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# SATURATED VAPOR PRESSURE OF IRIDIUM(III) ACETYLACETONATE

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## Abstract

The temperature dependency of the saturated vapor pressure of Ir(acac)$_3$ has been measured by the method of calibrated volume (MCV), the Knudsen method, the flow transpiration method, and the membrane method. The thermodynamic parameters of phase transition of a crystal to gas were calculated using each of these methods, and the following values of $\Delta H^\circ_\mathrm{T}$ (kJ mol$^{-1}$) and $\Delta S^\circ_\mathrm{T}$ (J mol$^{-1}$K$^{-1}$), respectively, were obtained:

- MCV: 101.59, 156.70
- Knudsen: 130.54, 224.40
- Flow transpiration: 129.34, 212.23
- Membrane: 95.45, 149.44

Coprocessing of obtaining data (MCV, flow transportation method and Knudsen method) at temperature ranges 110–200°C as also conducted: $\Delta H^\circ_\mathrm{T}$=127.9±2.1 (kJ mol$^{-1}$); $\Delta S^\circ_\mathrm{T}$=215.2± 5.0 (J mol$^{-1}$K$^{-1}$).

**Keywords:** iridium(III) acetylacetonate, saturated vapor pressure

## Introduction

Ability of β-diketonates of metals to transfer to the gas phase without the decomposition is broadly used in processes of depositing metallic coatings by the CVD method. In this connection in the literature greater attention is devoted to studying thermal stability of these compounds as well as study of such important characteristic as volatility that it is required for understanding processes of depositing and choice of modes of coating deposition. Systematic studies of temperature dependencies of saturated vapor pressure of metal β-diketonates has begun from Berg's work [1]. At present many experiments on studying the temperature dependencies of saturated vapor pressure of volatile metal chelates has been conducted by different methods. However, data of parameters of vaporization processes obtained by different methods for one and same compound often do not coincide between itself [2–4]. In this work for the clarification of reasons of such type of differences on the example of tris-(acetyl-

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acetonate)iridium(III) temperature dependency of the saturated vapor pressure of this compound were measured using four independent methods: the method of calibrated volume (MCV), the Knudsen method, the flow transpiration method, and the membrane method. Additionally, coprocessing of the obtained results was performed, and clarification of the resultant differences was attempted.

## Synthesis

Synthesis of iridium(III) acetylacetonate was produced on method developed by us [5]. Excess of acetylacetone was added to aqua-ion of Ir(III) in acid medium and iridium(III) acetylacetonate was obtained at heating and stirring during 1 h. Obtaining substance was purified by recrystallization (system a benzene-hexane) and binary multiply sublimation in vacuum at $P=5\cdot10^{-2}$ torr and $T=220°C$. Compound is identified on data of infrared (IR) spectroscopy, melting point and data of element chemical analysis for carbon and hydrogen content.

## Flow transportation method

Density of saturated vapor over the crystalline iridium(III) acetylacetonate in the interval of temperatures 423–473 K was measured by flow transpiration method with using an inert gas-carrier (helium). Experiments were conducted in quasi-equilibrium conditions and values of vapor density did not depend on rate of gas-carrier flow in the interval 0.5–6 L $h^{-1}$ (inaccuracy of speed measurement of flow did not exceed ±2%). Detailed description of methods of experiment is presented in [6]. Amount of compound transferred in the gas phase as well as transported in the cool area by the measured flow of helium was defined by a-weighting. Good agreement of both values indicates that $Ir(acac)_3$ sublimates without the decomposition in the investigated interval of temperatures. From obtained data values of saturated vapor pressure were calculated. Herewith it was expected that investigated compound is in monomolecular form in the gas phase. Experimental variance of determination of vapor pressure did not exceed ±5% (calibration on standard compounds was conducted beforehand), accuracy of measurement of temperature is ±0.5 K.

## Knudsen method

Measurements of partial vapor pressure of $Ir(acac)_3$ by the effusion Knudsen method and method of calibrated volume were carried out with the mass spectrometric registration of molecular composition of gas phase. At measurements by the effusion method known in the literature methods of full evaporation of certain amount of substance at different temperatures of effusion camera within one experiment was used for the calibration of mass-spectrometer. Cylindrical effusion camera by the diameter of internal cavity 0.8 cm and height 1 cm was made from stainless steels and it had an output hole by the diameter 0.02–0.04 cm with the length of channel 0.02 cm. Temperature was set by thermoregulator PIT-3 allowing to stabilize it in the stationary mode with accuracy ±0.1 K.

## Method of calibrated volume (MCV)

It is known that the effusion method of pressure measurement gives correct results in limited interval of pressures not exceeding at the best tenth shares of torr. For the pressure measurement in the broad interval of values we offered the method of calibrating volume, its essence is the selection of the gas portion based on the balance with condensing phase in steady-state conditions at the given temperature in beforehand calibrate reservoir. Then vapor from the calibrate reservoir moves on the pipe line in effusion camera forming molecular bunch in the ion source of mass-spectrometer. The temperature of effusion camera is defined by the condition that maximum vapor pressure of investigated compound at certain temperature did not exceed possible values dictated by conditions of the molecular current. Essentially concentrations of particles in selected portions of vapor are measured by the method of calibrating volume. Calibration of mass-spectrometer on each sort of the molecular forms of vapor is realized in analogy with the method of full evaporation of compound. Such description of methods of measurement of vapor pressure by MCV will be given in following publications. Values of pressure from experimental data obtained by MCV for monomolecular composition of vapor are calculated on the formula

$$P_{(\mathrm{torr})}=6.23\cdot 104 I_\mathrm{i}/SI_\mathrm{i}GT_\mathrm{i}/\mathrm{M}V_\mathrm{k}+C$$

where $G$ is the amount of evaporated compound (in g), $I_\mathrm{i}$ is the measured integral intensity of ion current corresponding to amount of molecules in $i$-portions of vapor, $T_\mathrm{i}$ is the temperature of evaporation, M is the molecular mass, $V_\mathrm{k}$ is the value of calibrating volume (in $\mathrm{m}^3$), and $C$ is a constant dependent on the sensitivity of mass-spectrometer to certain sort of molecules.

## Membrane method

Methods of static method with using of membrane zero-manometer and detailed description of experiments were earlier published and presented by us in work [7].

## Data processing

Experimental data of enumerated above methods processed under the special methodic [8] are presented as equation $\ln P(\mathrm{bar})=B-(A/T)$. From temperature dependencies of saturated vapor pressure for researched complex standard thermodynamic parameters $\Delta H^\circ_\mathrm{T}$ and $\Delta S^\circ_\mathrm{T}$ of processes of sublimation were calculated. Coprocessing the obtaining results was also conducted.

## Results and discussion

In Fig. 1 the temperature dependencies of saturated vapor pressure of iridium(III) acetylacetonate, obtained by methods described above, are presented. In Table 1, the parameters of sublimation processes $\Delta H^{\circ}_{T}$ and $\Delta S^{\circ}_{T}$ of iridium(III) acetylacetonate are presented.

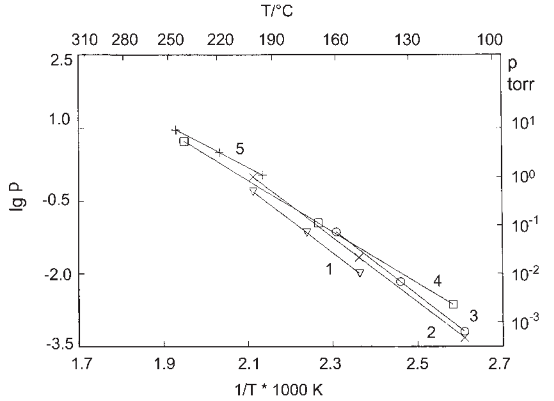

**Fig. 1** Dependencies of logarithm of saturate vapor pressure on reciprocal temperature for the complex $Ir(acac)_3$: 1 – flow method, 2 – coprocessing (MCV (1), Knudsen method, flow method) , 3 – Knudsen method, 4 – MCV, 5 – membrane method

Earlier it was noted repeatedly by us [7] that tris-acetylacetonate complexes of iridium(III) and rhodium(III) (specifically a complex of iridium(III)) have anomalous low values of enthalpy and entropy processes of sublimation in contrast with tris-acetylacetonates of chromium(III), ferric(III) and others. All these complexes have practically identical molecular structures and very close parameters of crystalline cells. Explanations of such differences supposed by us earlier were based on the following hypothesis. 'Heavy' central atom on the associate electronic system of chelate ring can influence on potentials of interaction of peripheral ligand atoms are responsible for the main contribution to intermolecular interaction. At calculations in the atom-atomic approximation set of potentials of interaction used by us for complexes of rhodium(III) and iridium(III) lead to values of energy of lattice (enthalpy of sublimation) close to similar data for complexes of chromium(III), ferric(III) and others. The structure of tris-acetylacetonate iridium(III) described by us [9] has shown that this complex does not possess particularities in packing of molecules in the crystalline lattice and in the molecular structure in contrast with similar complexes of 3p- and 3d-elements.

Thereby the question regarding the clarification of reasons of essential divergences between the chosen calculation model and experimental data became lock-and-key for us. Exactly this circumstance impelled us to conduct additional measurements of the temperature dependency of the vapor pressure of iridium(III) acetyl-

**Table 1** Sublimation parameters of Ir(acac)$_3$ obtained using various methods

| Method | $\ln P\pm\sigma=-(A/T)+B$ | | | $\Delta H^{\circ}_{T}$/ kJ mol$^{-1}$ | $\Delta S^{\circ}_{T}$/ J mol$^{-1}$K$^{-1}$ | $\Delta T$/°C | $n$ |
|---|---|---|---|---|---|---|---|
| | $A$ | $B$ | $\sigma^2$ | | | | |
| Flow | 15557 | 25.53 | $9954/T^2$<br>$-44.4/T$<br>$+0.050$ | 129.3±0.8 | 212.2±1.9 | 150–200 | 10 |
| Knudsen | 15701 | 26.99 | $162747/T^2$<br>$-796.0/T$<br>$+0.975$ | 130.5±3.4 | 224.4±8.2 | 110–160 | 11 |
| MCV | 12218 | 18.85 | $48773/T^2$<br>$-208.8/T$<br>$+0.225$ | 101.6±1.8 | 156.7±3.9 | 114–240 | 38 |
| MCV (1) | 14916 | 25.12 | $64076/T^2$<br>$-299.1/T$<br>$+0.350$ | 124.0±2.1 | 208.9±4.9 | 114–186 | 19 |
| MCV (2) | 9092 | 12.47 | $66221/T^2$<br>$-268.9/T$<br>$+0.273$ | 75.6±2.1 | 103.7±4.3 | 196–240 | 19 |
| Membrane [7] | 10397 | 15.65 | $17493/T^2$<br>$-69.8/T$<br>$+0.069$ | 86.6±1.7 | 130.0±4.2 | 195–245 | 22 |

acetonate by independent methods over an additional range of temperatures. This was done despite the fact that data obtained by us earlier on the vapor pressure of these compounds using the membrane method did not engender doubts. As independent corroboration, the Knudsen and flow transportation methods were used. Over temperature ranges of 110–160°C and 150–200°C, the following values of sublimation enthalpy for Ir(acac)$_3$ were obtained by Knudsen method and flow transportation method, respectively: $\Delta H^{\circ}_{T}$=130.5 kJ mol$^{-1}$, $\Delta H^{\circ}_{T}$=129.3 kJ mol$^{-1}$.

Obtained values were very close to the value for Cr(acac)$_3$ (127.2 kJ mol$^{-1}$) and sufficiently close to the accounting value 136.8 kJ mol$^{-1}$. Significant differences in values of sublimation enthalpy obtained by different methods over different temperature intervals exceed many times over the possible inaccuracies caused by the temperature dependency of heat capacity of condensed and gas phases were not taken into account in Clausius-Clapeyron equation. As an ‘arbitration’ method, the MCV method designed in our Institute was used, which is a variant of the static method, with mass spectrometric analysis of amount and composition of gas phase allowing measurement of vapor pressures over a very broad range: $10^{-5}$ to 10 torr. This method was approved for use with aluminum(III) and chromium(III) acetylacetonates (i.e., those compounds for which there is a significant number of independent and sufficiently reliable measurements of temperature dependency of vapor pressure using different methods). Data obtained by this method for Ir(acac)$_3$ were processed as in all interval of temperatures (MCV, Table 1) as in low and high temperatures [MCV (1) and MCV (2) from Table 1, respectively]. Mass spectrometric study of Ir(acac)$_3$ vapor pressure performed by the above methods showed that at temperatures of up to 440 K, the compound vaporizes in a manner similar to the good convergence of obtained results indicated in Fig. 1. At higher temperatures, deviance from single-line dependency is observed on curve ln$P$–1/$T$ for molecules of Ir(acac)$_3$. At like temperatures of the vapor source and calibrating volume above 440 K in mass spectrums, peaks of ions corresponding of molecules of free ligand are observed. Its concentration vastly increases with the increasing temperature. It is typical that molecules of free ligand are not observed in the gas phase at cooling selected vapor portions at high temperatures up to temperatures of 430–440 K. Besides, in these conditions, increasing a general amount of molecules of Ir(acac)$_3$ in selecting portions of vapor is observed in contrast with the amount measured at the high temperature in same portions of vapor. It should be noted that in vapor in conditions of experiment, other metal-containing forms are not discovered in the investigated interval of temperatures except molecules of Ir(acac)$_3$.

Analyzing the obtained results and thermostability data of Ir(acac)$_3$ it is possible to expect that at temperatures above 440 K local equilibria are observed which stipulated by concentration effects and connected with them changing the nature of adsorption. However, results for aluminum(III) and chromium(III) acetylacetonates obtained by the MCV method corresponded well with the most reliable data in all interval of measurement of vapor pressure: $10^{-4}$ to 10 torr. The temperature dependency of the vapor pressure of iridium(III) acetylacetonate and calculated values of enthalpy and entropy of sublimation measured by MCV (1) at low temperatures within inaccuracy comply with results both a flow transportation method and Knudsen method.

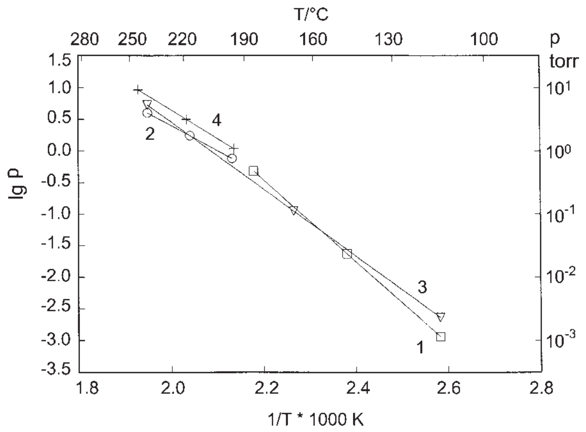

**Fig. 2** Dependencies of logarithm of saturate vapor pressure on reciprocal temperature for the complex Ir(acac)$_3$: 1 – MCV(1), 2 – MCV(2), 3 – MCV, 4 – membrane method

Coprocessing of obtained data by these methods gives the following results: $A$=15391; $B$=25.88; $\Delta H_T^o$=127.9±2.1 (kJ mol$^{-1}$); $\Delta S_T^o$=215.2±5.0 (J mol$^{-1}$K$^{-1}$) (Fig. 1). We obtained the following equation: ln$P$=25.88–15391/$T$ (temperature ranges 110–200°C).

In Fig. 2, temperature dependencies of saturated vapor pressure of Ir(acac)$_3$ obtained by MCV, MCV (1), MCV (2), and the membrane method are presented.

Additional studies performed using the method of high temperature mass spectrometry have shown that reversible thermal conversions of complex are observed in the closed volume at pressures in several torr in the gas phase for iridium(III) acetylacetonate. This mechanism requires a special study. It is possible to expect that in the closed volume under high concentrations in the gas phase a formation of associates with the greater molecular mass occurs that lead to reduction of vapor pressure. Formation of these associates cannot be explained within the framework of intermolecular interaction and rather it has a chemical nature. The data of high temperature mass spectrometry allowing to check a composition of gas phase obliquely confirm such a possibility. A similar situation is probably typical rhodium(III) acetylacetonate as well. Thereby hereinafter at comparing experimental data with calculated data, we shall use values of thermodynamic parameters of sublimation processes calculated from data on the vapor pressure measured by Knudsen method.

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