

Thermodynamics of chromium acetylacetonate sublimation

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Abstract

The equilibrium sublimation pressure $\text{Cr}(\text{acac})_3(\text{s})=\text{Cr}(\text{acac})_3(\text{g})$ was measured in the range $320 \leq T \text{ (K)} \leq 476$ 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 $\ln(P \text{ (Pa)})=39.197-15\,308.5/T$, enthalpy $\Delta_{\text{sub}}H^\circ(T)=127.28 \pm 0.22 \text{ kJ mol}^{-1}$ and entropy $\Delta_{\text{sub}}S^\circ(T)=230.1 \pm 0.5 \text{ J mol}^{-1} \text{ K}^{-1}$.

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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 $\text{Cr}(\text{acac})_3$. 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 ($\geq 10^3 \text{ Pa}$) recording the qualitative and quantitative composition of the gas phase with the help of mass spectrometry,
- investigation of $\text{Cr}(\text{acac})_3$ saturated vapor pressure,
- analysis of the entire set of experimental data on $\text{Cr}(\text{acac})_3$ vapor pressure.

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2. Experimental

2.1. Materials

The samples for investigation were synthesized using a known procedure [11,12] starting with $\text{CrCl}_3 \cdot 10\text{H}_2\text{O}$ 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 $\text{Cr}(\text{acac})_3$.

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 $\text{Cr}(\text{acac})_3$ 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:

$$P \text{ (Pa)} = \frac{m}{(Ksq t)(2\pi RT/M)^{1/2}} \\ = 2279.62 \left(\frac{T}{M} \right)^{1/2} \frac{m}{Ksq t} \quad (1)$$

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 Klause 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)

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

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 mea-

sured values

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

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)

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

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; 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, $S_{\text{eff}} = Ksq$.

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:

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

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 Klause factor. Provided that

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

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

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