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Low-temperature thermodynamic properties of $Ir(C_5H_7O_2)_3$: Connection of entropy with the molecule volume for tris-acetylacetonates of metals

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Abstract

The heat capacity of $Ir(C_5H_7O_2)_3$ has been measured by the adiabatic method within the temperature range (5 to 305) K. The thermodynamic functions (entropy, enthalpy, and reduced Gibbs free energy) at 298.15 K have been calculated using the obtained experimental heat capacity data. A connection has been found between the entropy and the volume of the elementary crystalline cell for β-acetylacetonates of some metals. The reasons for this interdependence are discussed. The values of entropies at $T = 298.15$ K have been calculated for all the metal acetylacetonates on which there are structural data.

Keywords: Molecular crystals; Thermodynamic functions; Structural characteristics

1. Introduction

Owing to a high pressure of vapor at moderate temperatures β-diketonates of metals are made use of as precursors in the processes of precipitating metal and oxide coatings from the (vapor + gas) phase [1–3]. They are considered to be prospective materials in the future technologies of nanoelectronics. At the present time, many properties of these compounds are not yet sufficiently studied including the thermodynamic ones. There are works devoted to the study of the enthalpy of formation [4–6], vapor pressures [5–9], and low-temperature heat capacity [10–15] of β-diketonates of metals.

The accumulation of experimental data on the thermodynamic properties lags considerably behind the requirements of practice. This particularly concerns the low-temperature thermodynamic properties, which are necessary for studying the nature of volatility, calculating the conditions of the crystal-gas system equilibrium, and in studying other properties of these compounds.

The possibilities of calculating the thermodynamic characteristics of these compounds within the framework of theoretical modeling [16–19] are now limited due to the absence of data on quite a number of force constants and the absence of reliable data on the parameters of interatomic interaction potentials. That is why along with the experimental determination of the thermodynamic properties of particular substances there is a need to search for empirical and semi-empirical regularities making it possible to evaluate and to approximately calculate these properties.

Presented in this paper are the results of the experimental research on the heat capacity of $Ir(C_5H_7O_2)_3$ in the temperature range of (5 to 305) K and the analysis of the known data on other β-diketonates [10,11,14,15] aimed at revealing the interdependence of the thermodynamic and structural characteristics of these objects.

2. Experimental

Iridium tris-acetylacetonate (pentane-2,4-dionate) $Ir(C_5H_7O_2)_3$ (or $Ir(AA)_3$) was obtained by the standard

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method [20]. $Ir(AA)_3$ was obtained from K_3IrF_6, resolved in hydrofluoric acid. On adding ligand (HAA) to this solution at 80 °C yellow precipitate of $Ir(C_5H_7O_2)_3$. The complex was extracted with benzol. After the benzol was evaporated the dry precipitate was sublimated in a vacuum gradient furnace ($P = 1.33$ Pa, $T = (450$ to $470)$ K).

Visually, the $Ir(AA)_3$ sample at room temperature is yellow crystalline powder with a mean crystallite size of ~0.3 mm. The melting point determined on a Boetius table is (543 ± 1) K, which is in good agreement with published data [20].

According to X-ray phase analysis, the crystalline compound is single phase; the structure of obtained crystals corresponds to the $Ir(AA)_3$ structure determined before [20] with lattice $a = (1.3900 \pm 0.0009)$ nm, $b = (1.6440 \pm 0.0011)$ nm, $c = (0.7494 \pm 0.0005)$ nm, $\gamma = (98.63 \pm 0.02)°$; space group $P2_1/b$. The calculated X-ray density is (1.920 ± 0.002) g · cm^{-3}, the experimental density (picnometric density at ambient temperature) is (1.920 ± 0.004) g · cm^{-3}. It is visible, that densities in limit of accuracies coincide. The chemical analysis of the refined compound showed its composition for C and H to correspond to the calculated one within the accuracy of the analysis (C, H – 0.2%). The derivatogram and the examination of IR spectra show the obtained compound to correspond to the class of tris-acetylacetonate of metals.

The heat capacity $C_p(T)$ of the sample $Ir(AA)_3$ was measured by the adiabatic method on the installation described in reference [11] using a demountable calorimeter [21]. A sample of 11.041 g was loaded into the calorimetric ampoule. The molar mass used in the calculation of the molar heat capacity was determined from the formula $Ir(C_5H_7O_2)_3$ as 489.548 g. The heat capacity has been measured at 77 points in the range (5 to 305) K. The obtained data are presented in table 1. The analysis of the functional dependence of the heat capacity has not revealed any peculiarities in its behavior.

The root-mean-square deviations of experimental points from a smoothed $C_p(T)$ curve are 0.56% (5 to 46 K), 0.08% (46 to 185 K), 0.27% (185 to 305 K). Standard molar entropy $S^\circ(T)$, difference of standard molar enthalpies $H^\circ(T)$–H° (0 K) and reduced standard molar Gibbs free energy $\Phi^\circ(T)$ within the range (5 to 305) K were obtained by numerical integration of the smoothed $C_p(T)$ dependence. Since there are no experimental data for the temperature below 5 K, in this range the heat capacity of the sample was assumed to obey the limiting Debye law ($C \sim T^3$). The values of these functions at the reference temperature 298.15 K are

$$C_p^\circ = 423.3 \pm 1.1 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1},$$
$$S^\circ = 500.0 \pm 0.4 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1},$$
$$H^\circ\text{–}H^\circ(0) = 73{,}509 \pm 19 \text{ J} \cdot \text{mol}^{-1},$$
$$\Phi^\circ = 253.5 \pm 0.3 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1},$$

where $\Phi^\circ = S^\circ(T) - [H^\circ(T) - H^\circ(0)]/T$. The uncertainties are due to experimental data scatter and the account of extrapolation of heat capacity to 0 K.

TABLE 1
Experimental values of heat capacity for $Ir(C_5H_7O_2)_3$ (molar mass: 489.548 g)

T/K	C_p/(J · mol^{-1} · K^{-1})	T/K	C_p/(J · mol^{-1} · K^{-1})	T/ K	C_p/(J · mol^{-1} · K^{-1})
5.45	2.074	53.62	105.50	147.09	270.4
6.87	3.975	57.02	113.67	159.56	284.6
8.06	5.961	60.12	121.03	165.53	291.7
9.30	8.024	63.12	127.99	171.85	298.3
10.45	9.966	66.25	135.17	178.53	305.4
11.59	11.83	69.67	143.02	185.09	312.1
12.77	13.91	73.47	151.19	190.64	316.9
13.92	15.97	77.41	159.71	197.04	322.1
15.01	18.28	80.66	166.42	203.35	330.8
16.10	20.31	82.15	169.48	209.61	336.7
17.35	22.67	84.70	174.84	215.79	343.2
18.80	25.60	87.46	180.23	221.89	346.5
20.44	28.80	92.40	189.29	227.90	350.7
22.23	32.52	97.05	198.01	234.23	358.4
24.22	36.85	99.23	202.18	240.90	366.2
26.35	41.36	101.48	205.70	247.43	372.3
28.54	46.23	105.78	213.01	259.66	384.5
30.84	51.36	109.91	219.51	266.26	390.8
33.24	56.94	113.87	225.57	272.53	398.2
35.68	62.93	117.72	231.36	275.46	400.1
38.17	68.37	119.36	233.73	280.13	404.1
40.64	74.94	121.47	236.68	286.32	413.3
43.15	79.84	125.13	241.78	292.45	417.8
45.67	86.13	126.61	243.78	298.52	423.2
48.17	92.14	133.64	254.12	304.52	430.2
50.63	98.21	140.50	262.14		