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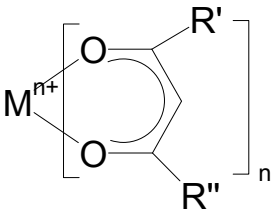
Volatile Precursors for Films Deposition: Vapor Pressure, Structure and Thermodynamics

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1. Introduction

At present the processes of chemical vapour deposition (MO CVD) and physical vapour deposition (PVD) are widely used to obtain the layers of different materials. A possibility to obtain materials of the required composition (elementary, complex, composite, etc.) is determined by the chemical nature of a precursor. By now a set of criteria for the precursors to meet the MO CVD and PVD standards have already been established (Maury, 1995). Among the parameters from which the choice of a precursor is made, the most important one is its ability to transfer to the gaseous phase at temperatures not exceeding the temperature of molecules decomposition, i.e., its volatility. The most important quantitative characteristic of volatility is the pressure of saturated vapour of the compound at defined temperature. A number of experimental data showing volatility of different classes of metal complexes with organic ligands are known. Practically all precursors crystallize in lattices of a molecular type. The relation to molecular crystals suggests that energy of intermolecular interaction is much less than the energy of intramolecular bonding. The structure of metal complexes with organic ligands is determined by different factors depending on the nature of metal and coordinated ligands.

The current review summarizes the data of saturated vapor pressure and thermodynamic parameters of the sublimation process of some complexes with organic ligands as reported in the literature as well as in our works. Dependence of volatility on type of substituents in the ligand, on central atom, and on donor atom in the ligand is discussed using metal β -diketonate (Chart 1) and phthalocyanine (MPc) derivatives as examples. The volatility of metal β -diketonates and phthalocyanines is analysed from the standpoint of their molecular and crystal structure. One important aspect of chemistry of precursors for MO CVD and PVD is a possibility to predict volatility from the data of the compound structure. A description of the microscopic model created in the framework of the statistical mechanics to describe the volatility of metal complexes with organic ligands is given. It follows from the structural studies that interatomic spacing in a molecule is comparable to interatomic spacing in different adjacent molecules. With such location of the molecules of complexes in the crystal lattice, it is necessary to take into account both van der Waals and electrostatic interactions. The correlation between these interactions determines the specific features of the behavior of this class of molecular crystals.



R'	R''	Name	Abbreviation
CH ₃	CH ₃	pentane-2,4-dionate (acetylacetonate)	aa
C(CH ₃) ₃	C(CH ₃) ₃	2,2,6,6-tetramethylheptane-3,5-dionate (dipivaloylmethanate)	dpm
CF ₃	C(CH ₃) ₃	1,1,1-trifluoro-5,5-dimethylhexane-2,4-dionate (pivaloyltrifluoroacetate)	pta
CH ₃	C(CH ₃) ₃	2,2-dimethylhexane-3,5-dionate (pivaloylacetonate)	pva
CF ₃	CF ₃	1,1,1,6,6,6-hexafluoropentane-2,4-dionate (hexafluoroacetylacetate)	hfa
C ₆ F ₁₁	C ₆ F ₁₁	1,5-di(undecafluorocyclohexyl)-pentane-2,4-dionate	dhfa
CF ₃	CH ₃	1,1,1-trifluoropentane-2,4-dionate (trifluoroacetylacetate)	tfa
C ₆ H ₅	C ₆ H ₅	1,3-diphenylpropane-1,3-dionate (dibenzoylmethanate)	dbm
C ₆ H ₅	CH ₃	1-phenylbutane-1,3-dionate (benzoylacetonate)	ba
C ₆ H ₅	CF ₃	1-phenyl-4,4,4-trifluorobutane-1,3-dionate (benzoyltrifluoroacetate)	btfa
CH ₃	CH ₃	pentane-2-on-4-iminate (ketoiminate) / N atom in place of one O atom	ki
CH ₃	CH ₃	pentane-2,4-diiminate (diiminate) / N atoms in place of O atoms	diim
CH ₃	CF ₃	1,1,1-trifluoropentane-2-on-4-iminate / N atom in place of one O atom	ktfa

Chart 1. Structure of metal β -diketonate molecules and notation conventions of the names of some metal β -diketonates

2. Experimental data on measuring temperature dependence of vapor pressure for metal complexes with organic ligands

2.1 General considerations, the macroscopic approach

The process of sublimation and evaporation of different compounds including complexes of metals with organic ligands is related to the phase transitions of the first order which are described in thermodynamic approach by the Clausius-Clapeyron (CC) equation (Callen, 1985). The temperature dependence of equilibrium pressure in the gaseous phase $P(T)$ is

derived from CC equation by integration after introduction of a number of assumptions (Callen, 1985):

$$\ln P(T) = q / RT + B \quad (1)$$

where heat of transition is chosen as $q = -\Delta_e h$, where $\Delta_e h$ is enthalpy of transition at a certain pressure and temperature T_o , while the constant of integration B is found in different models and is commonly chosen as $B = \Delta_e s / R$, where $\Delta_e s$ is entropy of crystal-vapor transition at $P(T) = 1$ atm and $R = N_o k$, where k is the Boltzmann constant and N_o is the Avogadro constant. Formula (1) makes it possible to find $\Delta_e h$ and $\Delta_e s$ from the experimentally obtained relationship $\ln P(T) = f(T)$. However, for unambiguous description of a thermodynamic system additional information on the composition of vapor is needed since different processes associated with changes of the molecular mass, eg. oligomerization or dissociation, may proceed in the gaseous phase.

2.2 Methods of vapor pressure measurements, limitations and specific features of compounds

The absolute value of measured pressure in the first place and thermal stability of the investigated compound in the second place are of crucial importance when the method for investigation of the saturated vapor pressure is chosen. There are well known methods for the study of heterogeneous equilibrium in which gaseous and condensed phases take part; those methods may be classified into static, quasistatic, dynamic (flow method and Langmuir method) and kinetic (Knudsen effusion) methods (Margrave, 1967; Ingram & Drauart, 1962). Different methods may be used to study different ranges of vapor pressure and temperatures. Most of the results of measurement of saturated vapor pressure for volatile compounds have been obtained by different variants of the static method, flow method and Knudsen method as well. All these methods in different modifications have been used for measurements of the temperature dependence of the saturated vapor pressure of precursors.

2.2.1 Static methods of vapor pressure measurements

In the static methods, measurement of vapor pressure is carried out in a closed vessel (Beech & Lintonbon, 1971; Margrave, 1967). The temperature of the vessel is maintained constant to establish equilibrium between the condensed phase and vapor. The equilibrium pressure is determined either directly with a measuring instrument – mercury, ionization, spiral, membrane or other type of manometer (direct methods), or by determination of the substance amount in the known volume (indirect methods). The method allows approaching the equilibrium both from the “bottom” and from the “top”, which is one of its main advantages. This method allows determining the overpressure arising in the system due to thermal dissociation of the precursor at a given temperature. The most acceptable range of pressure measured by this method is 1-760 Torr.

2.2.2 Flow method

In this method, a flow of inert gas is passed over a heated substance and carries the substance vapors into the condenser (Beech & Lintonbon, 1971; Margrave, 1967). The quantity is determined by the weight, chemical analytical or radiation method. The vapor pressure of the substance p is determined by the Henry law: $p = P^* n / (n + N)$, where P is the

total pressure; n is the number of moles of the transferred substance and N is the number of moles of the inert gas.

The method is applicable for measurement of low vapor pressures of precursors. The dynamic range of the measured pressures is from 10^{-3} to 1 Torr. The main advantage of the flow method is the possibility of measurement of the precursor partial pressure against a background of its decomposition. If the compound exists in several molecular forms in the vapor phase, the measured pressure is averaged. In this case for calculation of the thermodynamic parameters of vaporization it is necessary to know the ratio of these molecular forms in the vapor phase.

2.2.3 Knudsen method

Knudsen method is based on the measurement of the rate of effusion of the equilibrium vapor through a small orifice. It can be used for the measurement of extremely small values of vapor pressures - 10^{-7} – 10^{-1} Torr. Knudsen method has different modifications; the most powerful one is its combination with mass spectrometer. This variant allows controlling the composition of vapor phase during measurements.

2.2.4 Indirect methods of vapor pressure measurements

In a limited number of works, different variants of the thermal analysis (Logvinenko et al., 1998; Bublik et al., 1978) as well as gas-liquid chromatography (Irving & Ribeiro da Silva, 1976) are used for the calculation of vapor pressure values. Different calorimetric methods were also used to determine the value of sublimation enthalpy for different metal complexes with organic ligands (Ribeiro da Silva & Goncalves, 1998; Berg & Truempfe, 1960).

2.3 Analysis of adequacy of the experimental data on precursors vapor pressure

The measurement of vapor pressure for the same compounds carried out by different methods or sometimes even by the same method but performed by different investigators were not always in good agreement. The temperature dependences of vapor pressure $P(T)$ for chromium tris-acetylacetonate are presented in Fig. 1 and Table 1 for comparison.

The difference in $P(T)$ leads to rather important divergence in the values of enthalpies and entropies of sublimation. Moreover close values of the precursor vapor pressure are described by sets of thermodynamic parameters with quite different values (Table 1) in some independent measurements. In most published work neither structural modifications of the investigated complexes nor their purity were specified, while both factors have significant influence on the value of vapor pressure as well as on the value of sublimation enthalpy of the compounds. In the majority of published work the enthalpy of evaporation is used as the sole criterion for comparison of volatility of different compounds.

This approach is found to be incorrect because the differences in the volatility of various molecular complexes are described by different sets of thermodynamic parameters and the results of evaporation enthalpy change as well as entropy change should be considered. To analyze the reasons of these divergences the following parameters should be taken into account: 1 - characterizations the investigated compound (method of synthesis, purity, thermal properties); 2 - methods of vapor pressure measurement (technique details, pressure and temperature measurement errors, and limitations of the methods); 3 - analysis of observations. Hereafter, where applicable, data collection of independent measurements will be used.

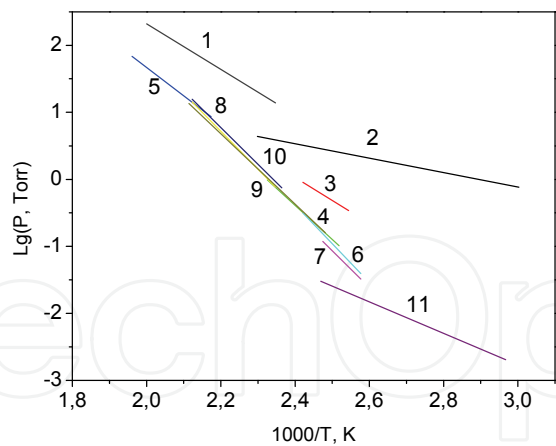


Fig. 1. LgP(1/T) dependence for Al(aa)₃ measured by different methods (Table 1)

N _o	Метод	ΔH, kJ/mol	ΔS ^o , J/K·mol	Range T, K	Ref
1	St (isoten.)	65.1	119.5	426-500	Berg & Truempe, 1960
2	St (isoten.)	20.5	4.16	333-435	Berg & Truempe, 1965
3	St (isoten.)	65.7	103.1	393-413	Fontain et. al., 1972
4	St (membr.)	96.9	170.0	397-430	Wolf et. al., 1972
5	St (membr.)	80.8±2.9	138±4	460-510	
6	St (membr.)	111±4	204	388-413	Sachinidis & Hill, 1980
7	St (bulb.)	105±2	187	388-404	Sachinidis & Hill, 1980
8	St (membr.)	108.4±1.8	197.1±3.8	426-471	Igumenov et. al., 1979
9	GLC	100.6	172.9	403-473	Bublik et. al., 1978
10	GLC	105.2	191.1	423-471	Mazurenko & Gerasimchuk, 1993
11	Knudsen	45.0±0.4	26.8±1.2	337-405	Techil et. al., 1981

Table 1. Enthalpy and entropy of sublimation of Al(aa)₃ obtained by different methods

2.4 Vapor pressure of metal β-diketonates

At present metal β-diketonate derivatives are one of the most widely used class of precursors for MO CVD. Metal β-diketonates are typical members of metal chelates. The metal β-diketonates are very good model objects because it is always possible to choose such series of compounds which have essentially different distribution of intramolecular electronic density and, accordingly, different energies of intermolecular interaction, but for all that they retain similar crystal and molecular structures.

The structure of homoligand metal β-diketonates (Chart 1) allows to change the peripheral surrounding of the molecule in the crystal lattice by variation of the type of substituents in ligand (R¹, R²=CH₃, CF₃, C(CH₃)₃, C₆H₅ etc.). It is also possible to change both the donor atom (X, Y =O, N, S) and the central metal while keeping the molecule geometric parameters and types of crystal packing very close.

2.4.1 Dependence of metal β-diketonate vapor pressure on type of substituents in ligand

Experimental data for metal β-diketonates demonstrate a very strong dependence of their saturated vapor pressure on the type of substitutes in ligand (Irving & Ribeiro da Silva, 1976;

Ribeiro da Silva & Goncalves, 1998). Typical temperature dependences of vapour pressure for Cu (Berg & Truempfe, 1960), and Pb (Fontain et. al., 1972) β -diketonates with different substitutes in ligand are given in Fig. 2. Table 2 provides the respective values of enthalpy and entropy of sublimation for these compounds. The data analysis reveals some empirical regularity in the change of saturated vapor pressure as a function of temperature depending on the type of substituents in ligand (CH_3 , CF_3 , $\text{C}(\text{CH}_3)_3$, C_3F_7 , C_6H_5 and their combinations). Substitution of both trifluoromethyl groups in ligand for methyl radicals leads to increase of the vapor pressure of monomeric β -diketonates by three or four orders of magnitude. The same order of pressure change is observed in bis- β -diketonates of Pt (Wolf et. al., 1972), Pd and tris-complexes of Al (Berg & Truemper, 1965), Ir and Rh (Sachinidis & Hill, 1980).

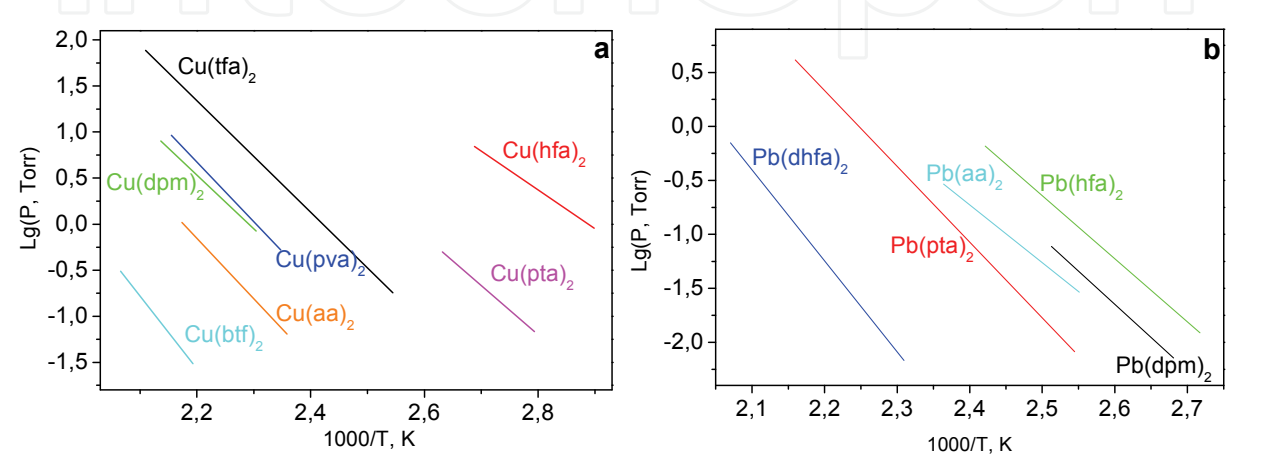


Fig. 2. $\text{LgP}(1/T)$ dependence for different Cu(II) (a) and for Pb(II) (b) β -diketonates

Compound	Method	ΔH , kJ/mol	ΔS° , J/K·mol	Range T, K
Cu(aa) ₂	membr.	125.5±9.2	218.0±20.1	424-460
Cu(tfa) ₂	membr.	115.9±0.8	225.5±2.5	393-474
Cu(hfa) ₂	membr.	80.8±1.8	178.2±5.4	345-372
Cu(dpm) ₂	membr.	111.7±4.6	200.8±8.8	434-468
Cu(pva) ₂	membr.	123.8±2.7	230.1±6.3	426-464
Cu(btf) ₂	flow	151.5±6.7	248.1±14.2	456-484
Cu(pta) ₂	flow	102.2±3.0	208.0±8.0	358-380
Pb(hfa) ₂	flow	111.7±1.3	211.8±3.2	368-413
Pb(dpm) ₂	flow	117.5±2.8	218.8±7.3	373-398
Pb(aa) ₂	flow	102.4±5.0	176.7±12.4	392-423
Pb(pta) ₂	flow	134.4±1.4	246.9±3.2	393-463
Pb(dhfa) ₂	flow	161.4±1.5	276.1±3.3	433-483

Table 2. Enthalpy and entropy of sublimation of different Cu(II) and Pb(II) β -diketonates

For zirconium tetrakis- β -diketonates (Igumenov et. al., 1979), the substitution of both trifluoromethyl groups for methyl ones leads to pressure increase by 4-4.5 orders of magnitude. Quite different situation is observed for lead bis- β -diketonates (Fig. 2b). The observed change is no more than 0.5 order at 100 °C. Moreover, the lead complex with fluorinated ligand has the lower vapor pressure than non-fluorinated one. This quite rare

situation seems to be caused by pseudo-polymeric structure of these lead complexes in the condensed phase (Mazurenko & Gerasimchuk, 1993). In the gas phase only monomeric molecules of these lead complexes have been detected. Decrease of vapor pressure with introducing fluorinated substituents was also observed for copper ethylene-diamine-bis-acetylacetonate derivatives (Techil et. al., 1981) and for dimethylgold(III) fluorinated ketoiminate derivatives (Wolf et. al., 1972). β -diketonate complexes with aromatic substitutes, eg. phenyl, have substantially lower vapor pressure. Thus, substitution of one trifluoromethyl group for phenyl group in copper hexafluoroacetylacetonate leads to decrease of the vapor pressure 5.5 orders of magnitude (Fig. 2a).

Therefore, analyzing all data presented above, we can formulate the following regularity. The vapor pressure increases with consequential introduction of fluorinated substituents into the ligand if strong specific interaction is absent in the condensed phase for bis-, tris- and tetrakis- metal β -diketonates. Introduction of bulky tert-butyl substituents into the ligand also increases the volatility insignificantly in most cases.

2.4.2 Dependence of metal β -diketonates vapor pressure on central atom

The central atom has a strong influence on the value of vapor pressure of monomeric β -diketonates. Temperature dependences of vapor pressure of different metal β -diketonates with identical ligands are shown in Fig. 3. Enthalpy and entropy of sublimation of acetylacetonates and dipivaloylmethanates of different metals are given in Table 3. The pressure change at 100 °C is 1.5 orders of magnitude for acetylacetonate derivatives (Fig. 3a) and up to 3 orders for metal hexafluoroacetylacetonates (Fig. 3c).

The aluminum and zirconium complexes are the most volatile while the platinum and iridium complexes are characterized by the lowest volatility. Lead β -diketonates demonstrate different behaviour. $\text{Pb}(\text{aa})_2$ is one of the most volatile, while $\text{Pb}(\text{hfa})_2$ has the lowest volatility among the respective derivatives.

As a whole, it is possible to claim that complexes having a planar structure possess the lower vapor pressure than the tris-complexes. This conclusion is also confirmed by the measurements of temperature dependence of vapor pressure for noble metal diethyldithiocarbamates (Igumenov et. al., 1978).

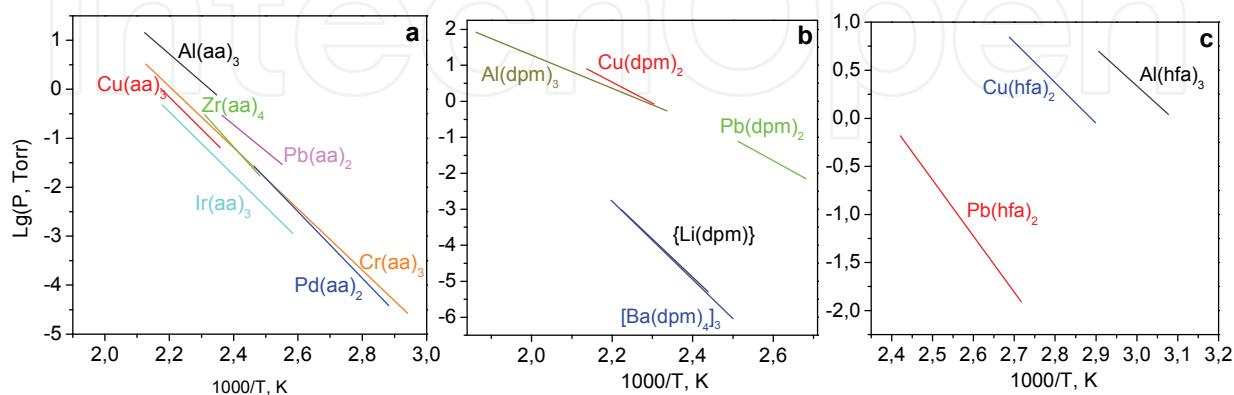


Fig. 3. $\text{Lg}P(1/T)$ dependence for acetylacetonates (a), dipivaloylmethanates (b) and hexafluoroacetylacetonates (c) of different metals

Complex	Method	ΔH , kJ/mol	ΔS° , J/K·mol	Range T, K	Ref.
Al(aa) ₃	membr.	108.4±1.8	197.1±3.8	426-471	Igumenov et al., 1979
Cr(aa) ₃	5 methods	119.7±	209.3±	340-470	Fedotova et al., 1999
Cu(aa) ₂	flow	125.5±9.2	218.0±20.1	424-460	Igumenov et al., 1978
Zr(aa) ₄	flow	138.8±4.0	255.4±9.1	403-433	Morozova et al., 1996
Pd(aa) ₂	Knudsen	130.1±2.8	235.2±7.1	347-406	Zharkova et al., 2000
Ir(aa) ₃	MCV	124.0±2.1	208.9±4.9	387-459	Igumenov et al., 1985
Pb(aa) ₂	flow	102.4±5.0	176.7±12.4	392-423	Krisyuk et al., 1998
{Li(dpm)} ₄	Knudsen	192.2±7.2	312.2±7.3	410-450	Filatov et al., 2006
Al(dpm) ₃	membr.	87.3±0.7	143.7±1.4	360-385	Igumenov et al., 1979
Cu(dpm) ₂	membr.	111.7±4.6	200.8±8.8	434-468	Igumenov et al., 1978
Pb(dpm) ₂	flow	117,5.±2.8	218.8±7.3	373-398	Krisyuk et al., 1998
[Ba(dpm) ₂] ₃	Knudsen	208.7±5.4	350.9±2.5	400-455	Alikhanyan et al., 1994

Table 3. Enthalpy and entropy of sublimation of acetylacetonates and dipivaloylmethanates of different metals

2.5 Vapor pressure of metal phthalocyanines

The literature devoted to the investigation of thermal behaviour in the gaseous phase and vapor pressure data is available only for a limited number of phthalocyanines. The detailed review of vapor pressure of some phthalocyanines is given in (Basova et. al., 2010). It was shown that the crystal structure of the investigated compound plays a significant role during these measurements. The results are expected to be largely distorted if α -MPc or the mixture of different phthalocyanine crystalline modifications are used for the measurement of saturated vapor pressure, since the $\alpha \rightarrow \beta$ phase transition is expected to proceed during these experimental conditions. In order to avoid such highly possible distortion of results, thermally stable crystal modifications were used during all our investigations; namely β -ZnPc, β -CuPc (Brown, 1968) and triclinic modification (phase ϕ_{II}) of VOPc (Ziolo et. al., 1980).

The temperature dependence of the saturated vapor pressure of the unsubstituted phthalocyanines without additional ligands in axial positions as well as those of vanadyl and titanyl phthalocyanines are presented in Fig. 4. The calculated thermodynamic parameters of vaporization are listed in Table 4. The phthalocyanines with additional ligands in axial positions M(IV)Cl₂Pc, where M=Si, Sn, or Ge, have lower vapor pressure in comparison with Sn(II)Pc which doesn't have axial ligands (Bonderman et. al., 1970; Shaulov et. al., 1972; Shaulov et. al., 1975). This is not only due to their larger molecular weights but also due to features of their crystal structure (Basova et. al., 2010).

While saturated vapor pressure data of some unsubstituted phthalocyanines are already available in the literature, data on substituted phthalocyanines in gaseous phase are scarce. The vapor pressure of only two halogen-substituted phthalocyanines, hexadecachloro- and hexadecabromophthalocyanines (H₂PcCl₁₆ and H₂PcBr₁₆) has however been studied (Bonderman et. al., 1970). Data on vapor pressure for hexadecafluorinated phthalocyanines MPcF₁₆ have been obtained for the first time by our research group and were published recently (Semyannikov et. al., 2006; Kol'tsov et. al., 2004; Semyannikov et. al., 2008). Measurements on vapor pressure for MPcF₁₆, M=Cu, Zn, VO and their unsubstituted analogues are presented in Fig. 4. The order of volatility for some unsubstituted

phthalocyanines is as follows: CuPc > ZnPc > VOPc. However, the volatility order for the fluorinated analogues of the same compounds is in the following order; CuPcF₁₆ ~ VOPcF₁₆ > ZnPcF₁₆. The ΔH_T and ΔS^o_T of these phthalocyanines increase from CuPcF₁₆ to ZnPcF₁₆. The introduction of 16 electron-acceptor fluorine atoms into the phthalocyanine ring leads to the decrease of the volatility of CuPcF₁₆ and ZnPcF₁₆ in comparison with their unsubstituted analogues while the volatility of VOPcF₁₆ becomes higher than that of unsubstituted VOPc.

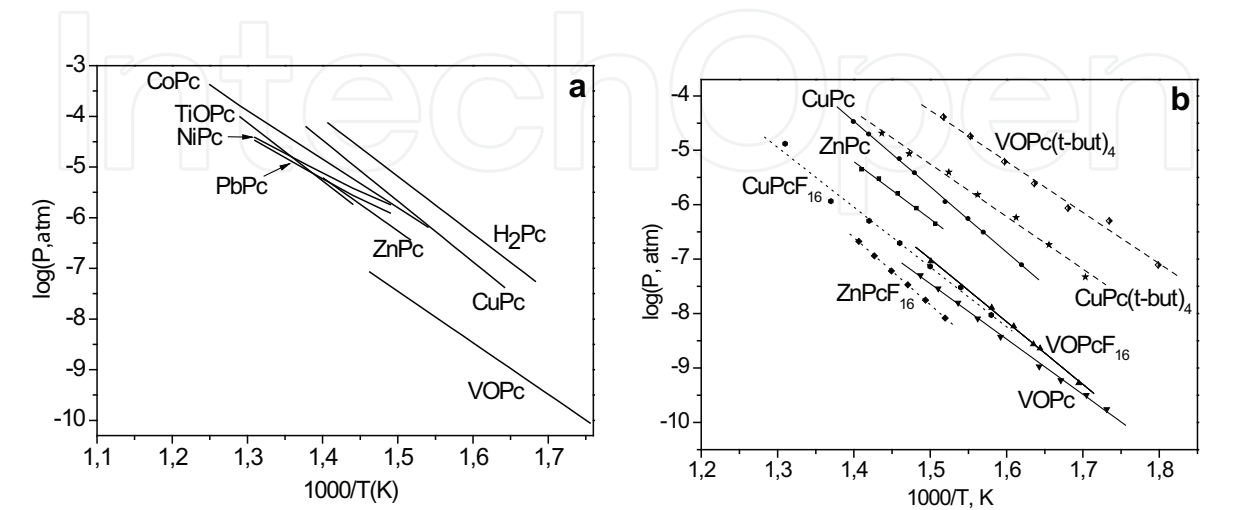


Fig. 4. Temperature dependence of saturated vapor pressure of some unsubstituted (a) and substituted (b) phthalocyanines

Compound	ΔH _T , kJ/mol	ΔS ^o _T , J/mol·K	T, °C	Ref.
β-H ₂ Pc	223.8±1.3	236.4±2.1	325-425	Semyannikov et. al., 2000
β-CuPc	231.8±2.1	238.9±2.9	345-440	Semyannikov et. al., 2000
β-ZnPc	201.3±7.9	182.4±11.3	390-438	Semyannikov et. al., 2006
CoPc	183.7±13.8	164.8±18.8	375-527	Bonderman et. al., 1970
NiPc	144.6	-	400-490	Yase et. al., 1995
PbPc	156.3	-	400-490	Yase et. al., 1995
VOPc	194.6±3.3	149.4±5.0	305-400	Semyannikov et. al., 2006
TiOPc	220.9	-	420-500	Yase et. al., 1995
AlClPc	236.4±1.7	252.7±2.5	315-430	Semyannikov et. al., 2000
AlFPc	266.9±2.5	253.9±3.7	385-495	Semyannikov et. al., 2000
(AlPc) ₂ O	509.6±2.9	527.6±3.7	485-565	Semyannikov et. al., 2000
SiCl ₂ Pc	151.0±11.7	-	341-410	Shaulov et. al., 1972
GeCl ₂ Pc	148.1±12.6	-	327-438	Shaulov et. al., 1972
SnCl ₂ Pc	218.4±17.6	196.2±25.1	427-496	Bonderman et. al., 1970
CuPcF ₁₆	200.8±7.1	163.2±9.2	360-490	Kol'tsov et. al., 2004
ZnPcF ₁₆	236.4±1.7	204.6±2.5	385-440	Semyannikov et. al., 2008
VOPcF ₁₆	220.5±4.2	197.1±7.1	320-400	Semyannikov et. al., 2008
H ₂ PcCl ₁₆	141.0±17.6	227.6±41.4	127-182	Bonderman et. al., 1970
H ₂ PcBr ₁₆	109.2±16.3	131.8±36.4	153-230	Bonderman et. al., 1970
CuPc(t-but) ₄	185.7±6.3	177.8±9.6	310-440	Plyashkevich et. al., 2010
VOPc(t-but) ₄	179.5±7.5	187.4±12.6	315-440	Plyashkevich et. al., 2010

Table 4. Thermodynamic parameters of sublimation of phthalocyanines

The difference in MPc and MPcF₁₆ (M=Cu, Zn) volatility may be explained by different crystal packing and therefore different intermolecular bonding in the solids. While the crystal structures of unsubstituted phthalocyanines are well described in the literature (Engel, 2002), the crystal structure of their fluorinated derivatives is still unknown due to some difficulties in growing their single crystals.

The suggestion that the intermolecular interaction in the unit cell of ZnPcF₁₆ is stronger than that for unsubstituted ZnPc derivative (Schlettwein et. al., 2000) was made on the basis of analysis of the electron absorption spectra using exciton model described by Kasha (Kasha, 1965) for molecular crystals of aromatic compounds. This was further confirmed by measurements and calculations found in the literature (Schlettwein et. al., 1999). Another behavior was observed for VOPc and its fluorinated derivative VOPcF₁₆. While VOPc is a nonplanar polar molecule with the vanadyl group located perpendicular to the macrocycle, the outer phenyl rings making an angle of about 7° with respect to the C-N inner ring (Ziolo et. al., 1980). Both the nonplanarity and the dipolar character of VOPc molecule result in a specific polymorphism that differs significantly from that of planar phthalocyanines (Mizugushi et. al., 1995).

Measurements of vapor pressure for Cu(II) and vanadyl tetra-tertbutyl phthalocyanines (MPc(t-but)₄) are also presented in Fig. 4 (Plyashkevich et. al., 2010). The introduction of four branched tert-butyl substituents leads to the increase of vapor pressure and the decrease of sublimation enthalpy (Table 4) in comparison with their unsubstituted analogues.

2.6 Effect of donor atoms in ligand on vapor pressure

Only the limited number of reliable data is available in literature which allows to demonstrate the influence of donor atoms on the saturated vapor pressure of the complexes. These are copper β-diketonates and their imino-derivatives (Fig. 5) as well as β-diketonates complexes of dimethylgold(III) and their imino- and thio-analogues (Semyannikov, 1988). In these examples, substitution of oxygen for another donor atom does not lead to change of the molecular structure of the complexes but influences on their vapor pressure.

In Cu(II) complexes, substitution of one of the oxygen atoms in ligand for nitrogen leads to increase of vapor pressure in the case of aliphatic ligands (Fig. 5, curves Cu(aa)₂ and Cu(ki)₂). For complexes with chelate node (O₄) and (N₄) (curves Cu(aa)₂ and Cu(NH,NH)₂, respectively), vapor pressure is practically the same. A considerable narrowing of the range of volatility change is observed for ketoiminate complexes with different type of substituents in ligand.

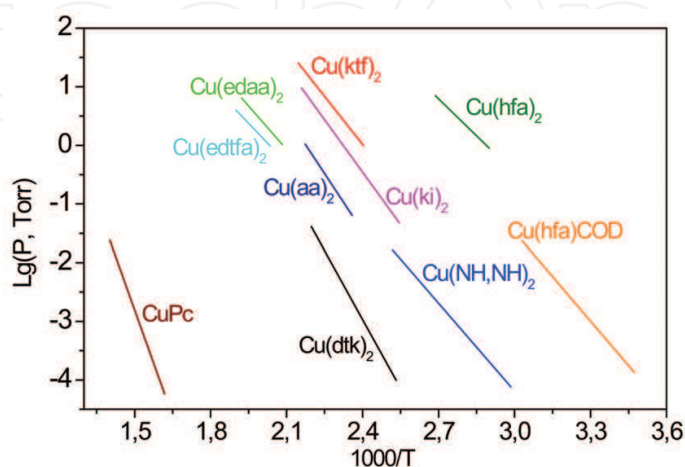


Fig. 5. Temperature dependence of vapor pressure of different Cu(II) complexes

Even more considerable changes of the volatility are observed for tetradentate ligands of 02N2 type. The structure of the copper complex with ethylendiamine-bis-acetylacetone differs from that of the ketiminate complex only by ethylene bridge CH₂-CH₂- binding two ketoimine ligands. However, even this insignificant change in the molecular structure leads to decrease of vapor pressure by one order of magnitude. Substitution of one methyl group in this ligand for trifluoromethyl one (Fig. 5, curves Cu(edaa)₂ and Cu(edtfa)₂, respectively) decreases the vapor pressure significantly.

It is also interesting to compare the vapour pressure of copper(II) β-diketonates with that of the complexes belonging to different classes. The temperature dependence of saturated vapor pressure for copper(II) β-diketonates, and their imino-derivatives, as well as copper(II) dithiocarbamate, and copper phthalocyanine are also presented in Fig. 5. Thermodynamic parameters of their sublimation are presented in Table 5.

Compound	Method	ΔH, kJ/mol	ΔS, J/K·mol	Range T, K	Refs.
Cu(aa) ₂	membr.	125.5±9.2	218.0±20.1	424-460	Igumenov et. al., 1978
Cu(ki) ₂	membr.	114.2±1.3	210.2±3.0	393-463	Chumachenko et. al., 1979
Cu(ktf) ₂	membr.	104.6±1.7	196.2±4.2	416-466	Chumachenko et. al., 1979
Cu(edaa) ₂ *	membr.	94.6±2.0	142.2±5.0	480-520	Chumachenko et. al., 1979
Cu(hfa) ₂	membr.	80.8±1.8	178.2±5.4	345-372	Igumenov et. al., 1978
Cu(edtfa) ₂ *				490-525	Chumachenko et. al., 1979
Cu(hfa)cod	Knudsen	97.1±1.4	207.9±18.4	288-330	Liskovskaya et. al., 2001
Cu(NH,NH) ₂	Knudsen	95.8±13.4	152.0±5.0	335-397	Unpublished results
Cu(dtk) ₂	flow	149.9±3.1	247.7±7.5	395-455	Zemskova et. al., 1998
CuPc	Knudsen	231.8±2.1	238.9±2.9	618-713	Semyannikov et. al., 2000

Table 5. Thermodynamic parameters of sublimation of different volatile Cu (II) complexes

Phthalocyanines are characterized by the lowest volatility and maximum value of sublimation enthalpy (Table 5) among the above mentioned compounds. The difference between the vapor pressure of Cu(hfac)₂ and CuPc is more than 7 orders of magnitude.

In the case of dimethylgold(III) β-diketonates (Semyannikov, 1988), the introduction of trifluoromethyl group increases the vapor pressure while for ketoiminate complexes the introduction of trifluoromethyl radical leads to its decrease. In general the ketoiminate complexes possess the lower vapor pressure than the corresponding β-diketonate derivatives. The substitution of oxygen in ketoimenes for sulfur atom leads to further decrease of vapor pressure. Therefore, the order of volatility for dimethylgold complexes depending on the type of donor atoms of ligand is as follows: (O,O) > (O,N) > (N,S).

It is possible to conclude on the basis of the available data on vapor pressure of different precursors that substitution of oxygen for sulfur leads to considerable decrease of volatility. The substitution of oxygen for nitrogen may lead both to insignificant increase of vapor pressure and to its decrease.

3. Structural aspects of metal complexes with organic ligands

3.1 Features of the interaction of molecules in crystal lattice

The volatile metal complexes with organic ligands are crystallized in lattices of a molecular type. The approaches of the classic organic crystal chemistry are applicable for their

description, namely, the van der Waals radii, theory of closest packing of molecules and atom-atomic approximation (Kitaigorodsky, 1971).

The structure of metal complexes with organic ligands depends on the nature of metal and coordinated ligands. The main difference between metal volatile complexes with organic ligands and organic compounds is a specific intramolecular distribution of electronic density with a positive charge localized on the central metal atom and a negative charge localized mostly on donor atoms and partially on atoms of the carbon moiety of the ligand. Therefore it is necessary to take into account not only van der Waals interaction but also electrostatic one. Obviously, the specificity and anisotropy of intermolecular contacts are more distinct for metal complexes with organic ligands than for organic molecules. However, no systematic crystal chemical analysis of the regularities of precursor molecules packing in crystals and their nearest intermolecular contacts has been done even for single class of the compounds. The analysis of some interaction features will be done using metal β -diketonates as model compounds.

The main contribution to the energy of crystal lattice is made by van der Waals (nonspecific) contacts of peripheral atoms of adjacent molecules. The number and type of these contacts are determined by molecules packing in the crystal. Structure of complexes depends on electronic and dimensional factors and primarily on the central atom radius and the radical size in ligand. Bulky substitutes in the ligand side chain cause in a number of cases the suppression of polymerization and formation of monomeric complexes sometimes with the lower coordination number. For example, the substitution of methyl radicals to tert-butyl ones in the acetylacetonates of the metals of the first transition series leads to formation of the monomeric complexes. The latter have a higher vapor pressure which is caused by the following reasons: decrease of the coordination number from 6 to 4; decrease of total intermolecular contacts; decrease of precursor molecular weight. However, different situation is observed in the case of metals with big ionic radii and high coordination numbers, eg. alkaline-earth metals. For example, barium dipivaloylmethanate, which is widely used as a precursor in MO CVD, is a tetramer (Otvay & Rees, 2000), while introducing more bulky substitutes ($R^1 = -C(n-C_6H_{13})(CH_3)(OCH_3)$, $R^2 = -CH(n-C_4H_9)(CH_3)$) into the ligand leads to decrease of the oligomerization extent to 2 (Igumenov et. al., 1996). Although the molecular weight of the latter barium complex decreases substantially, its volatility remains lower than that of barium dipivaloylmethanate.

In Ref. (Baidina, 2001) the crystal chemical analysis of over than 30 complexes of Cu(II) with β -diketones is performed. The symmetry of crystals is various - from triclinic $P1$ to tetragonal $I4_1/a$. Most of the investigated complexes have a trans-configuration. Cys-configuration is observed only for five complexes. In all considered complexes the central copper atom is bidentately coordinated by two oxygen atoms of β -diketonate ligand (L) with formation of the six-membered chelate metallocycle. Cu^{2+} ion tends, as a rule, to complete its coordination environment to pyramidal (4+1) and bipyramidal (4+1+1) or (4+2), adding oxygen, carbon or fluorine atoms of the neighboring molecules to axial positions. As a result various types of molecules association arise, eg. dimers, stacks and chains. The formation of dimers is typical for heteroligand and cys-complexes. As a rule, atoms of metal cycle participate in their formation, and the molecules are bound in dimers via their center of symmetry. Cu...Cu distance is in the range 3.39-5.46 Å.

The formation of one-dimensional infinite stacks of identical molecules is typical for homoligand trans-isomers. The planes of coordination squares of copper atoms are parallel in the stack. The angle formed by these planes with the stack axis is in the range of 41.3–

60.4° and Cu...Cu distance varies from 4.4 to 8.3 Å. Carbon atoms (C_γ) of metallocycles often take part in the stacks formation. In this case Cu...C_γ distance is within 3.01-3.44 Å. The chains of complexes are formed as a rule due to additional coordination of the copper atom with atoms of the end groups of adjacent molecules. Comparing to the stacks, a wider range of atoms belonging to end groups takes part in the formation of the chains and the complexes themselves can be rotated relative one another. Among the uniform chains (with the same Cu...Cu distances) it is possible to identify linear and zigzag ones. Cu...Cu distance is in the range from 6.9 to 9.1 Å in all chain structures.

Compound	Structure	Interaction with closest molecule			E _{shv} , energy of shortest contacts	E _{rep.,} repulsion of all atoms	E, energy of Van der Waals interaction
		E _M , kJ/mol	shortest contact				
			r, Å	E, kJ/mol	kJ/mol		
Cu(aa) ₂	P2 ₁ /n, Z=2	-19,1	3.017...C _γ	2,9	5,8	92,1	-101,1
Cu(ba) ₂	P2 ₁ /n, Z=2	30,9	3.013...C _{Ph}	3,0	5,9	84,1	-138,9
Cu(dbm) ₂	I2 ₁ /c, Z=4	-37,3	3.145...C _{Ph} 3.367...C _{Ph}	2,1 0,3	3,4	114,2	-193,3
Cu(thd) ₂	P2 ₁ /b, Z=2	-18,4	-	-	-	64,0	-147,3
Cu(btfa) ₂	P2 ₁ /n, Z=2	-37,2	3.251...C _{Ph} 3.389...C _{Ph}	0,3 0,2	1,8	62,6	-153,1
Cu(aa)(hfa)	P(-1), Z=2	-15,4 -24,9	2.704...O 3.186...C _γ	5,4 1,1	6,5	66,2	-100,8
Cu(aa) ₂	P2 ₁ /n, Z=2	-24,8	3.124...C _γ	1,7	3,3	80,7	-120,5
Cu(3-Meaa) ₂	P(-1), Z=1	-26,0	3.434...C _{Me}	1,2	4,3	103,2	-120,1
Cu(3-Phaa) ₂	P2 ₁ /c, Z=2	-26,0	-	-	-	79,3	-168,4

Table 6. Energy characteristics of copper(II) β-diketonates

The presence of shortened contacts in the copper β-diketonate crystals causes mutual repulsion between the neighboring molecules. The contribution of this type of interaction to the total energy of crystal lattice was calculated for a number of complexes (Table 6). The copper complexes considered above have different vapor pressure. The differences in the saturated vapour pressure value may reach some orders of magnitude and are determined by Van der Waals and electrostatic interaction of peripheral atoms of adjacent molecules, as well as by specific interactions.

3.2 Molecular structure in the gaseous phase

Only a few works devoted to investigation of the structure of metal complexes with organic ligands in the gaseous phase are known (Shibata et. al., 1986; Giricheva et. al., 1999). These works are devoted to β-diketonate derivatives. Unfortunately the analysis of these studies does not allow us to make unambiguous conclusions. However it is possible to mention that upon transition of the compound from the crystal to gaseous phase the M...O distance slightly increases within the measurement error if the molecule symmetry and coordination of the central atom do not change. M...O distance may decrease sufficiently if the molecule symmetry and coordination number change. The structural parameters of ligands change

only slightly for the most structures. In some cases the angle of chelate cycle bending in the O...O line may also change.

In general the obtained electronographic data show that the structure of precursor molecules does not practically change in the gaseous phase. It means that the data on spatial arrangement of atoms in the molecules obtained from the data of X-ray structural analysis may be used for description of the molecule in the gaseous phase.

3.3 Dependence of thermodynamic parameters of sublimation processes on the structure of complexes

The analysis of the total thermodynamic data for sublimation processes of metal complexes with organic ligands shows that the values of sublimation enthalpy change within 80-150 kJ/mol and the entropy changes to 250 J/K·mol for most of the investigated compounds. These values are quite comparable with the respective thermodynamic parameters for organic crystals having close molecular weight (300-500 a.u.).

Substitution of one $-C_6H_5$ group for $-CF_3$ in copper complexes leads to a difference in vapor pressure by 5.5 orders of magnitude. The sublimation enthalpies for $Cu(hfa)_2$ and $Cu(btf)_2$ are equal to 80.8 and 151.5 kJ/mol (Table 2), respectively. Their sublimation entropies are 178.2 and 248.1 J/K·mol. That is, the differences of 70.7 kJ/mol and 69.9 J/K·mol in thermodynamic parameters determine the above mentioned difference in the vapor pressure of these complexes.

It is possible to estimate the influence of enthalpy and entropy on the saturated vapor pressure of metal β -diketonates, assuming averaged values of thermodynamic parameters typical for this class of compounds. Let $\Delta H_T = 105$ kJ/mol, $\Delta S_T = 188$ J/K·mol and $T = 423$ K, then at $S_T = \text{const}$ the change of ΔH_T by 8 kJ/mol leads to a change of the saturated vapor pressure by 1 order of magnitude. At $H_T = \text{const}$ the respective pressure changes are caused by the difference in entropy by 19 J/K·mol. Therefore, the enthalpy could change the vapor pressure of the considered copper complexes by 8.6 orders of magnitude and the entropy – by 3.4 orders of magnitude. This estimation is quite close to the observed difference in the saturated vapor pressure of $Cu(hfa)_2$ and $Cu(btf)_2$ (5.5 orders of magnitude). A regular decrease of the thermodynamic parameters values is observed for the following order: $M(aa)_n - M(tfa)_n - M(hfa)_n$ which is parallel to change of the volatility of these chelates.

It is interesting to mention that similar differences of the volatility of acetylacetonate and hexafluoroacetylacetonate complexes are described by different sets of thermodynamic parameters. In the majority of published work the enthalpy is used as the sole criterion for comparison of volatility of different compounds. These data indicate that such approach is found to be incorrect because the differences in the volatility are described by different sets of thermodynamic parameters and the results of evaporation enthalpy change as well as entropy change should be considered (Zharkova et. al., 2000; Igumenov et. al., 1985).

4. Theoretical calculation of enthalpy and entropy of sublimation, and correlation with experiment

4.1 Microscopic theory of the volatility of metal complexes with organic ligands

For characterization of the dependence of equilibrium pressure of the gaseous phase over the crystal it is possible to use microscopic description of both gaseous and crystal phases in the framework of statistical thermodynamics. The equilibrium pressure $P(T)$ in the gaseous phase is found from the condition of equality of chemical potentials of the gaseous μ^{gas} and

crystal μ^{solid} phases. In order to find the chemical potentials of gaseous and crystal phases, the rigid molecules approximation in which the contributions of the intramolecular freedom degrees of molecules are neglected should be used. It has already been shown that the molecule structure in gaseous and crystal phase changes insignificantly. Therefore, this change can be neglected. In consideration of the binary equilibrium, only contributions of rotational and translatory motion of molecules into thermodynamic functions of the gaseous phase are taken into account. In the case of thermodynamic functions of crystal phase the intermolecular interaction should also be considered.

In the method of lattice dynamics in harmonic (quasi-harmonic) approximation, the analytical expressions describing dependence of the thermodynamic function of solid on parameters of intermolecular interaction is well known. The chemical potential of the crystal phase can be written as follows:

$$\mu^{solid} = \frac{1}{N} [F(V, T) + PV], \quad (2)$$

where N is the number of molecules in crystal; V is the crystal volume and $F(V, T)$ is free energy of the crystal presented as:

$$F(V, T) = U + E_{vib}(V, T) - kTs_{vib}^{solid}(V, T) \quad (3)$$

where U is the potential energy of the crystal; $E_{vib}(V, T)$ is the crystal vibrational energy and $s_{vib}^{solid}(V, T)$ is the crystal entropy that can be found from the well known formula (Leifried & Ludwig, 1961, Belosludov et. al., 1994):

$$E_{vib}(V, T) = 6N\hbar \int d\omega \coth(\hbar\omega / 2kT) \omega g(\omega) \quad (4)$$

$$s_{vib}^{solid}(V, T) = 6N \int d\omega \left\{ \frac{\hbar\omega}{2kT} \coth\left(\frac{\hbar\omega}{2kT}\right) - \ln[2 \sinh\left(\frac{\hbar\omega}{2kT}\right)] \right\} g(\omega) \quad (5)$$

In (4), (5) $g(\omega)$ is the density of the phonon state of the crystal presented as:

$$g(\omega) = \frac{1}{6N} \sum_{\vec{q}j} \delta(\omega - \omega_j(\vec{q})) \quad (6)$$

where $\omega_j(\vec{q})$ are the frequencies of crystal vibrations which are expressed by the following system of equations in rigid molecules approximation:

$$\begin{aligned} m_k \omega^2(q) U_{\alpha}^t(k, q) &= \sum_{k'\beta} D_{\alpha\beta}^t(q, k, k') U_{\beta}^t(k', q) + D_{\alpha\beta}^{tr}(q, k, k') U_{\beta}^r(k', q) \\ \sum_{\beta} I_{\alpha\beta}(k) \omega^2(q) U_{\beta}^r(k, q) &= \sum_{k'\beta} D_{\alpha\beta}^{rt}(q, k, k') U_{\beta}^t(k', q) + D_{\alpha\beta}^{rr}(q, k, k') U_{\beta}^r(k', q) \end{aligned} \quad (7)$$

where $D_{\alpha\beta}^{ii'}(q, k, k')$, $(\alpha, \beta = x, y, z)$ are translational ($i, i' = t$), rotational ($i, i' = r$) and mixed ($i = t, i' = r$ or $i = r, i' = t$) elements of the molecular crystal dynamic matrix, the expressions for which are presented in Refs. (Belosludov et. al., 1988; Belosludov et. al., 1994). $U_{\alpha}^i(k, q)$, $(\alpha, \beta = x, y, z)$ is the vibration amplitude, m_k and $I_{\alpha\beta}(k)$ are the mass and inertia tensor of the k -th molecule in the unit cell.

In the quasiharmonic approximation, the free energy of crystal has the same form as in the harmonic approximation but the structural parameters at fixed volume depend on temperature. If the vapor phase is seen as the ideal gas, it is possible to use the known expressions for enthalpy h^{gas} and entropy s^{gas} of the ideal gas in rigid molecules approximation to find the chemical potential μ^{gas} (Stull et al., 1969):

$$\mu^{gas} = kT \ln P + h^{gas}(T) - kTs^{gas}(T) \quad (8)$$

$$h^{gas}(T) = \frac{5}{2}kT \quad (9)$$

$$s^{gas}(T) = 3 + \ln \left[kT \left(\frac{mkT}{2\pi\hbar} \right)^{3/2} \right] + \ln \frac{(kT)^{3/2} [8\pi I_1 I_2 I_3]^{1/2}}{\sigma \hbar^3} + \ln(8\pi^3 k I_r T)^{1/2} \quad (10)$$

where m is molecule mass, I_1, I_2, I_3 are the molecule inertia moments; σ is the symmetry number; I_r is the moment of fragment rotation around its axis.

Using (3)-(5) and (8), the equation (1) can be write as follows:

$$\ln P(T) = -\Delta_e h / kT + \Delta_e s \quad (11)$$

where enthalpy of phase transition $\Delta_e h$ and entropy of phase transition $\Delta_e s$ are:

$$\Delta_e h = \frac{5}{2}kT - \frac{U}{N} - 6\hbar \int d\omega \coth(\hbar\omega / 2kT) \omega g(\omega) - \frac{PV_{solid}}{N} \quad (12)$$

$$\begin{aligned} \Delta_e s = & 3 + \ln \left[kT \left(\frac{mkT}{2\pi\hbar} \right)^{3/2} \right] + \ln \frac{(kT)^{3/2} [8\pi I_1 I_2 I_3]^{1/2}}{\sigma \hbar^3} + \ln(8\pi^3 k I_r T)^{1/2} - \\ & - 6 \int d\omega \left\{ \frac{\hbar\omega}{2kT} \coth \frac{\hbar\omega}{2kt} - \ln \left[2 \sinh \frac{\hbar\omega}{2kT} \right] \right\} g(\omega) \end{aligned} \quad (13)$$

Therefore, on the basis of the parameters of molecular and crystal structure and atom-atom potential functions, formulas (12) and (13) allow us to estimate enthalpy and entropy of the crystal-gas transitions and equilibrium pressure of the gaseous phase of precursor.

4.2 Calculation of Van der Waals contribution to enthalpy of sublimation

Analysis of equation (12) shows that the main contribution to the enthalpy $\Delta_e h$ is made by the potential energy of crystal U . Other members of the equation (12) are connected with the kinetic energy of the gas phase and vibration energy of the crystal. In the first approximation these members can be neglected. $\Delta_e h$ is approximately equal to the potential energy of crystal and can be presented as:

$$\Delta_e h = -U / N = -(U_{vvi} + U_{EI}^{mol}) / N \quad (14)$$

where U_{vvi} and U_{EI}^{mol} are van der Waals and electrostatic interactions of the molecular crystal, respectively. The electrostatic interaction is determined by the interaction of unlike charges non-uniformly distributed over precursor molecules.

To find the van der Waals portion of intermolecular interaction energy for molecular crystals, the atom-atom method of potential functions (AAP) is commonly used. This method is based on the assumption that energy of molecules interaction is equal to sum interactions of atoms in the molecule (additivity). It is also assumed that interaction potentials are of a universal character, depending only on the sort of atom and not depending either on molecule composition or on oxidation degree of the central atom.

The method of atom-atom potential (AAP) functions and its application have been described in different reviews and monographs (Kitaigorodsky et. al., 1971; Dashevskii et.al., 1982; Timofeeva et. al., 1980). Thus, eg. calculation of the lattice energy of molecular crystals comes to determination of all possible distances between pairs of nonvalency bound atoms and to calculation of the lattice sums of attraction and repulsion. Obviously such a procedure presupposes the use of positional parameters of atoms, i.e., it is necessary to know molecular and crystal structure of the investigated compound.

Van der Waals interaction was calculated with use of interatomic potential $V_{mn}(r_{ij})$ between i and j atoms of different n and m molecules.

$$U_{vvi} = \frac{1}{2} \sum_{nm} \sum_{ij} V_{mn}(r_{ij}) \quad (15)$$

Calculations of the intermolecular interaction energy were carried out in the framework of AAP method. Semiempirical Buckingham potential $V_{mn}(\tilde{r}_{ij})$ was used (abbreviated as “6-exp” potential):

$$V_{mn}(r_{ij}) = B_{mn} \exp(-\alpha_{mn} r_{ij}) - \frac{A_{mn}}{r_{ij}^6} \quad (16)$$

where the first term characterizes repulsion and the second one characterizes attraction; indexes m and n indicate the sort of atoms; A , B and α are empirical parameters; r_{ij} is the interatomic space between i and j atoms of different molecules. The choice of this potential is determined by ease of calculations of energetic and dynamic properties of crystal.

Let's consider some features of the calculation of van der Waals interaction contribution to the molecular crystal lattice energy. The “6-exp” potentials were calculated by equalities of Kitaigorodsky (Kitaigorodsky & Mirsky, 1961).

$$A = 1.79 \varepsilon_0 r_0^6, \quad B = 6.364 \cdot 10^2 \varepsilon_0, \quad \alpha = 13.6 / r_0 \quad (17)$$

where ε_0 and r_0 are the depth of the potential well and equilibrium distance between the atoms. Interaction potentials of light atoms were taken from (Gordon & Kim, 1972). Parameters for metal-metal interactions were estimated from $\varepsilon_0=f(N)$ dependence (where N is the number of metal atoms), that was plotted using the known parameters for noble gases (Timofeeva et. al., 1980; Crowell & Chang, 1963).

4.3 Contribution of electrostatic interaction

Historically two approaches are used for the estimation of electrostatic energy of crystal: calculation taking into account the interactions of charges on atoms (ion crystals) and calculations on the basis of multipoles of molecules (molecular crystals). However, the specific structural features of the molecules of metals complexes with large organic ligands

and their arrangement in the crystal lattice violate a condition of applicability of multipoles–multipole approximation at $a \ll r$, where a is the largest space between charges in molecule; r is the least distance between the charges of different molecules.

The long-range Coloumb potential must be taken into account along with the van der Waals interaction. Calculation of electrostatic interaction can be performed by direct summation of interactions of all pairs of electric charges of different molecules since the multipole expansion is impossible for metal β -diketonates. The summation of interactions of all pairs of electric charges $\langle ij \rangle$ of different molecules can be written as follows:

$$U_{El}^{mol} = \frac{1}{2} \sum_{\langle ij \rangle} \frac{Z_i Z_j}{r_{ij}} \quad (18)$$

where Z_i is the effective charge of i -atom.

The formula allowing to find the electrostatic energy of molecular crystal (18) from specified distribution of molecule charges have been obtained in Ref. (Belosludov et.al., 1988).

$$U_{El}^{mol} = \frac{1}{2} (\vec{E} \vec{P}) + Z_{\min}^2 \frac{\alpha(r)}{r} \quad (19)$$

where \vec{E} is the macroscopic field, \vec{P} is the dipole moment of elementary cell, r is the least distance between centers of inertia of molecules, Z_{\min} is the least in absolute value charge in the molecule, $\alpha(r)$ is the Madelung constant for molecular crystal which can be found from the equation (20):

$$\alpha(r) = \frac{c}{2} \sum_{l', k, k', m, m'} \xi_m \xi_{m'} H(c |\vec{x}(l'k'm' - \vec{x}(km))| / r) + O(c^3) \quad (20)$$

where $H(x)$ is integral of errors (21):

$$H(x) = \frac{2}{\sqrt{\pi}} \frac{1}{x} \int_x^\infty e^{-x^2} dx, \quad (21)$$

$Z_{\min} = Z_{\min} \xi_m$ is the m -th point charge of molecule; $\vec{x}(lkm)$ is the radius-vector of the point charge of the k -th molecule found in the 1st cell; index 1 is the set of three indices (l_1, l_2, l_3) of the cell ($l_i = 0, \pm 1, \pm 2, \dots$), $\vec{x}(km) = \vec{x}(0km)$, $\vec{x}(m) = \vec{x}(0m)$, c is an arbitrary small parameter chosen so as to satisfy the following inequality:

$$c \ll r |\vec{x}(m') - \vec{x}(m)|^{-1} < 1, \quad r / a_{\max} \leq 1, \quad (21)$$

In calculations of the contribution of electrostatic interaction to the energy of crystals lattice of metal β -diketonates the following assumptions were used:

1. the charge of the central atom was calculated from $q\text{Me}^{n+} = nq\text{H}^+$, where q is the charge of enol hydrogen atom in uncoordinated ligand;
2. in varying the central atom charge based on the principle of electrical neutrality, the compensating charges were distributed only within the chelate cycle, and the charges of the peripheral atoms were not changed;
3. calculations were carried out using one geometry for the complexes of the same type. Only complexes with known positional parameters of all atoms were chosen for calculations.

The charge distribution in metal β -diketonate molecules was calculated by quantum chemical methods (Schaaf et. al., 1976). The calculation results of the electrostatic energy of some metal β -diketonates are given in Table 7.

Chelate	Z_e	-U. kJ/mol
Fe(aa) ₃	0.51	11.97
Fe(aa) ₃	1.17	12.02
Fe(aa) ₃	2.10	9.88
Fe(tfa) ₃	0.40	9.17
Fe(tfa) ₃	1.20	7.95
Fe(tfa) ₃	2.04	6.68
Fe(hfa) ₃	1.23	11.39
Fe(dbm) ₃	1.08	8.08
Cu(dbm) ₂	0.72	7.30

Table 7. Electrostatic energy of some β -diketonate crystals (Z_e is the charge on metal atom)

The results show that the variation of charge inside the chelate ring has not substantial influence on the intermolecular interaction energy of metal β -diketonates. Therefore the main contribution to the electrostatic energy is made by interaction between peripheral parts of molecules, and the electrostatic energy is not practically dependent on the type of ligand substituents and the nature of central metal. For this reason, the contribution of electrostatic interaction to sublimation enthalpy was taken equal to 10 kJ/mol for all compounds.

4.4 Entropy of sublimation of molecular crystals

4.4.1 Entropy of crystal

The entropy of crystal phase can be estimated if the density of phonon states $g(\omega)$ which can be calculated using the method of lattice dynamics (Belosludov et. al., 1994) is known. In this method, frequencies of crystal vibrations $\omega_j(q)$ are found from equations of motion (7). These equations describe the motion of mass centers of molecule and molecule rotation. Interaction between molecules was described by the potential in atom-atom approximation. As in the case of calculation of sublimation enthalpy, van der Waals interaction including both repulsion of molecules at a close distance and long-range dispersive attraction as well as electrostatic interaction were considered. The same parameters of the potentials as in the case of calculation of sublimation enthalpy were also used.

4.4.2 Entropy of gaseous phase

The entropy of vapor phase was calculated using eq. 10. For calculation of the moments of inertia and the moments of molecule rotation the positional atom parameters (x,y,z) were used. The values of rotation barriers of molecule fragments were chosen according to the recommendations presented in Ref. (Stull et. al., 1969).

4.5 Comparison between experimental and calculated data on vapor pressure

Structural data for the investigated acetylacetonates were taken from Cambridge Structural Data Base (CSDB). All known structural data for Al(III), Cr(III), Fe(III) and Ir(III) tris-acetylacetonates are presented in (Prokuda et. al., 2006). The structures determined by X-

Ray diffraction method with reasonably low R-factors and all defined atoms including hydrogen were chosen for calculations.

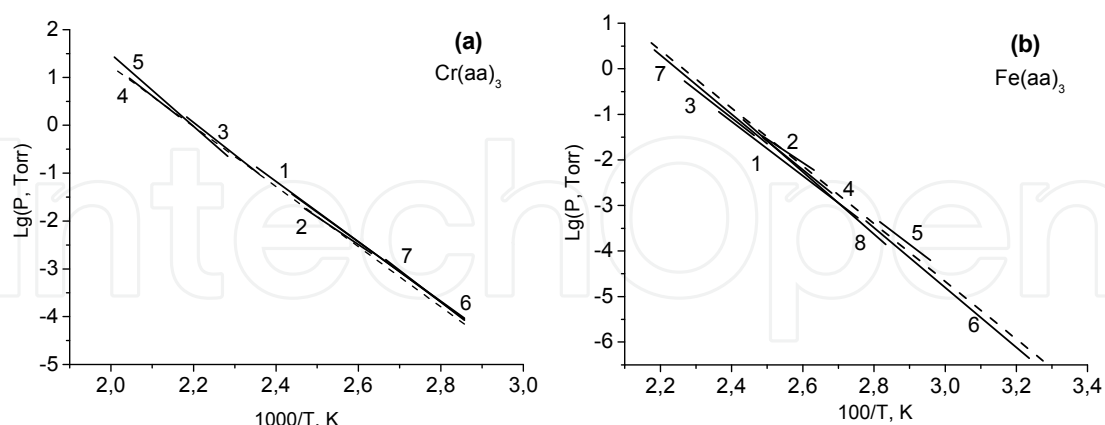


Fig. 6. Comparison of the experimental (—) and calculated (---) $\text{LgP}(1/T)$ dependence for $\text{Cr}(\text{aa})_3$ (a): 1 – flow method (Götze et. al., 1970); 2 – (Melia & Merrifield, 1970); 3 – membrane method (Wolf et. al., 1972); 4 – membrane method (Techil et.al., 1981); 5 – chromatography (Bublik et al., 1978); 6 – Knudsen method (Malkerova et. al., 1990); 7 – Knudsen method (Semyannikov et.al., 2001) and for $\text{Fe}(\text{aa})_3$ (b): 1 – flow method (Götze et. al., 1970); 2 – (Melia & Merrifield, 1970); 3 – Knudsen method; 4 – (Sachinidis et. al., 1980); 5 – Langmuir method (Fedotova et. al., 1993); 6 – Knudsen method (Malkerova et. al., 1990); 7 – Knudsen method (Stabnikov et.al., 2001); 8 – flow method (Stabnikov et.al., 2001)

Dynamic and thermodynamic properties for different metal acetylacetonate crystals were calculated. A comparison of the experimental and calculated data on temperature dependence of saturated vapor pressure for $\text{Cr}(\text{aa})_3$ and $\text{Fe}(\text{aa})_3$ is given as an example in Figs. 6(a) and 6(b), respectively. The experimental data obtained by different methods are shown in these graphs. Good agreement between the experimental and calculated dependencies confirms the reliability of the obtained data.

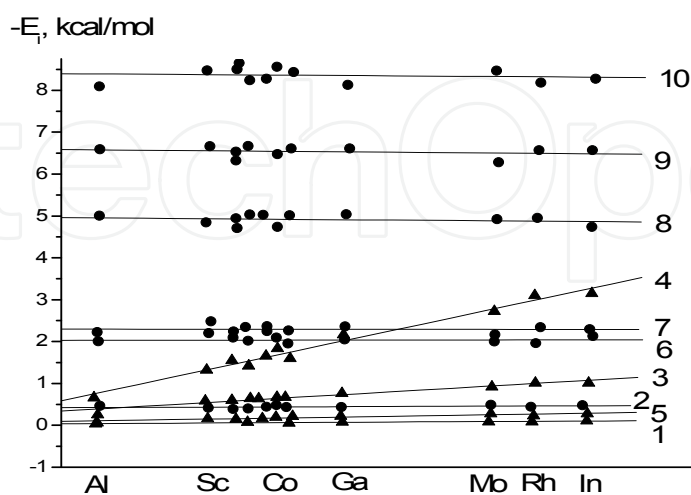


Fig. 7. Contribution of different types of interaction into the energy of Van der Waals interaction for metal tris-acetylacetonates: 1 - M-M; 2 - M-O; 3 - M-C; 4 - M- CH_3 ; 5 - O-O; 6 - O-C; 7 - C-C; 8 - O- CH_3 ; 9 - CH_3 - CH_3 ; 10 - CH_3 -C

Contribution of different types of interaction into the energy of Van der Waals interaction for metal tris-acetylacetonates is presented in Fig. 7. The existing evaluation of parameters of metal-metal interactions using known e and r values for inert gases is a suitable technique but it should be supported by experimental data. Table 8 presents experimental and calculated values of enthalpy and entropy of sublimation for some metal acetylacetonates.

Complex		$-\Delta H$, kJ/mol	ΔS° , J/(K·mol)
Cu(aa) ₂	experiment	125.5±9.2	218.0±20.1
	calculation	107.9	202.3
Al(aa) ₃	experiment	104.5	188.4
	calculation	112.9	
Cr(aa) ₃	experiment	119.7	203.9
	calculation	120,4	222.4
Ir(aa) ₃	experiment	127.9	215
	calculation	139	
Fe(aa) ₃	experiment	124.4	224.3
	calculation	121.4	220.9

Table 8. Experimental and calculated values of enthalpy and entropy of sublimation of metal acetylacetonates

The values of enthalpy and entropy were obtained by averaging of experimental data on enthalpy of the investigated metal acetylacetonates presented in literature. The calculations of sublimation enthalpy were carried out using “6-exp” potential (eq. 15). The calculations of entropy of sublimation for Cu(aa)₂ and Cr(aa)₃ were carried out according to equation 13. Contribution of electrostatic interaction to lattice energy was taken as a constant value 10 kJ/mol in the calculations.

5. Conclusions

A systematic analysis of experimental data on temperature dependencies of vapor pressure of molecular complexes with organic ligands using metal β -diketonates and phthalocyanines as examples was performed. The volatility of β -diketonates and phthalocyanines was analysed from the standpoint of their molecular and crystal structure. The complexes considered in this review are characterized by different vapor pressure. The differences in the saturated vapor pressure value may reach some orders of magnitude and are determined by the Van der Waals and electrostatic interaction of the peripheral atoms of adjacent molecules, as well as by a specific interaction, the type and number of which depend on the type of molecules packing in the crystal. Along with other volatile metal complexes with organic ligands the phthalocyanines crystallize in the molecular type lattices. Approaches of classical organic crystal chemistry such as the Van der Waals radii algorithm, theory of closest packing of molecules and atom-atom approximation are usually used for their description. The structure of complexes depends on electron and size factors, most of all, on the type of central metal atom and on the type of substituents in the phthalocyanine ring. The vapor pressure is described by enthalpy and entropy of sublimation; in the majority of published work the enthalpy of evaporation is used as the sole criterion for comparison of

volatility of different compounds. This approach is found to be incorrect because the differences in the volatility of various phthalocyanines are described by different sets of thermodynamic parameters and the results of evaporation enthalpy change as well as entropy change should be considered.

The general theoretical approach to the quantitative description of the volatility of precursors for MO CVD has been developed on the basis of statistical thermodynamics. Numerical procedures for calculating temperature dependencies of vapor pressure in the atom-atom approximation on the basis of the known crystal chemical data have been proposed and realized for a number of precursors. Good agreement between the experimental and calculated dependencies confirms the reliability of the suggested approach.

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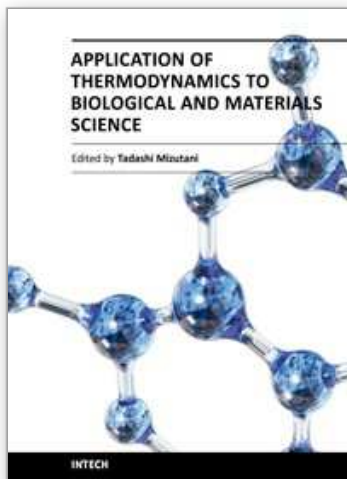
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