Piv})_4$  and  $\text{Cd}_4\text{O}(\text{Piv})_6$  is another direct evidence of congruent sublimation of complex **II** [23].

Using the found thermodynamic characteristics of vaporization of  $\text{Cd}_2(\text{Piv})_4$ ,  $\text{Cd}_4\text{O}(\text{Piv})_6$ , and  $\text{Cd}_4(\text{Piv})_8$  molecules, the standard enthalpy of reaction (6) for congruent sublimation of compound  $\text{CdPiv}_2 \cdot \text{Cd}_4\text{O}(\text{Piv})_6$   $\Delta_S H_{298}^\circ = 297.0 \pm 12.1$  kJ/mol and the standard enthalpy of the dissociation reaction of the  $\text{Cd}_4(\text{Piv})_8$  tetrameric molecule were calculated:



$$\Delta_D H_{298}^\circ = 139.7 \pm 16.8 \text{ kJ/mol.}$$

The last thermodynamic characteristic was calculated according to the third law of thermodynamics. In the calculation, the entropy change in the dissociation reaction was taken equal to 146.4 J/(mol K); the equilibrium constant at  $T = 508$  K was found from the partial pressures given in Table 4. The dissociation enthalpy calculated in this way was found to be  $126.6 \pm 14.3$  kJ/mol. The coincidence of values of this thermodynamic characteristic obtained by two independent methods indicates the correctness of the saturated vapor composition found by us over congruently sublimated complex **II**.

Based on the experimental data, the equation of the dependence of the total pressure (Pa) of saturated vapor over the  $\text{CdPiv}_2 \cdot \text{Cd}_4\text{O}(\text{Piv})_6$  complex in a closed volume on temperature can be represented as follows:

$$\log p = -(10400 \pm 500)/T + 19.33 \pm 0.16, \quad (8)$$

$$470 \leq T \leq 530 \text{ K.}$$

## CONCLUSIONS

The thermodynamic characteristics of vaporization of cadmium complex  $\text{CdPiv}_2 \cdot \text{Cd}_4\text{O}(\text{Piv})_6$  found here allow us to recommend this compound as a precursor in the CVD method for the preparation of oxide films or coatings. This is due to its high volatility, the relatively simple composition of saturated vapor, the

congruent character of vaporization, the constancy of thermodynamic properties over a long storage period, and the simplicity of synthesis.

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#### CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

#### REFERENCES

1. C. A. Hoel, T. O. Mason, J.-F. Gaillard, and K. R. Poepelmeier, *Chem. Mater.* **22**, 3569 (2010). <https://doi.org/10.1021/cm1004592>
2. A. A. Shubin, A. V. Sidorak, and V. V. Ivanov, *Russ. J. Appl. Chem.* **87**, 258 (2014). <https://doi.org/10.1134/S1070427214030021>
3. J. Chang, V. V. Todkar, R. S. Mane, et al., *Physica E* **41**, 1741 (2009). <https://doi.org/10.1016/j.physe.2009.05.005>
4. A. Abrutis, G. Valincius, G. Baltrunas, et al., *Thin Solid Films* **515**, 6817 (2007). <https://doi.org/10.1016/j.tsf.2007.02.075>
5. F. Z. Henari and A. A. Dakhel, *Laser Phys.* **18**, 1557 (2008). <https://doi.org/10.1134/S1054660X08120281>
6. C. P. Liu, Y. Foo, M. Kamruzzaman, et al., *Phys. Rev. Appl.* **6**, 064018 (2016). <https://doi.org/10.1103/PhysRevApplied.6.064018>
7. A. A. Dakhel, *J. Sol–Gel Sci. Technol.* **85**, 311 (2018). <https://doi.org/10.1007/s10971-017-4567-9>
8. Ch. V. Reddy, B. Babu, and J. Shim, *J. Phys. Chem. Solids* **112**, 20 (2018). <https://doi.org/10.1016/j.jpics.2017.09.003>
9. V. G. Syrkin, *The CVD Method. Chemical Vapor-Phase Deposition* (Nauka, Moscow, 2000) [in Russian].
10. S. Samoilenov, M. Stefan, G. Wahl, et al., *Chem. Vap. Dep.*, No. 8, 74 (2002). [https://doi.org/10.1002/1521-3862\(20020304\)8:2<74::AID-CVDE74>3.0.CO;2-B](https://doi.org/10.1002/1521-3862(20020304)8:2<74::AID-CVDE74>3.0.CO;2-B)
11. D. B. Kayumova, I. P. Malkerova, M. A. Shmelev, et al., *Russ. J. Inorg. Chem.* **64**, 125 (2019). <https://doi.org/10.1134/S0036023619010121>
12. D. B. Kayumova, I. P. Malkerova, M. A. Shmelev, et al., *Russ. J. Coord. Chem.* **44**, 728 (2018). <https://doi.org/10.1134/S1070328418120035>
13. N. Kuzmina, I. Malkerova, A. Alikhanyan, et al., *J. Phys.* **IV**, No. 11, r3645 (2001). <https://doi.org/10.1051/jp4:2001382>
14. A. C. Jones and M. L. Hitchman, *Chemical Vapor Deposition: Precursors, Processes and Applications* (Royal Soc. Chem., 2009).
15. I. P. Malkerova, N. N. Kamkin, Zh. V. Dobrokhotova, et al., *Zh. Neorg. Khim.* **59**, 873 (2014). <https://doi.org/10.7868/S0044457X14070216>
16. N. P. Kuz'mina, A. E. Altsybeev, I. P. Malkerova, et al., *Russ. J. Inorg. Chem.* **51**, 1750 (2006). <https://doi.org/10.1134/S0036023606110118>
17. E. Iljina, A. Korjeva, N. Kuzmina, et al., *Mater. Sci. Eng. B* **18**, 234 (1993). [https://doi.org/10.1016/0921-5107\(93\)90139-E](https://doi.org/10.1016/0921-5107(93)90139-E)
18. D. B. Kayumova, N. N. Kamkin, and N. G. Yaryshev, *Zh. Neorg. Khim.* **58**, 946 (2013). <https://doi.org/10.7868/S0044457X13070131>
19. N. V. Gogoleva, A. A. Sidorov, Yu. V. Nelyubina, et al., *Russ. J. Coord. Chem.* **44**, 473 (2018). <https://doi.org/10.1134/S107032841808002X>
20. E. A. Morozova, I. P. Malkerova, and M. A. Kiskin, *Russ. J. Inorg. Chem.* **63**, 1436 (2018). <https://doi.org/10.1134/S0036023618110128>
21. J. W. Otwsos and D. P. Stevenson, *J. Am. Chem. Soc.* **78**, 536 (1956).
22. J. B. Mann, *J. Chem. Phys.* **46**, 1646 (1967).
23. L. N. Sidorov, M. V. Korobov, and L. V. Zhuravleva, *Mass-Spectrometric Thermodynamic Investigations* (Moscow Univ. Press, Moscow, 1985) [in Russian].

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