

Thermodynamics of sublimation of aluminium triacetylacetonate

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Received 12 May 2006; received in revised form 27 July 2006; accepted 11 August 2006

Available online 26 August 2006

Abstract

The equilibrium sublimation pressure $\text{Al}(\text{acac})_3(\text{s}) = \text{Al}(\text{acac})_3(\text{g})$ was measured in the range $376 \leq T/\text{K} \leq 467.5$ by two procedures. One of them is mass spectrometric procedure “calibrated volume method” (CVM), which helped us to expand the possibilities of the effusion method toward the high pressure range. The second is the static method with quartz null Novikov–Suvorov manometers. Experimental data are in good agreement with each other.

For this process, we obtained $\ln(P/\text{Pa}) = 35.67 - 13,207/T$, calculated according to the second law of thermodynamics, enthalpy $\Delta_{\text{sub}}H^\circ(298.15) = 121.8 \pm 1.5 \text{ kJ mol}^{-1}$ and entropy $\Delta_{\text{sub}}S^\circ(298.15) = 235.5 \pm 4.3 \text{ J mol}^{-1} \text{ K}^{-1}$; according to the third law, $122 \pm 1.5 \text{ kJ mol}^{-1}$ and $235.0 \pm 5 \text{ J mol}^{-1} \text{ K}^{-1}$.

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Keywords: β -Diketonates; Pressure; Enthalpy; Entropy; Mass spectrometry

1. Introduction

Unique physicochemical properties of aluminium acetylacetonate determine the promising character of its use to obtain heat- and corrosion-resistant coatings, materials for electronics, special ceramics, highly pure materials by means of gas-phase decomposition at relatively low temperatures.

However, the published data on sublimation pressure and the fundamental thermodynamic characteristics of $\text{Al}(\text{acac})_3$, which are necessary to develop technological processes involving this compound; are conflicting data, this is due to complexities connected with the investigation of this compound (see Fig. 1).

The goal of the present work was to obtain reliable information on temperature dependence of vapour pressure above the solid $\text{Al}(\text{acac})_3$ and on thermodynamics of vaporization of aluminium acetylacetonate.

2. Experimental

2.1. Materials

The samples for investigation were synthesized using the known procedure [12] and characterized by means of chem-

ical analysis, DSC, IR spectroscopy, mass spectrometry and X-ray phase analysis. Within the sensitivity of these methods, the synthesized samples were monophasic compounds of the stoichiometric composition.

2.2. Experimental procedure

Pressure of $\text{Al}(\text{acac})_3$ saturated vapour was measured using the effusion and static procedures.

In the version of effusion method used by us, that is, the calibrated volume method, relative error of pressure measurement was 10%, error of temperature measurement was $\pm 1^\circ$. A detailed description of the set-up and measurement procedure was presented in [13].

Measurement of pressure using the static procedure was carried out with the help of Novikov–Suvorov quartz membrane manometers [14]. A scheme of the set-up is shown in Fig. 2.

The substance under investigation is kept in the working volume 1 of the membrane null manometer. A flat membrane 2, which is a sensitive element of the device, separates the working volume and the compensating one. The latter chamber (3) contains a mechanical amplifier of transference 4 with displacement indicator 5, as well as the reference thread 6. Pressure in the system under investigation causes membrane flexure with respect to the zero position. The membrane flexure can be compensated with changes in the external pressure; this pressure

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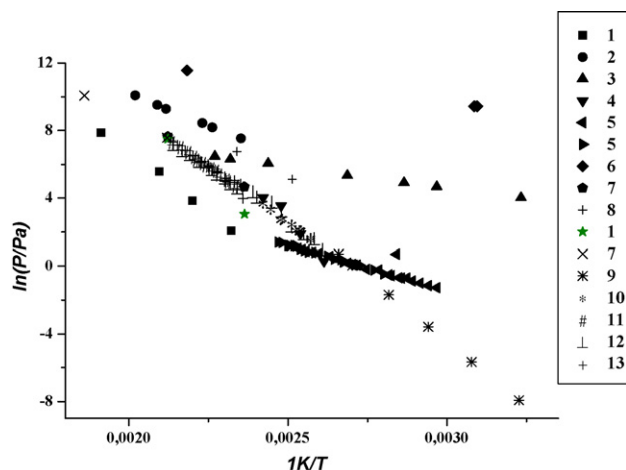


Fig. 1. Temperature dependence of $\text{Al}(\text{acac})_3$ vapour pressure. Series 1–11 are literature data [1–11], series 12 and 13 are the results of the present investigation with tensimetric and CVM methods, correspondently.

can be measured with a mercury manometer of inner diameter 25 mm 7 and cathetometer KM-8 with an error of less than 4 Pa. The indications of the manometer were reduced to the values at 273.15 K and the normal gravity acceleration. In order to fix

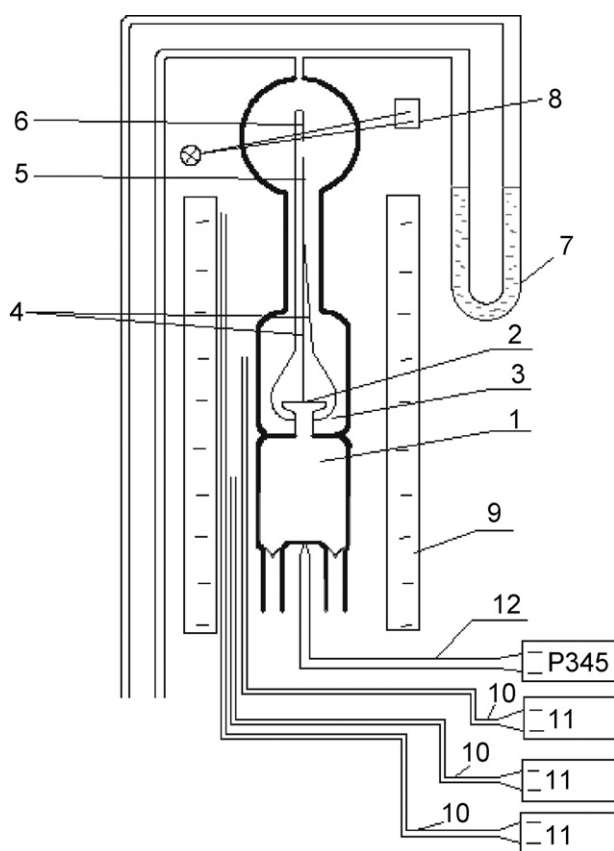


Fig. 2. A schematic of tensimetric set-up: 1, working volume of the membrane null manometer; 2, a flat sensitive quartz membrane; 3, compensating chamber; 4, a mechanical amplifier of transference; 5, displacement indicator; 6, reference thread; 7, mercury manometer and cathetometer KM-8; 8, an optical system recording the zero position of the membrane; 9, a three-sectional resistance furnace; 10, thermocouple sensors; 11, isodromic thermoregulator PIT-3; 12, measuring Pt–Pt/Rh thermocouple.

the zero point more accurately, an optical system was used to register the zero position of membrane 8. The projection of the displacement indicator and of the reference thread onto a matte screen at a magnification of $30\times$ ensured compensation of pressure with an accuracy to 6 Pa. The limiting error of pressure measurements taking into account the compensation error and the error of measurement with a cathetometer did not exceed 27 Pa.

In order to heat the membrane null manometers, a three-sectional resistance furnace 9 was used; each of its windings was controlled independently with its own sensor thermocouple and PIT-3 thermoregulator. Such a design allowed us to maintain the same temperature in three points of the furnace. Deviations from this temperature at the length of 140 mm did not exceed 0.5 K, which was established with the help of special measurements with a measuring Pt–Pt/Rh thermocouple 12, which was moving inside the working zone of the furnace. The measuring thermocouple was preliminarily calibrated with the reference substances (In, Pb, Cd, Sb). Calibration of the measuring thermocouple in the working mode was carried out basing on the pressure of saturated vapour of standard compounds – naphthalene and mercury – with the help of membrane null manometers. In addition, the set-up was calibrated with the help of the gas thermometer of constant volume, which was a membrane null manometer filled with argon.

Pressure measurements have been recorded after reaching an equilibrium for a given temperature. The time of the solid phase–gas equilibrium establishment was 10–15 min. Measurements were carried out only in the forward direction, that is, from lower temperature to higher one. Small residual pressure was observed at the end of each experiment. Nevertheless, after the experiments the substance present in the working chamber was well formed druses of the transparent crystals of aluminium acetylacetonate.

Changes in the pressure of ballast gas with temperature were accepted to be corresponding to the behaviour of an ideal gas and the measured pressure was described with equation:

$$P/P_{\text{st}} = \exp\left(\frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}\right) + \frac{C_j RT}{P_{\text{sb}}}$$

$$C_i \neq C_i(T) \text{ for each } j \text{ experiment}$$

where P is the measured pressure at a temperature of T/K , P_{st} is standard pressure expressed in the units accepted in the present work (1 atm, 760 Torr, 1.0133×10^5 Pa).

Saturated vapour pressure was determined on the basis of the difference $P/P_{\text{st}} - C_j RT/P_{\text{st}}$.

3. Results and discussion

The experimental data obtained using the calibrated volume method (18 points) and the static procedure (23 points) within temperature range 376–467.5 K are shown in Table 1 and in Fig. 1.

One can see in the figure that our data are in excellent agreement between the two methods and with the published data [10,11] obtained within the same temperature range using

Table 1
Sublimation pressure for Al(acac)₃

Static procedure		CVM	
T/K	P/Pa	T/K	P/Pa
467.45	1730	376.15	1.9
423.94	60	383.15	2.8
434.22	170	387.15	5.3
449.15	510	392.15	7.0
443.96	380	398.15	11.1
443.96	380	403.15	27
448.75	520	408.15	46
454.25	760	416.15	61
459.2	1060	418.15	84
464.29	1430	427.15	100
425.25	140	431.15	140
434.17	180	434.15	190
434.16	180	439.15	240
444.3	430	442.15	320
424.07	100	450.15	500
423.61	120	456.15	770
428.71	180	461.15	960
428.7	160	467.15	1400
434.07	200		
444.16	410		
449.01	560		
439.01	290		
439.17	310		

the static procedure with membrane null manometers of the spoon type. One can also see that our data are in good agreement with low-temperature measurements [9]. The work was carried out using Knudsen effusion method with mass spectrometric analysis of the gas phase composition within temperature range 350–375 K. Pressure is low for this temperature range, so Knudsen method gives reliable results. Because of this, when determining thermodynamic characteristics of the process under investigation, we processed our data together with the indicated literature data since this broadens the temperature range investigated and therefore the accuracy of determination of the sought parameters increases.

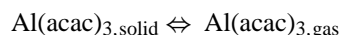
As far as other literature data shown in Fig. 1 are concerned, it should be noted that all the data overestimated in comparison with the present work were obtained with the help of isoteniscope [2–4,8]. Incorrectness of the application of this procedure for the investigation of β -diketonates has been mentioned more than once in literature [9]. Most probably, the authors did not take into account the residual pressure connected with desorption of gases and moisture from the walls of the device, which occurs during heating of a closed vessel with the substance.

The authors of [1,6,7] used the method, which they called chromatographic. The method is based on a quantitative connection between the retention volume, obtained by means of gas chromatographic analysis, and pressure of the vapour of compound under chromatographic analysis. The method was tested with aluminium tris-hexafluoroacetylacetonate. Temperature dependencies of sublimation pressure for this compound were obtained using the static and chromatographic methods. According to the authors, the “chromatographic” data are overestimated by not more than 1.5% within the entire temperature

range investigated (327–398 K). The results of measurements of vapour pressure for Al(acac)₃ are plotted (3 points) and presented as an equation $\log P = f(1/T)$. These data do not agree with each other. The absence of any information about the identification of the compound under investigation, weak validity of the reliability of the procedure involved, inconsistency of the reported data did not allow us to use the results of these works for calculating thermodynamic characteristics of the sublimation of Al(acac)₃.

Sharply different from our data are the results reported in [5] which were obtained by effusion-torsion method. In the region of low temperatures (335 K) pressure values are overestimated by a factor of 15, at the maximal temperature involved in measurements (405.4 K) pressure is underestimated by a factor of 4.8. Most probably, there was a systematic measurement error related to the design of the device. It is known that the most vulnerable aspect of the effusion-torsion method is manufacture of a chamber with the orifices of strictly definite diameter and position. Nevertheless, according to the authors, the measured pressure of sulphur and mercury vapour was comparable with the published data.

When choosing the physicochemical model of the process under investigation, the basis was the analysis of temperature dependence of the mass spectra of Al(acac)₃; according to these data, relative intensity of the fragments in the mass spectrum of Al(acac)₃ does not change within the whole temperature range investigated. This circumstance proves the presence of mainly monomeric Al(acac)₃ molecules in the gas phase. Therefore, vaporization process can be represented as follows:



In this case, pressure of sublimation is expressed by equation:

$$P = P_{\text{st}} \exp \left[\frac{-\Delta H^{\circ} T_0}{RT} + \frac{\Delta S^{\circ} T_0}{R} + \varphi(\Delta C_p, T) \right]$$

where P_{st} is standard pressure expressed in the accepted system of units (1 atm, 760 Torr, 101.325 kPa), $\Delta H^{\circ} T_0$, $\Delta S^{\circ} T_0$ are enthalpy and entropy of sublimation, respectively, at a definite fixed temperature T_0 , $\varphi(\Delta C_p, T)$ (where $\Delta C_p = C_{p(\text{gas})} - C_{p(\text{condensed phase})}$) is some known function of temperature which is determined by changes in the heat capacities during sublimation, R is the gas constant.

Calculations were carried using the criterion function:

$$\varphi = \sum_{i=1}^N \frac{\{p_i(\text{exp}) - p_i(\text{calc})\}^2}{\Delta p_i^2 + (\partial p / \partial T)^2 \Delta T_i^2}$$

where N is the number of experimental points, $p_i(\text{exp})$ is experimental pressure, $p_i(\text{calc})$ is pressure calculated using Eq. (1), Δp_i and ΔT_i are limiting errors of pressure and temperature measurements. The use of the target function in the treatment of results provides more reliable estimation of the desired parameters. The errors of the values to be determined were calculated taking into account Student's coefficient for the 95% confidence

Table 2

Entropy S° (298) and temperature dependence of the heat capacity of aluminium acetylacetonate in the solid and gaseous states $C_p^0(T) = A + BT + \frac{C}{T^2} + \frac{D}{T}$, $\text{J mol}^{-1} \text{K}^{-1}$

Phase	S° (298)	A	B	C	D	References
Solid	267.49	263.0	0.19600		−24.0587	Our treatment of experimental data [5]
Gas	502.48	−138.73	1.01310	1106110		Our treatment of experimental data [5]

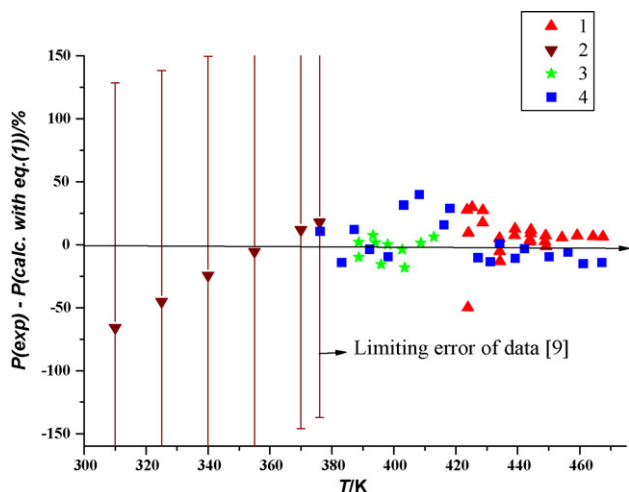


Fig. 3. Deviations (in percent) of the experimental data from pressure values calculated according to Eq. (1). Series 1, 4 are our tensimetric and "calibrated volume method" (CVM) data, series 2, 3 are literature data [2,3], correspondently.

interval.

$$\ln(P/\text{Pa}) = 35.67 - \frac{13207}{T} \pm 2\delta \quad (1)$$

$$\delta = 8238/T^2 - 37.93/T + 0.04382, \quad (310 < T/\text{K} < 467).$$

Processing of the experimental data (see above) was carried out on the basis of the II and III laws of thermodynamics. In the first case, heat capacity of the process was considered to be known, while enthalpy and entropy attributed to 298.15 K were the sought quantities. When carrying out the treatment according to the III law, heat capacity and entropy of the process were considered to be known. Standard entropy values and temperature dependencies of heat capacities of aluminium triacetylacetonate in the solid and gaseous states, which are necessary for calculations, are shown in Table 2, calculation results are presented in Fig. 3 and in Table 3.

The deviations of the experimental saturated vapour pressure values (involved in the treatment) from the quantities calculated according to Eq. (1) are shown in Fig. 3.

Table 3

Thermodynamic characteristics of sublimation of aluminium acetylacetonate, calculated with the joint processing of experimental data obtained in the present investigation and taken from [9–11]

Law	$\Delta_{\text{diss}}H^\circ$ (298) (kJ mol^{-1})	$\Delta_{\text{diss}}S^\circ$ (298) ($\text{J mol}^{-1} \text{K}^{-1}$)
2	121.8 ± 1.5	235.5 ± 4.3
3	122 ± 1.5	235.0 ± 5

See Eq. (1).

Random character of scattering of the deviations within temperature range 360–467 K is an evidence of the absence of essential systematic errors in the data obtained in the present work and in [10,11]. For temperature range 300–340 K, the experimental data obtained in [9] are lower than the calculated ones, but the deviations do not exceed the limiting measurement error indicated by the authors.

The calculated thermodynamic characteristics of sublimation are shown in Table 3.

It follows from the Table that within the indicated error limits a good similarity between the results of treatment according to the II and III laws of thermodynamics is observed. This circumstance confirms the correctness of the chosen physicochemical model and serves as one more confirmation of the absence of substantial systematic errors both in the chosen experimental data and in the calculations of absolute entropy and heat capacity $\text{Al}(\text{acac})_3$ based on molecular constants.

4. Conclusion

A good agreement between the experimental data obtained by different authors using different methods, as well as coincidence of the results of treatment according to the second and the third laws of thermodynamics allow us to recommend thermodynamic characteristics of $\text{Al}(\text{acac})_3$ sublimation listed in Table 3 as the most reliable ones at present.

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