# Introduction

Metal compounds and complexes are invaluable precursors for the chemical vapor deposition (CVD) or metal organic chemical vapor deposition (MOCVD) of metal and non-metal thin films. In general, the precursor compounds are chosen on the basis of their relative volatility and their ability to decompose to the desired material under a suitable temperature regime. Unfortunately, many readily obtainable (commercially available) compounds are not of sufficient volatility to make them suitable for CVD applications. Thus, a *prediction* of the volatility of a metal-organic compounds as a function of its ligand identity and molecular structure would be desirable in order to determine the suitability of such compounds as CVD precursors. Equally important would be a method to determine the vapor pressure of a potential CVD precursor as well as its optimum temperature of sublimation.

It has been observed that for organic compounds it was determined that a rough proportionality exists between a compound's melting point and sublimation enthalpy; however, significant deviation is observed for inorganic compounds.

Enthalpies of sublimation for metal-organic compounds have been previously determined through a variety of methods, most commonly from vapor pressure measurements using complex experimental systems such as Knudsen effusion, temperature drop microcalorimetry and, more recently, differential scanning calorimetry (DSC). However, the measured values are highly dependent on the experimental procedure utilized. For example, the reported sublimation enthalpy of $Al(acac)_3$ (Figure a, where M = Al) varies from 47.3 to 126 kJ/mol.

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(a)	(b)	(c)	(d)
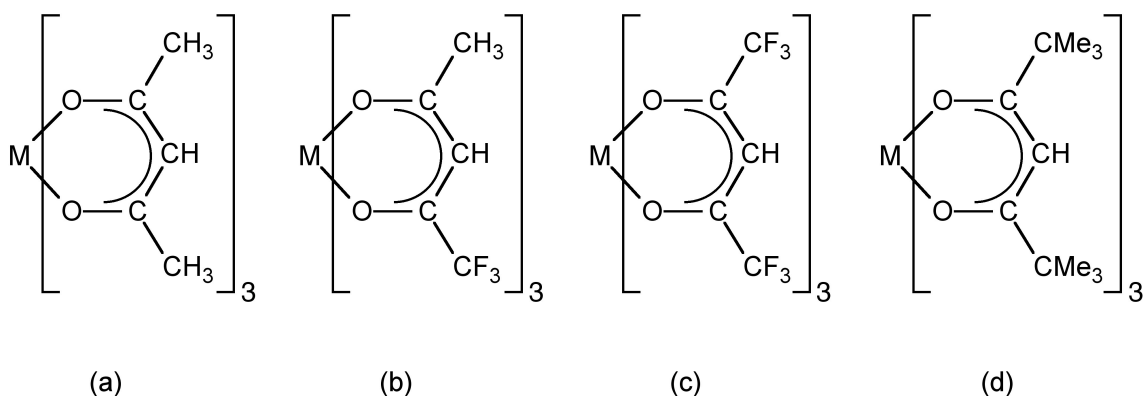
Structure of a typical metal β-diketonate complex. (a) acetylacetonate (acac); (b) trifluoro acetylacetonate (tfac), (c) hexafluoroacetylacetonate (hfac), and (d) tetramethylheptanedionate (tmhd).

Thermogravimetric analysis offers a simple and reproducible method for the determination of the vapor pressure of a potential CVD precursor as well as its enthalpy of sublimation.

Determination of sublimation enthalpy

The enthalpy of sublimation is a quantitative measure of the volatility of a particular solid. This information is useful when considering the feasibility of a particular precursor for CVD applications. An ideal sublimation process involves no compound decomposition and only results in a solid-gas phase change, i.e., Eq.

$$[M(L)_n]_{(solid)} \rightarrow [M(L)_n]_{(vapor)}$$
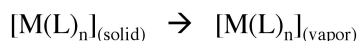
Since phase changes are thermodynamic processes following zero-order kinetics, the evaporation rate or rate of mass loss by sublimation (m_{sub}), at a constant temperature (T), is constant at a given temperature, Eq. Therefore, the m_{sub} values may be directly determined from the linear mass loss of the TGA data in isothermal regions.

$$m_{sub} = \frac{\Delta[mass]}{\Delta t}$$

The thermogravimetric and differential thermal analysis of the compound under study is performed to determine the temperature of sublimation and thermal events such as

melting. Figure shows a typical TG/DTA plot for a gallium chalcogenide cubane compound (Figure).
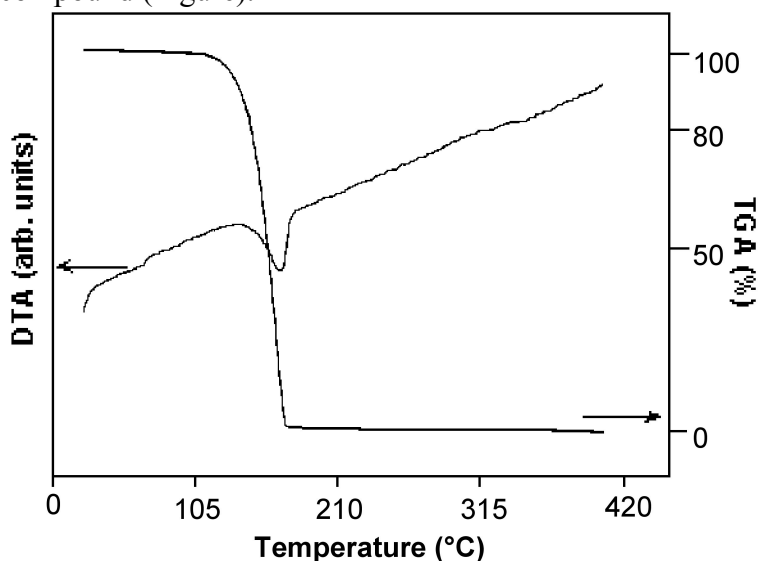
A typical thermogravimetric/differential thermal analysis (TG/DTA) analysis of [(EtMe$_2$C)GaSe]$_4$, whose structure is shown in Figure. Adapted from E. G. Gillan, S. G. Bott, and A. R. Barron, *Chem. Mater.,* 1997, **9**, 3, 796.
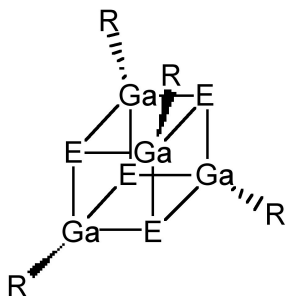

Structure of gallium chalcogenide cubane compound, where E = S, Se, and R = CMe$_3$, CMe$_2$Et, CEt$_2$Me, CEt$_3$.

Data collection

In a typical experiment 5 - 10 mg of sample is used with a heating rate of ca. 5 °C/min up to under either a 200-300 mL/min inert (N$_2$ or Ar) gas flow or a dynamic vacuum (ca. 0.2 Torr if using a typical vacuum pump). The argon flow rate was set to 90.0 mL.min^{-1} and was carefully monitored to ensure a steady flow rate during runs and an identical flow rate from one set of data to the next.

Once the temperature range is defined, the TGA is run with a preprogrammed temperature profile (Figure). It has been found that sufficient data can be obtained if each isothermal mass loss is monitored over a period (between 7 and 10 minutes is found to be sufficient) before moving to the next temperature plateau. In all cases it is important to confirm that the mass loss at a given temperature is linear. If it is not, this can be due to either (a) temperature stabilization had not occurred and so longer times should be spent at each isotherm, or (b) decomposition is occurring along with sublimation, and lower temperature ranges must be used. The slope of each mass drop is measured and used to calculate sublimation enthalpies as discussed below.
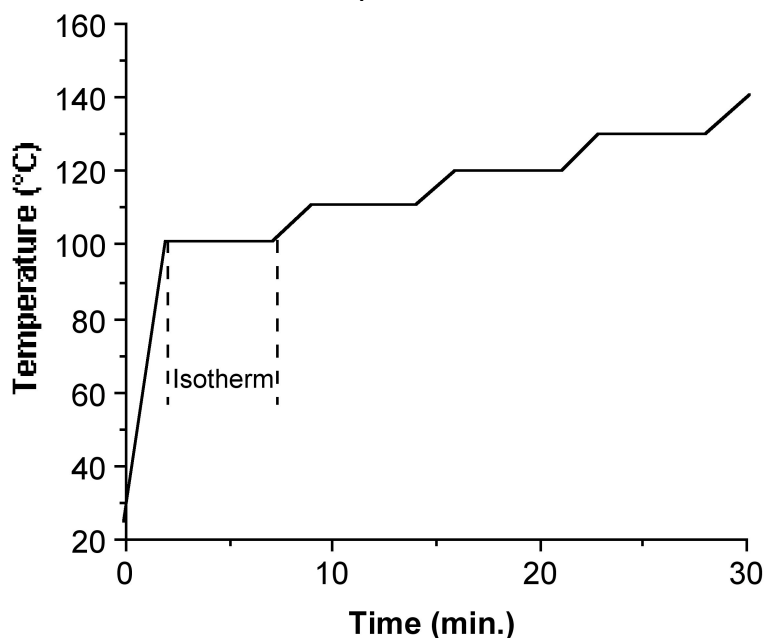
Typical temperature profile for determination of isothermal mass loss rate.

As an illustrative example, Figure displays the data for the mass loss of Cr(acac)$_3$ (Figure a, where M = Cr) at three isothermal regions under a constant argon flow. Each isothermal data set exhibits a linear relation ($R^2 > 0.99$). As expected for an endothermal phase change, the linear slope, equal to m_{sub}, increases with increasing temperature.
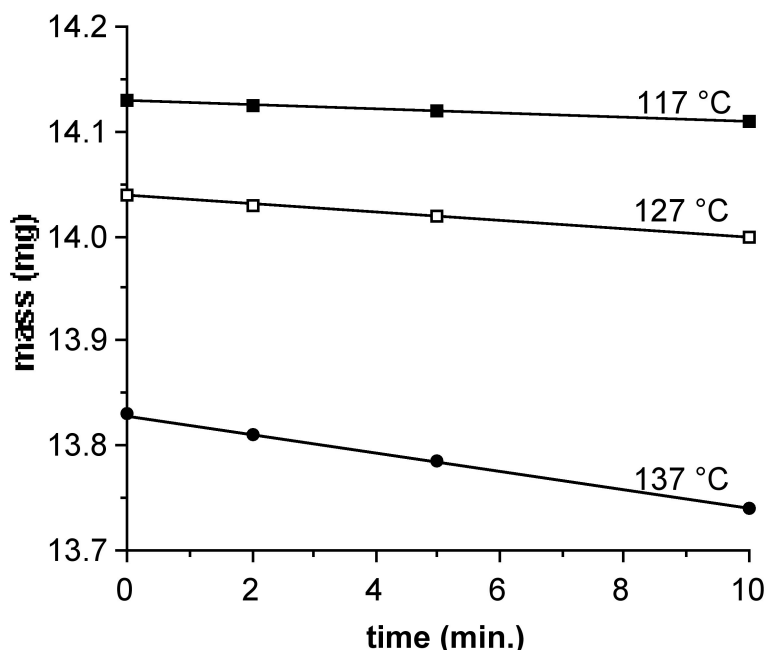
Plot of TGA results for Cr(acac)$_3$ performed at different isothermal regions. Adapted from B. D. Fahlman and A. R. Barron, *Adv. Mater. Optics Electron.*, 2000, **10**, 223.

Note: Samples of iron acetylacetonate (Figure a, where M = Fe) may be used as a calibration standard through ΔH_{sub} determinations before each day of use. If the measured value of the sublimation enthalpy for Fe(acac)$_3$ is found to differ from the literature value by more than 5%, the sample is re-analyzed and the flow rates are optimized until an appropriate value is obtained. Only after such a calibration is optimized should other complexes be analyzed. It is important to note that while small amounts (< 10%) of involatile impurities will not interfere with the ΔH_{sub} analysis, competitively volatile impurities will produce higher apparent sublimation rates.

It is important to discuss at this point the various factors that must be controlled in order to obtain meaningful (useful) m_{sub} data from TGA data. First, the sublimation rate is independent of the amount of material used but may exhibit some dependence on the flow rate of an inert carrier gas, since this will affect the equilibrium concentration of the cubane in the vapor phase. While little variation was observed we decided that for consistency m_{sub} values should be derived from vacuum experiments only. Second, the

surface area of the solid in a given experiment should remain approximately constant; otherwise the sublimation rate (i.e., mass.time^{-1}) at different temperatures cannot be compared, since as the relative surface area of a given crystallite decreases during the experiment the apparent sublimation rate will also decrease. To minimize this problem, data was taken over a small temperature ranges (*ca*. 30 °C), and overall sublimation was kept low (*ca*. 25% mass loss representing a surface area change of less than 15%). In experiments where significant surface area changes occurred the values of m_{sub} deviated significantly from linearity on a log(m_{sub}) versus 1/T plot. Third, the compound being analyzed must not decompose to any significant degree, because the mass changes due to decomposition will cause a reduction in the apparent m_{sub} value, producing erroneous results. With a simultaneous TG/DTA system it is possible to observe exothermic events if decomposition occurs, however the clearest indication is shown by the mass loss versus time curves which are no longer linear but exhibit exponential decays characteristic of first or second order decomposition processes.

Data analysis

The basis of analyzing isothermal TGA data involves using the Clausius-Clapeyron relation between vapor pressure (p) and temperature (T), Eq, where ΔH_{sub} is the enthalpy of sublimation and R is the gas constant (8.314 J/K.mol).

$$\frac{d \ln(p)}{dT} = \frac{\Delta H_{sub}}{RT^2}$$

Since m_{sub} data are obtained from TGA data, it is necessary to utilize the Langmuir equation, Eq, that relates the vapor pressure of a solid with its sublimation rate.

$$p = \left[\frac{2\pi RT}{M_w}\right]^{0.5} m_{sub}$$

After integrating Eq in log form, substituting in Eq, and consolidating the constants, one obtains the useful equality, Eq.

$$\log(m_{sub}\sqrt{T}) = \frac{-0.0522(\Delta H_{sub})}{T} + \left[\frac{0.0522(\Delta H_{sub})}{T_{sub}} - \frac{1}{2}\log\left(\frac{1306}{M_w}\right)\right]$$

Hence, the linear slope of a $\log(m_{sub}T^{1/2})$ versus $1/T$ plot yields ΔH_{sub}. An example of a typical plot and the corresponding ΔH_{sub} value is shown in Figure. In addition, the y intercept of such a plot provides a value for T_{sub}, the calculated sublimation temperature at atmospheric pressure.
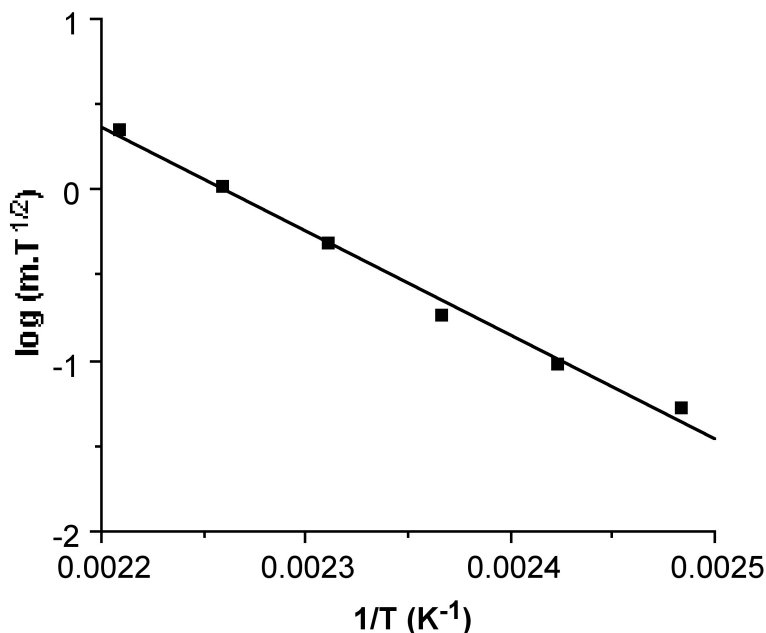
Plot of $\log(m_{sub}T^{1/2})$ versus $1/T$ and the determination of the ΔH_{sub} (112.6 kJ/mol) for Fe(acac)$_3$ ($R^2 = 0.9989$). Adapted from B. D. Fahlman and A. R. Barron, *Adv. Mater. Optics Electron.*, 2000, **10**, 223.

Table lists the typical results using the TGA method for a variety of metal β-diketonates, while Table lists similar values obtained for gallium chalcogenide cubane compounds.

Compound	ΔH_{sub} (kJ/mol)	ΔS_{sub} (J/K.mol)	T_{sub} calc. (°C)	Vapor pressure @ 150 °C (Torr)
Al(acac)$_3$	93	220	150	3.261
Al(tfac)$_3$	74	192	111	9.715
Al(hfac)$_3$	52	152	70	29.120
Al(tmhd)$_3$	88	213	140	3.378
Cr(acac)$_3$	91	216	148	3.328
Cr(tfac)$_3$	71	186	109	9.910

Cr(hfac)$_3$	46	134	69	29.511
Cr(tmhd)$_3$	85	207	137	3.432
Fe(acac)$_3$	112	259	161	2.781
Fe(tfac)$_3$	96	243	121	8.340
Fe(hfac)$_3$	60	169	81	25.021
Fe(tmhd)$_3$	111	263	150	2.910
Co(acac)$_3$	138	311	170	1.059
Co(tfac)$_3$	119	295	131	3.319
Co(hfac)$_3$	73	200	90	9.132
Co(tmhd)$_3$	132	305	161	1.211

Selected thermodynamic data for metal β-diketonate compounds determined from thermogravimetric analysis. Data from B. D. Fahlman and A. R. Barron, *Adv. Mater. Optics Electron.*, 2000, **10**, 223.

Compound	ΔH_{sub} (kJ/mol)	ΔS_{sub} (J/K. mol)	T_{sub} calc. (°C)	Vapor pressure @ 150 °C (Torr)
[(Me$_3$C)GaS]$_4$	110	300	94	22.75
[(EtMe$_2$C)GaS]$_4$	124	330	102	18.89
[(Et$_2$MeC)GaS]$_4$	137	339	131	1.173
[(Et$_3$C)GaS]$_4$	149	333	175	0.018
[(Me$_3$C)GaSe)]$_4$	119	305	116	3.668
[(EtMe$_2$C)GaSe]$_4$	137	344	124	2.562
[(Et$_2$MeC)GaSe]$_4$	147	359	136	0.815
[(Et$_3$C)GaSe]$_4$	156	339	189	0.005

Selected thermodynamic data for gallium chalcogenide cubane compounds determined from thermogravimetric analysis. Data from E. G. Gillan, S. G. Bott, and A. R. Barron, *Chem. Mater.,* 1997, **9**, 3, 796.

A common method used to enhance precursor volatility and corresponding efficacy for CVD applications is to incorporate partially (Figure b) or fully (Figure c) fluorinated ligands. As may be seen from Figure this substitution does results in significant decrease in the ΔH_{sub}, and thus increased volatility. The observed enhancement in volatility may be rationalized either by an increased amount of intermolecular repulsion due to the additional lone pairs or that the reduced polarizability of fluorine (relative to hydrogen) causes fluorinated ligands to have less intermolecular attractive interactions.

Comparison with other methods

Table lists a comparison of typical ΔH_{sub} values obtained from the TGA method with those obtained by traditional methods. The value determined for $Fe(acac)_3$ shows a difference of less than 4% relative to the literature value. However, the values determined for $Cr(acac)_3$ and $Co(acac)_3$ differ from previously reported values, however, the accuracy of the isoteniscopic and sublimation bulb techniques used have long been questioned.

Compound	Method	ΔH_{sub} (kJ/mol)
$Fe(acac)_3$	TGA	112
$Fe(acac)_3$	isoteniscopic and sublimation bulb	113
$Cr(acac)_3$	TGA	91
$Cr(acac)_3$	isoteniscopic and sublimation bulb	123
$Co(acac)_3$	TGA	138
$Co(acac)_3$	isoteniscopic and sublimation bulb	118
$Cu(acac)_2$	TGA	120
$Cu(acac)_2$		116

Comparison of enthalpy of sublimation determined by different methods.

Determination of sublimation entropy

The entropy of sublimation is readily calculated from the ΔH_{sub} and the calculated T_{sub} data, Eq.

$$\Delta S_{sub} = \frac{\Delta H_{sub}}{T_{sub}}$$

Table and Table show typical values for metal β-diketonate compounds and gallium chalcogenide cubane compounds, respectively. The range observed for gallium chalcogenide cubane compounds ($\Delta S_{sub} = 330 \pm 20$ J/K.mol) is slightly larger than values reported for the metal β-diketonates compounds ($\Delta S_{sub} = 130 - 330$ J/K.mol) and organic compounds (100 - 200 J/K.mol), as would be expected for a transformation giving translational and internal degrees of freedom. For any particular chalcogenide, i.e., $[(R)GaS]_4$, the lowest ΔS_{sub} are observed for the Me_3C derivatives, and the largest ΔS_{sub} for the Et_2MeC derivatives, see Table. This is in line with the relative increase in the modes of freedom for the alkyl groups in the absence of crystal packing forces.

Determination of vapor pressure

While the sublimation temperature is an important parameter to determine the suitability of a potential precursor compounds for CVD, it is often preferable to express a compound's volatility in terms of its vapor pressure. However, while it is relatively straightforward to determine the vapor pressure of a liquid or gas, measurements of solids are difficult (e.g., use of the isoteniscopic method) and few laboratories are equipped to perform such experiments. Given that TGA apparatus are increasingly accessible, it would therefore be desirable to have a simple method for vapor pressure determination that can be accomplished on a TGA.

Substitution of Eq into Eq allows for the calculation of the vapor pressure (p) as a function of temperature (T). For example, Figure shows the calculated temperature dependence of the vapor pressure for $[(Me_3C)GaS]_4$. The calculated vapor pressures at

150 °C for metal β-diketonates compounds and gallium chalcogenide cubane compounds are given in Table and Table.

The TGA approach to show reasonable agreement with previous measurements. For example, while the value calculated for Fe(acac)$_3$ (2.78 Torr @ 113 °C) is slightly higher than that measured directly by the isteniscopic method (0.53 Torr @ 113 °C); however, it should be noted that measurements using the sublimation bulb method obtained values much lower (8 x 10^{-3} Torr @ 113 °C). The TGA method offers a suitable alternative to conventional (direct) measurements of vapor pressure.
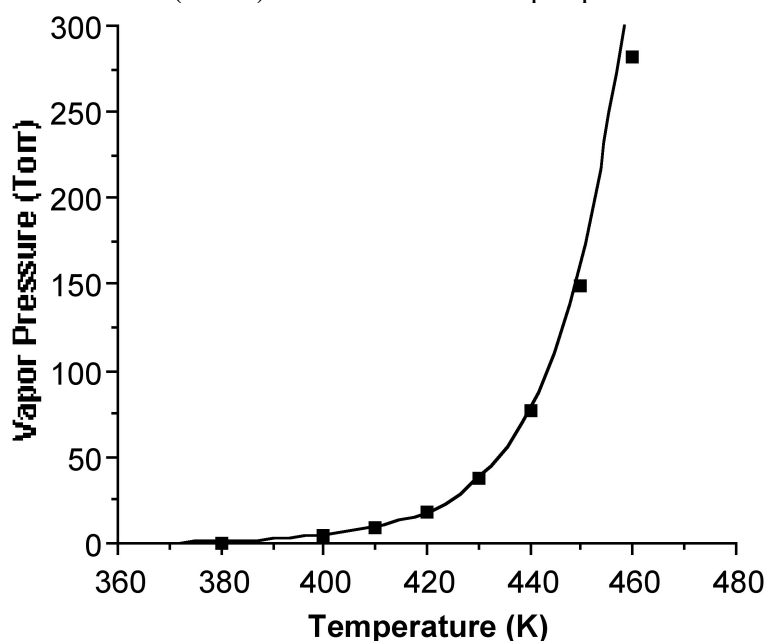
A plot of calculated vapor pressure (Torr) against temperature (K) for [(Me$_3$C)GaS]$_4$ [p = 3.0980 x 10^{-13} * 10$^{(0.0326)T}$, R = 0.997].

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