Available online at www.sciencedirect.com
SCIENCE DIRECT®
Thermochimica Acta 432 (2005) 91–98
thermochimica acta
www.elsevier.com/locate/tca

Thermodynamics of chromium acetylacetonate sublimation

P.P. Semyannikov, I.K. Igumenov,
S.V. Trubin, T.P. Chusova*, Z.I. Semenova

*Siberian Branch of Russian Academy of Sciences, Nikolaev Institute of Inorganic Chemistry,
Ac Lavrentyev Prospect 3, 630090 Novosibirsk, Russia Federation*

Received 1 December 2004; received in revised form 12 February 2005; accepted 16 February 2005

Abstract

The equilibrium sublimation pressure $Cr(acac)_3(s) = Cr(acac)_3(g)$ was measured in the range $320 \leq T$ (K) ≤ 476 by two procedures. One of them is Knudsen's effusion procedure with mass spectrometric analysis of the composition of the gas phase, which proved to be good in measuring low pressure. The second is mass spectrometric procedure "calibrated volume method" (CVM), which helped us to expand the possibilities of the effusion method toward high pressure range. Experimental data are in good agreement with each other.

For this process were obtained $\ln(P\ (\mathrm{Pa})) = 39.197 - 15\ 308.5/T$, enthalpy $\Delta_{\mathrm{sub}}H^\circ\ (T) = 127.28 \pm 0.22\ \mathrm{kJ\,mol^{-1}}$ and entropy $\Delta_{\mathrm{sub}}S^\circ\ (T) = 230.1 \pm 0.5\ \mathrm{J\,mol^{-1}\,K^{-1}}$.

© 2005 Elsevier B.V. All rights reserved.

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

1. Introduction

The processes of chemical vapor deposition (metal organic chemical vapor deposition MO CVD and atomic layer deposition ALD) attract increasing attention of researchers during the recent years. This attention depicts modern trends in developing the methods for the synthesis of new film materials under as low temperature as possible. By present, the set of criteria for the choice of precursors meeting the requirements of MO CVD and ALD processes has been already formed. One of the most important parameters, according to which a compound is chosen, is its ability to pass into the gas phase without decomposition at moderate temperature. At present, metal β-diketonates are one of the most widely used kinds of precursors for MO CVD processes. In particular, a large number of processes is known in which metal β-diketonates are used to obtain metal, oxide, superconducting, ferroelectric and other film materials.

One of the most perspective β-diketonates is tris-acetylacetonate $Cr(acac)_3$. However, at present fundamental thermodynamic characteristics which are necessary for the development of technological processes are tentative and often contradictory, which is connected with the complexity of investigations of the above-indicated compound [1–11]. If one compares thermodynamic parameters calculated on the basis of these data, the necessity of a detailed analysis of the entire set of published data for the purpose of obtaining reliable information will become evident.

In view of the above considerations, the main goal of the present work is

- development of a method to measure saturated vapor pressure within a broad pressure range ($\geq 10^3$ Pa) recording the qualitative and quantitative composition of the gas phase with the help of mass spectrometry,
- investigation of $Cr(acac)_3$ saturated vapor pressure,
- analysis of the entire set of experimental data on $Cr(acac)_3$ vapor pressure.

---

* Corresponding author. Tel.: +7 3832 309259; fax: +7 3832 309489.
E-mail address: chu@che.nsk.su (T.P. Chusova).

0040-6031/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2005.02.034

2. Experimental

2.1. Materials

The samples for investigation were synthesized using a known procedure [11,12] starting with $CrCl_3{\cdot}10H_2O$ and the (Hacac) ligand neutralized with NaOH, in water-alcohol medium. The product was purified by means of vacuum sublimation. The resulting substance was characterized by means of chemical analysis, IR spectroscopy, derivatography, mass spectrometry and X-ray phase analysis. The results of examinations showed that the synthesized substance was a one-phase compound of the stoichiometric composition $Cr(acac)_3$.

2.2. Knudsen mass spectrometric effusion procedure

In our work, we use mass spectral effusion method to investigate temperature dependence of vapor pressure. The published data [7,9,10] on the temperature dependence of $Cr(acac)_3$ vapor pressure obtained using this method deviate from each other. The majority of researchers using this procedure carry out the measurements at a constant temperature and use Hertz–Knudsen equation for calculations:

$$P\,(\mathrm{Pa}) = \frac{m}{(Ksqt)(2\pi RT/M)^{1/2}} = 2279.62\left(\frac{T}{M}\right)^{1/2}\frac{m}{Ksqt} \quad (1)$$

where m is the mass of matter (g) removed as a result of effusion through the hole within time t (s) at constant temperature T, K is Klausing coefficient depending on the ratio of the length of the effusion channel to its diameter, sq is the area of the effusion hole, M is molecular mass, R is gas constant.

In the mass spectrometric experiment, the equation connecting vapor pressure in the effusion chamber with the measured intensity of the corresponding ion current I is generally written down as

$$P = CIT \quad (2)$$

where the constant $C = k/\sigma$; k is the constant of the instrument's sensitivity to a given kind of ions, σ is the cross section of molecule ionization under the electron impact.

The constant C is determined by substituting (2) into (1)

$$C = \frac{2279.62m}{KsqM^{1/2}\int IT^{1/2}\,\mathrm{d}t} \quad (3)$$

The integral appears here because temperature and intensity are changed when the effusion chamber reaches the required temperature regime and at the final stage of the experiment, when the substance is no longer present in the chamber. Substituting the constant C (3) into Eq. (2) we obtain an equation for calculating pressure on the basis of experimentally measured values

$$P = \frac{2279.62mIT}{KsqM^{1/2}\int IT^{1/2}\,\mathrm{d}t} \quad (4)$$

The main disadvantage of experiments carried out at one fixed temperature is complexity of controlling the sensitivity of mass spectrometric instrument during measurements, which requires much time.

For experiments with mass spectrometric recording of the amount of effusing substance, the possibility exists to carry out measurements at several fixed temperature points within one experiment[13] with simultaneous measurements of the intensity of ion current and temperature. For this case, pressure is calculated using Eq. (4)

$$P_i = \frac{2279.62mI_iT_i}{S_{\mathrm{eff}}M^{1/2}\sum_i\int_0^t I_iT_i{}^{1/2}\,\mathrm{d}t} \quad (5)$$

where P_i is vapor pressure under isothermal conditions at a temperature T_i, m (g) is the amount of the substance evaporated during the whole experiment; $\boldsymbol{I_i}$ is the intensity of ion current at the established temperature T_i; M is molecular mass, I_i and T_i are current values of the intensity of ion current and temperature, $S_{\mathrm{eff}} = Ksq$.

In comparison with an experiment at one fixed temperature, the use of this procedure provides a substantial decrease in the time consumed for investigating temperature dependence of vapor pressure. In addition, in these experiments, temperature of the effusion chamber can be changed stepwise in any direction: rise, then decrease and vice versa, exposing the substance under isothermal conditions during the necessary time interval. This allows monitoring the sensitivity of mass spectrometer during the experiment, because equality of the recorded ion current measured for equal temperature with such a scanning procedure is a criterion of the stability of the sensitivity of instrumentation.

Since the substance is sampled from the vapor phase during an experiment, in order to maintain the state close to the equilibrium one it is necessary that the rate of effusion be negligibly small in comparison with the rate of saturation of the volume with the vapor. In a general case, the equilibrium vapor pressure in the effusion chamber is described by equation:

$$P_{\mathrm{eq}} = P_{\mathrm{exp}}\left(\frac{1+Ksq}{A\alpha}\right) \quad (6)$$

where P_{eq} is the equilibrium saturated vapor pressure, P_{exp} is the observed pressure calculated according to the Hertz–Knudsen equation from effusion experiments, A is the surface area of the material under investigation (which is unknown in the majority of cases), α is evaporation coefficient, K is Klausing factor. Provided that

$$\left(\frac{Ksq}{A\alpha}\right) \ll 1, \quad P_{\mathrm{eq}} = P_{\mathrm{exp}}$$

It is possible to measure the evaporation coefficient α experimentally; however, it is difficult to measure the surface

Table 1
Coefficients in equation $\ln(P/\mathrm{Pa}) = B - A/T$ for Cr(acac)$_3$ vapor pressure measured with different diameters (d) of effusion hole, and correction factor

d (mm)	Temperature range T (K)	A	B	Number of points	Correction $(1 + Ksq/A\alpha)$
0.2	320–388	15350 ± 90	39.30 ± 0.10	13	1.028
0.3	323–386	15280 ± 240	39.05 ± 0.07	10	1.075
0.4	327–383	15330 ± 90	39.14 ± 0.07	10	1.145
0.45	327–380	15450 ± 210	39.40 ± 0.10	17	1.195

area of the substance to be evaporated. The $A\alpha$ value can be determined by measuring vapor pressure at the same temperature for different dimensions of the effusion hole. Using Eq. (6) one can determine the Aα value on the basis of experimental data according to equation

$$A\alpha = \frac{\Delta(P_{\mathrm{exp}}Ksq)}{\Delta P_{\mathrm{exp}}} = \frac{\mathrm{d}(P_{\mathrm{exp}}Ksq)}{\mathrm{d}P_{\mathrm{exp}}} \qquad (7)$$

In the present work, in order to determine α we applied the procedure involving measurements of vapor pressure at several fixed temperature points in one experiment with the help of mass spectrometric instrumentation [13,14], We investigated Cr(acac)$_3$ vapor pressure in the effusion chamber with the holes (d = 0.2, 0.3, 0.4, 0.45 mm) and the length of the channel 0.2 mm within temperature range 320–388 K. A cylindrical effusion chamber with the inner cavity diameter 8 mm 5 mm high was made of molybdenum. In order to measure the surface area of the evaporating substance, Cr(acac)$_3$ was evaporated through a mask 6 mm in diameter onto silicon substrates. A substrate was placed on the bottom of the effusion chamber. The temperature of the chamber was set with a precise sensitive isodromic thermoregulator PIT-3, which allowed maintaining constant temperature with an accuracy of 0.1°. A reference calibrated Pt/PtRh thermocouple was attached to the central part of the bottom of the effusion chamber. The amount of matter in the films was varied within (1.2–2) mg.

The results typical for these experiments are shown in Fig. 1 for the effusion hole 0.2 mm and the amount of substance on the film 2 mg.

The data shown in Fig. 1 indicate that the sensitivity of instrumentation did not change during the experiment. Similar results were obtained in experiments with other effusion chambers.

Eq. (5) was used to calculate pressure. The results of measurements are listed in Table 1. Using the obtained data and Eq. (7), we calculated the mean of evaporation coefficient $\alpha \leq 0.02$ for $A \geq 28.3\,\mathrm{mm}^2$. A correcting factor by which the measured pressure should be multiplied, depending on the size of effusion hole, is listed in the last column of the Table taking into account the α value.

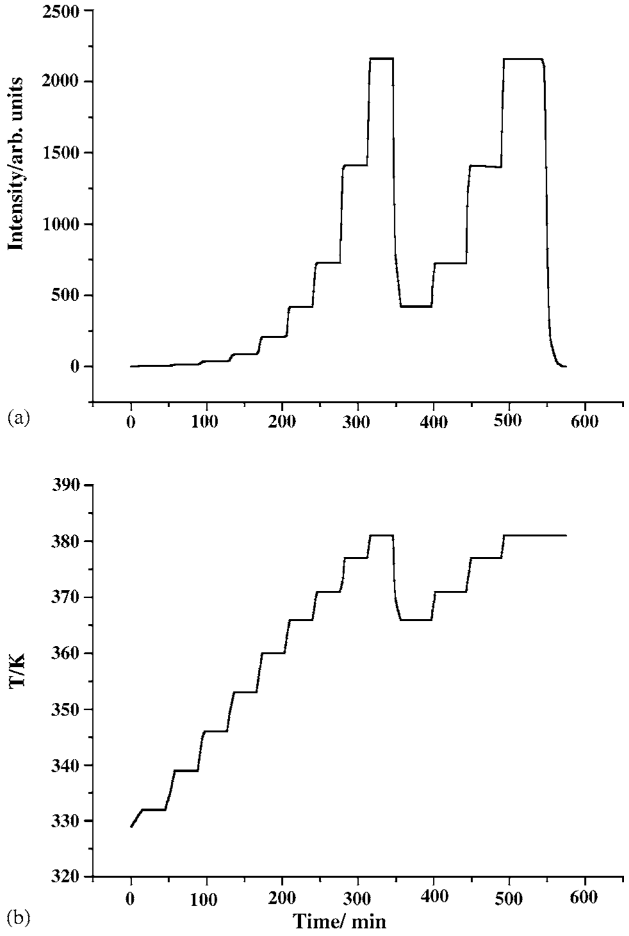

Fig. 1. The profile of intensity of the ion current of Cr(acac)$_3$ (a) and temperature (b) with stepwise temperature scanning.

Taking into account correction $Ksq/A\alpha$ in Eq. (6), saturated vapor pressure values for Cr(acac)$_3$ at a temperature of 330 and 380 K are shown in Table 2.

Table 2
Pressure P (Pa) of saturated Cr(acac)$_3$ vapor measured in effusion chamber with different hole diameters (d, mm), taking into account correction factor $(1 + Ksq/A\alpha)$

T (K)	$P = f(d)$				Average value P
	d = 0.2	d = 0.3	d = 0.4	d = 0.45	
330	7.55×10^{-4}	7.56×10^{-4}	7.46×10^{-4}	7.26×10^{-4}	7.45×10^{-4}
380	0.343	0.34	0.344	0.341	0.342

Saturated vapor pressure measured using effusion procedure is limited from above by 0.1–1 Pa. In many cases it is necessary to known the composition of the gas phase at higher vapor pressure of the substances used in the processes during their purification by means of vacuum sublimation and during MOCVD procedure.

2.3. *The calibrated volume method (CVM) for measuring saturated vapor pressure*

In order to broaden the possibilities of mass spectrometry for measuring saturated vapor pressure in the region of several thousand Pa, we propose mass spectral method of measuring partial pressure of saturated vapor: “calibrated volume method” (CVM).

The essence of the proposed method is sampling a portion of vapor which is in equilibrium with condensed substance into a batch of calibrated volume, followed by measuring the amount of vapor in this portion with the help of mass spectrometer. Actually, the proposed method of measuring saturated vapor pressure is a version of the static method. A set-up which is shown schematically in Fig. 2 was developed to implement this method.

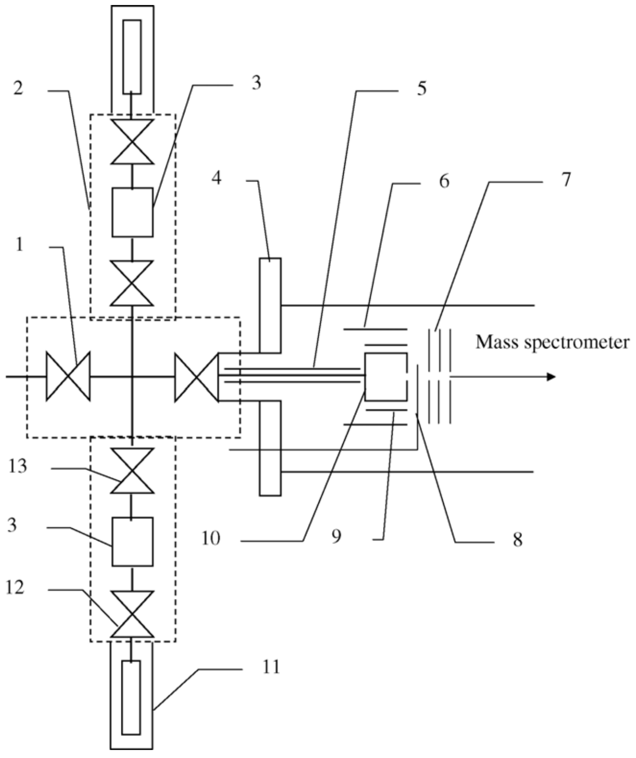

Fig. 2. A scheme of the set-up in which vapor pressure is measured by means of CVM. (1) Vacuum valve; (2) thermostats; (3) batcher; (4) flange to the ion source of mass spectrometer; (5) gas pipeline heater; (6) cooled screen; (7) ion source; (8) damper; (9) heater of the effusion chamber; (10) effusion chamber; (11) evaporator; (12) valve connecting evaporator with the batcher; (13) valve connecting batcher with the system of substance input into mass spectrometer.

The substance under investigation is placed into one of evaporators 11, it is evacuated to the working pressure in the mass spectrometer under the required temperature of evaporator, thermostat and tubing connecting the evaporator with the effusion chamber. Then, with the closed valve 13, which cuts the batcher off the tubing, temperature of evaporator and thermostat is set. After the system reaches its temperature regime, the equilibrium vapor pressure is established in the evaporator and in batcher. After that, the evaporator is cut off the batcher by valve 12; the sampled vapor portion is fed from the batcher to mass spectrometer. A criterion of established equilibrium is constancy of the integral intensity of the corresponding ion current for different exposure of the evaporator-batcher system. Such a procedure is carried out for each predetermined temperature of the substance. Temperature of thermostat can be equal to the temperature of evaporator or higher than it, which is dictated by experiment. Temperature of effusion chamber forming the molecular beam into the ion source of mass spectrometer is kept constant during the whole experiment and is chosen so that the saturated vapor pressure of the substance under investigation does not exceed 0.67 Pa, while the constant temperature for the tubing through which the vapor is admitted into the effusion chamber is set at a higher level. With such an arrangement of the experiment, the measured pressure value is almost unlimited from above, because, provided that vapor pressure in the evaporator is higher than 0.67 Pa, partial condensation of the vapor in the effusion chamber occurs; quasi-equilibrium pressure corresponding to the temperature of the effusion chamber is established. In order to monitor the sensitivity of mass spectrometer during experiment, the same compound or standard is placed in another evaporator. Temperature of this evaporator is kept constant during the whole experiment, that is, vapor pressure in it is constant.

In our experiments on investigation of $Cr(acac)_3$ vapor pressure, we used this compound also to monitor the sensitivity.

The isotherms of time dependence of the ion current intensity for the molecular peak of $Cr(acac)_3$ are shown in Fig. 3. The B, C, D curves describe the case when the pressure of the substance in the evaporator is below 1.33 Pa, the F, G, H curves describe the behavior of the ion current intensity at higher pressure.

Keeping in mind that the integral intensity of ion current is proportional to the number of molecules passing through the ionization zone of the ion source of mass spectrometer during time t, we may write down the following equation

$$N_i = c \int I_i \, \mathrm{d}t + N_\mathrm{d} \qquad (8)$$

where i relates to temperature of the substance, c is a constant, N_d is a constant number of molecules remaining in the volume of the inlet system, including batcher, the concentration of which is beyond the limits of sensitivity of the instrument.

It is evident that the number of molecules that passed through mass spectrometer in i portions during the whole

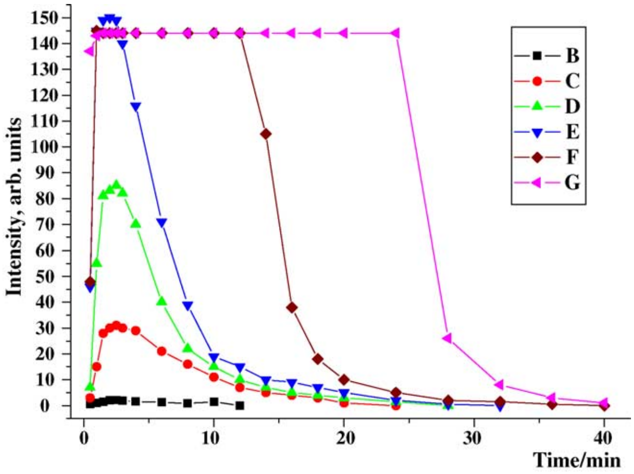

Fig. 3. Time dependencies of the ion current intensity for the molecular peak of Cr(acac)$_3$ for the portions of the equilibrium vapor sampled under equal temperature of evaporator and batcher: (B) 393 K, (C) 425 K, (D) 435 K, (E) 440 K, (F) 458 K, (G) 468 K. Temperature of the effusion chamber is constant and equal to 388 K.

time of experiment is equal to the sum of N_i (8); N_i can be easily determined on the basis of the experimental data if the mass of the evaporated substance W is known.

$$N_i = \frac{mN_\mathrm{A}(N_\mathrm{d} + \int I_i\,\mathrm{d}t)}{M\sum(N_\mathrm{d} + \int I_i\,\mathrm{d}t)} \tag{9}$$

Here N_A is Avogadro number.

Having divided this equation by V (cm^3) — the volume of the batcher, we obtain the concentration of saturated vapor at the substance temperature point number i. Using equation for pressure $P = nkT$ and keeping in mind that temperature of the batcher can be higher than the temperature of the substance, we obtain an equation to calculate pressure on the basis of the experimental data obtained by means of the CVM

$$P = \frac{6.23 \times 10^4 m(T_iT_v)^{1/2}(N_\mathrm{d} + \int I_i\,\mathrm{d}t)}{MV\sum(N_\mathrm{d} + \int I_i\,\mathrm{d}t)} \tag{10}$$

where T_i and T_v are temperature of evaporator and batcher, respectively, $T_v \geq T_i$.

The volume of batcher was (2 ± 0.002) cm^3 in our experiments, the volume of the inlet system V_s with the batcher was 10 cm^3, the sensitivity of instrument was 0.3×10^{-4} Pa. Calculation indicates that for this instrument at the vapor pressure of 0.133 Pa the contribution from N_d is 0.1% of this value, that is, much smaller than the experimental error. Because of this, pressure measured by means of the CVM is limited from below in our case by the values ≥0.133 Pa. In the general case, the contribution from N_d into the final result changes with changing vapor pressure inversely proportionally to the measured value.

Experimental data obtained by the CVM are shown in Table 3. In one case, temperature of batcher was equal to that of the evaporator $T_v = T_i$, while in another case the batcher temperature was $T_v = \text{const} = 500$ K. The last column of Table 3 shows the results of the effusion experiment for the chamber with the hole 0.2 mm in diameter.

3. Results and discussion

Analysis of temperature dependence of the mass spectra indicated that relative intensities of the fragments in the mass spectrum of Cr(acac)$_3$ remains unchanged within the whole temperature range investigated. This circumstance proves the presence of mainly monomer Cr(acac)$_3$ molecules in the gas phase. Therefore, vaporization process can be represented as follows:

$$\mathrm{Cr(acac)}_{3,\mathrm{s}} = \mathrm{Cr(acac)}_{3,\mathrm{gas}}$$

Table 3
Sublimation pressure for chromium acetylacetonate

"CVM" procedure				Effusion procedure	
Series no. 1, $T_v = 500\,^\circ\mathrm{C} = \text{const}$		Series no. 2, $T_v = T_i$		Series no. 3	
T (K)	P (Pa)	T (K)	P (Pa)	T (K)	P (Pa)
384.15	0.556	387.15	0.653	320.15	1.6799E−4
391.15	1.109	404.15	3.733	327.15	5.0662E−4
402.15	3.066	409.15	5.866	333.15	0.00127
404.15	3.586	421.15	18.26	341.15	0.00333
409.15	5.693	432.15	41.99	348.15	0.00840
421.15	17.60	442.15	97.72	355.15	0.02053
432.15	42.13	452.15	212.0	362.15	0.04600
442.15	98.79	458.15	330.6	369.15	0.10972
452.15	220.0	463.15	466.6	376.15	0.22531
458.15	334.0			382.15	0.43996
463.15	480.0			388.15	0.7626
468.15	639.0				
476.15	1109.0				

In this case, saturated vapor pressure is expressed by equation:

$$P = k\ \exp\left[-\frac{\Delta H^\circ(T_0)}{RT} + \frac{\Delta S^\circ(T_0)}{R} + \varphi(\Delta C_\mathrm{p}, T)\right] \qquad (11)$$

Here P is measured pressure at temperature T, k 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, $\varphi(\Delta C_\mathrm{p}, T)$ (where $\Delta C_\mathrm{p} = C_{\mathrm{p(gas)}} - C_{\mathrm{p(condensed\ phase)}}$) is some function of temperature, determined by changes in heat capacity during vaporization, T is temperature in K.

Experimental data shown in Table 3 (33 points) were processed using the criterion function

$$\psi = \frac{\sum_i^N (P_{i(\mathrm{exp})} - P_{i(\mathrm{calc})})^2}{W_i} \qquad (12)$$

$$W_i = \Delta P_i^2 + \left(\frac{\mathrm{d}P}{\mathrm{d}T}\right)_i^2 \Delta T_i^2$$

where N is number of points in the experiment, $P_{i(\mathrm{exp})}$ is experimental pressure, $P_{i(\mathrm{calc})}$ is pressure calculated using Eq. (11).

The criterion function (12) is a sum of squares of standardized digressions; their dispersions at correctly chosen ΔP_i and ΔT_i are almost independent of temperature and accuracy of measurements, while averages of distribution are equal to zero. Point estimates obtained using the criterion function (12) meet the principle of maximal likelihood. The use of the criterion function (12) for processing the data provides obtaining more reliable estimations of enthalpy and entropy of vaporization which are to be determined.

Search for a minimum of ψ was carried out with the help of the program based on the algorithm of the modified Newton–Gauss procedure.

Errors of the sought quantities were calculated taking into account Student coefficients for the 95% confidence interval.

The data were processed according to the second law, that is, the sought values were $\Delta_\mathrm{sub}H^\circ$ (T) and $\Delta_\mathrm{sub}S^\circ$ (T), $\varphi(\Delta C_\mathrm{p}, T)$ was accepted to be zero because of the absence of reliable data on thermal capacity for solid and gaseous chromium(III) acetylacetonate. The result of calculations was: $\Delta_\mathrm{sub}H^\circ$ $(T) = 127.28 \pm 0.22\ \mathrm{kJ\ mol^{-1}}$ and entropy $\Delta_\mathrm{sub}S^\circ$ $(T) = 230.1 \pm 0.5\ \mathrm{J\ mol^{-1}\ K^{-1}}$.

$$\ln P\,(\mathrm{Pa}) = 39.197 - 15308.5T \quad 320 \le T\,(\mathrm{K}) \le 476 \quad (13)$$

Deviations (in per cent) of the experimental data from pressure values calculated according to Eq. (13) are shown in Fig. 4

One can see from the figure that scattering of points within the entire temperature range is random from one series to another. This fact points to the absence of any essential systematic errors in the experiments performed both with the help of the effusion method and by the CVM.

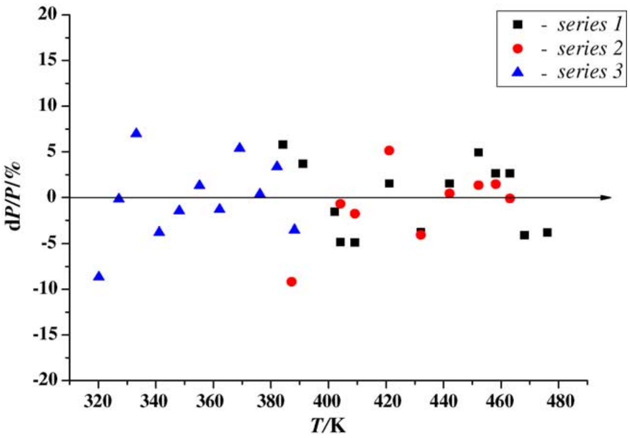

Fig. 4. Deviations (in %) of the experimental data from pressure values calculated according to Eq. (13).

The data on sublimation pressure of $\mathrm{Cr(acac)_{3,s}}$ obtained in the present investigation and also the values available from literature are shown in Fig. 5.

One can see that our results are in good agreement with the data [7] obtained by means of Knudsen's effusion method with mass spectral analysis of the composition of the gas phase within temperature range 350–375 K. Pressure is low within this temperature range, and Knudsen's method gives reliable results.

Within the medium temperature region (about 360 K) rather good agreement is observed (within 5–20%) with the data of the works [1,2], but for increased temperature 400–421 K the deviation increases sharply (the values obtained in [1,2] are 60–120% lower than our results). The authors of [1] used spectrophotometry. The reliability of the applied procedure is insufficiently substantiated. For instance, the method was verified using benzoic acid

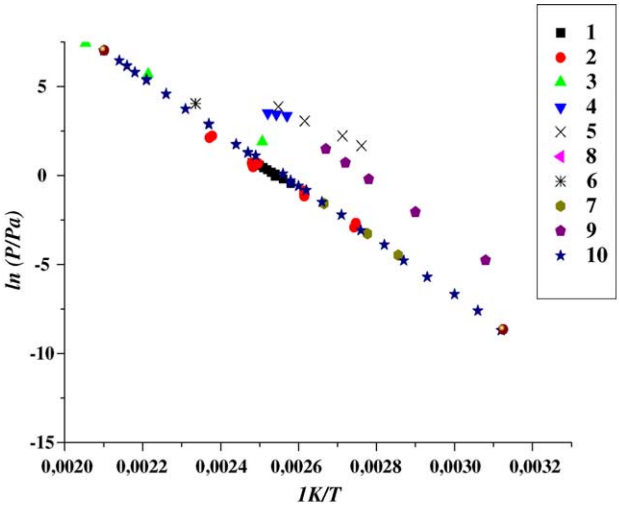

Fig. 5. Temperature dependence of $\mathrm{Cr(acac)_3}$ vapor pressure. Series 1–9 are literature data, series 10 are the results of the present investigation.

within temperature range 338–370 K, while measurements for $Cr(acac)_{3,s}$ were carried out within the range 383–403 K. The melting point of the sample investigated by these authors is somewhat overvalued 489 K.

The authors of [2] apply the flow procedure and determine the amount of the substance carried off; ultraviolet spectroscopy was involved. Quantitative data concerning the purity of the sample are not reported, but, according to the authors' statement, the upper temperature limit of investigation 421.7 K is due to the start of decomposition of the sample (for comparison, let us remind that in our work the upper limit of measurements was 476 K; no indices of decomposition were observed). It should also be noted that there are no proofs of the achievement of equilibrium in the experiments, which are obligatory when the dynamic methods are used.

Within the medium temperature range, there are three more works reporting the values much larger than those obtained by us [4,5,9]. Isoteniscope procedure is used in the works [4,5]; incorrectness of its application has already been discussed [9]. It is difficult to explain the reasons of deviations with the results of the work [9]. We may only note that the results of the same authors on $Cr(acac)_3$ sublimation reported in their next publication [7] are in very good agreement with our data. The data obtained by the authors of [10] are in satisfactory agreement with our data in the absolute value of pressure within the medium temperature range; however, thermodynamic parameters reported by these authors are lower than those obtained by us. Since the cited investigation dealt with vapor pressure studying it by means of effusion using small weighed portions of the crystal compound, the deviations are explained by a decrease in the surface of the substance during its evaporation, which inevitably causes a decrease in the pressure value calculated according to Eq. (5).

Within the high temperature range, there are three papers [3,6,8] published by one research team. The research procedure is chromatographic, based on the connection between retention time measured in chromatographic analysis and the pressure of vapor of the substance under chromatographic examination. The results obtained in the newest work [6] are most close to the values obtained by us. The values obtained by the authors within the whole temperature range investigated 428–483 K are larger than our results by 40%. The absence of any information about identification of the substance under investigation, poor validity of the reliability of the procedure used in the investigation, discordance between the reported data (pressure of $Cr(acac)_3$ sublimation at a temperature of 483 K, calculated using the equation for sublimation), is equal to 3253 Pa, while the value reported in the same paper, calculated using the evaporation equation at the same temperature 483 K, is 1106 Pa can be the reasons of deviations from out data. $Cr(acac)_3$ vapor was measured also using the static method using a membrane zero manometer [11]. The results of this work are in good agreement with our data.

4. Conclusion

With regard to

- the reasons of possible systematic errors in the cited works were revealed in the analysis of the available literature data;
- experimental data obtained in the present investigation with the help of two procedures (one of them is Knudsen's effusion procedure with mass spectrometric analysis of the composition of the gas phase, which proved to be good in measuring low pressure; the second is CVM, which helped us to expand the possibilities of the effusion method toward high pressure range) are in good agreement with each other;
- the measurements were carried out within a broad temperature range $320 \leq T\,(\mathrm{K}) \leq 476$, which allowed simultaneous determination of enthalpy and entropy of the process with high accuracy,

we recommend to use the results of the present investigation as reference values in modeling the processes participated by chromium(III) acetylacetonate.

Some advantages of the proposed mass spectrometric procedure CVM for the investigation of partial pressure of saturated vapor of complicated compounds in comparison with the generally accepted Knudsen effusion method should be mentioned:

- broad range of the measured saturated vapor pressure values with simultaneous identification of the composition of the gas phase;
- absence of errors connected with the necessity to take into account the parameters of the effusion chamber;
- possibility to investigate small weighed portions of not easily available compounds.

It should be noted that the procedure involving dosated sampling of the gas phase (CVM procedure) can be used to investigate saturated vapor pressure without using the effusion chamber. In this case, pressure can be measured within a broad range for thermally stable compounds, if the size of batcher and condensing device are chosen properly. In addition, if temperature dependence of saturated vapor pressure is known, the proposed method of vapor sampling allows admitting precisely dosed substance into the reactor during guided synthesis of film structures.

References

[1] T.P. Melia, R. Merrifield, J. Inorg. Nucl. Chem. 32 (1970) 1489.
[2] H.-J. Gotze, K. Bloss, H. Molketin, Z. Phys. Chem. (Frankfurt am Main) 73 (1970) 314.
[3] Zh.N. Bublik, E.A. Mazurenko, S.V. Volkov, Ukr. Khim. Zhurn. 44 (1978) 1214.
[4] J.L. Wood, M.M. Jones, Inorg. Chem. 3 (1964) 1553.
[5] R. Fontaine, C. Pommier, G. Guiochon, Bull. Soc. Chim. Fr. 8 (1972) 3011.

[6] E.A. Mazurenko, A.I. Gerasimchuk, Ukr. Khim. Zhurn. 59 (1993) 526.
[7] I.P. Malkerova, A.S. Alikhanyan, V.G. Sevastyanov, Ya.Kh. Grinberg, V.I. Gorgoraki, J. Inorg. Chem. USSR 35 (1990) 413 (Engl. Transl.).
[8] S.V. Volkov, E.A. Mazurenko, Zh.N. Bublik, Ukr. Khim. Zhurn. 44 (1978) 570.
[9] A.S. Alikhanyan, I.P. Malkerova, Ya.Kh. Grinberg, V.B. Lazarev, V.A. Bogdanov, V.I. Gorgoraki, V.A. Shreides, Russ. J. Phys. Chem. 292 (1987) 376 (Engl. Transl.).
[10] P.P. Semyannikov, I.K. Igumenov, S.V. Trubin, I.P. Asanov, J. Phys. IV 11 (2001) 995 (France).
[11] I.K Igumenov, Yu.V. Chumachenko, S.V. Zamskov, in: V.I. Spitzin (Ed.), Problems of Chemistry and Application of Metal β-Diketonates, Moscow, Nauka, 1982, pp. 100–120.
[12] V.N. Naumov, G.I. Frolova, V.V. Nogteva, P.A. Stabnikov, V.A. Nadolinny, Yu.G. Shvedenkov, I.K. Igumenov, Chem. Sustainable Dev. 8 (2000) 185.
[13] L.N. Sidorov, M.V. Korobov, L.V. Zhuravleva, Mass Spectrometric Thermodynamic Investigations, Publishing House of the Moscow University, Moscow, 1985, p. 208.
[14] V.M. Grankin, P.P. Semyannikov, Pribory e Technika Experimenta 4 (1991) 125 (Devices and Experimental Technology, Engl. Transl.).