

Vapor Pressures of the Copper and Yttrium β -Diketonate MOCVD Precursors

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The vapor pressures and vapor molecular weights of the copper and yttrium β -diketonate MOCVD precursors $\text{Cu}(\text{C}_{11}\text{H}_{19}\text{O}_2)_2$ (c) and $\text{Y}(\text{C}_{11}\text{H}_{19}\text{O}_2)_3$ (c) were measured by a torsion-effusion/mass-loss method in the ranges (346 to 375) K and (361 to 387) K, respectively. The molecular weight data indicate that the saturated vapors of both precursors are highly monomeric. Vapor pressures, estimated to be accurate within 5%, are presented in equation form for reliable extrapolation to higher temperatures. The results are compared with other determinations in the literature.

Introduction

The β -diketonate complexes, and their derivatives, of a number of metals are routinely employed as convenient, relatively inexpensive precursors for the metal–organic chemical vapor deposition (MOCVD) of thin films of superconducting phases¹ as well as other electrical materials. Of particular current interest is the use of copper β -diketonate derivatives for copper metallization via MOCVD in integrated circuits.² Although such precursor materials are usually available commercially, their vapor pressures are generally not known accurately, thereby making it difficult to establish optimum deposition conditions. Of interest here are the β -diketonate complexes of copper and yttrium, $\text{Cu}(\text{TMHD})_2$ (c) (TMHD: 2,2,6,6-tetramethyl-3,5-heptanedionato, $\text{C}_{11}\text{H}_{19}\text{O}_2$), and $\text{Y}(\text{TMHD})_3$ (c). Published vapor pressure data for these materials^{2–7} show considerable scatter or are available at only one temperature. In one instance,⁷ the vapor pressures were reported in graphical form only and are of limited quantitative use. We report here new measurements of the vapor pressures of high-purity $\text{Cu}(\text{TMHD})_2$ (c) and $\text{Y}(\text{TMHD})_3$ (c) made by the torsion-effusion method. This technique is an accurate and reliable method for the determination of total vapor pressure; when coupled with concurrent mass-loss measurements, it yields useful information about vapor composition. We have used this method extensively to obtain accurate vapor pressure and vapor composition data and to elucidate the sublimation/decomposition and monomer/dimer vaporization processes for many inorganic and organic materials.^{8–10}

Experimental Methods

The torsion vapor pressure system, Figure 1, is basically an effusion manometer in which a cell with opposed, offset orifices is suspended from a Pt–10% Ni ribbon attached to the arm of a microbalance, all within an evacuated enclosure. Effusion of vapor induces a recoil force and consequent angular rotation of the cell. This is a purely mechanical device that yields absolute total pressure in terms of the torsion constant of the filament, the observed

angular deflection, and the geometrical constants of the cell. Since the effusion pressure evaluated from mass loss alone requires knowledge of the vapor molecular weight, M , then determination of torque angle and mass loss together allows one to evaluate M directly. Effusion measurements have an upper pressure limit of about 10 Pa because of mean-free path restrictions for maintaining free molecular flow through the exit orifice. All of the measurements reported here were made with Pt–Rh effusion cells, having orifice diameters of 0.06 cm (denoted P-1) and 0.11 cm (denoted P-2), at a constant system pressure of 1.3×10^{-5} Pa. Temperatures were measured with a Pt, Pt–Rh thermocouple of accurately established calibration. Mass-loss determinations were made using a Cahn RH automatic electrobalance with a sensitivity of 0.01 mg for a 1-g sample. Frequent checks with laboratory vapor pressure standards such as Ag, Sn, and KCl have shown that both absolute pressures and vapor molecular weights are accurate to within 5% and that second law slope enthalpies can regularly be measured with an accuracy of ≈ 4 kJ mol⁻¹. The torsion-effusion system and microbalance arrangement for simultaneous measurement of effusion recoil force and sample mass loss has been described in the literature.^{8–10}

The $\text{Cu}(\text{TMHD})_2$ and $\text{Y}(\text{TMHD})_3$ samples were obtained from Strem Chemicals, Inc., and were further purified by successive vacuum sublimation cycles at low temperature to remove excess ligand and other impurities. Each resublimed sample was quickly loaded into the torsion cell in air. The cell was then transferred to the torsion apparatus and the system was evacuated. During the course of the measurements, the sample pressures proved to be very stable and reproducible, indicative of high sample purity and congruent vaporization. The samples remained solid over the temperature range employed.

Results

Total vapor pressures and vapor molecular weight data for $\text{Cu}(\text{TMHD})_2$ and $\text{Y}(\text{TMHD})_3$ obtained with cells P-1 and P-2 are listed in Tables 1 and 2. It is important to note that these data are recorded in the temporal order in which they were taken; data of this kind are best measured in a random temperature sequence to identify hysteresis effects

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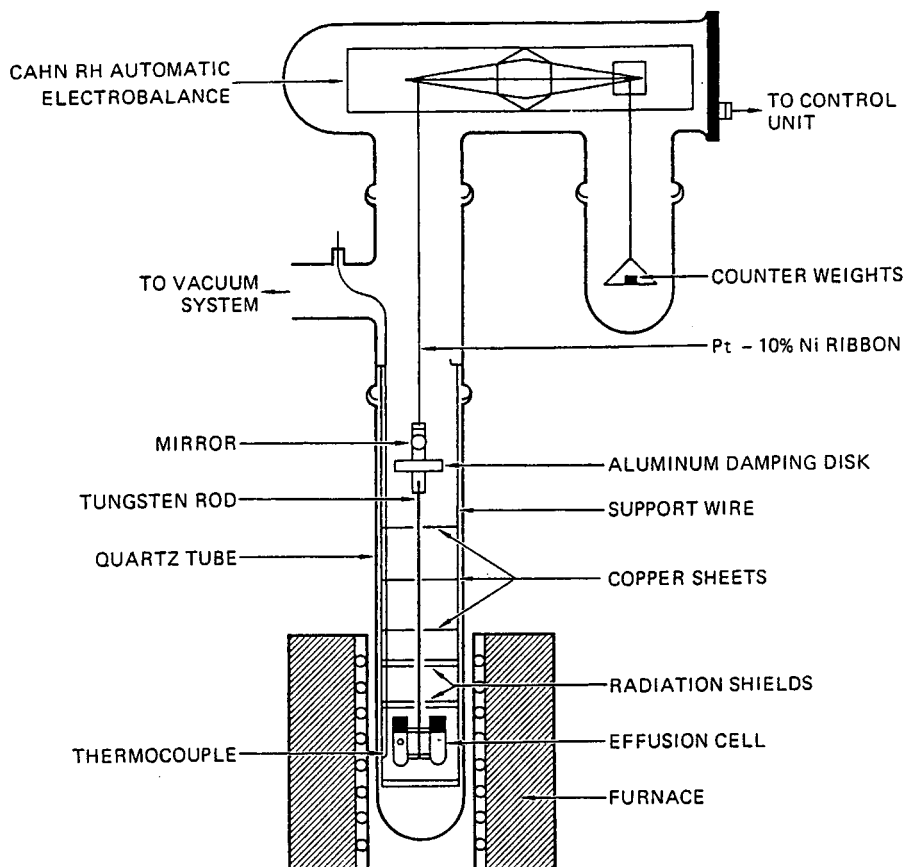
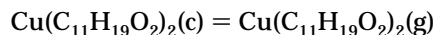
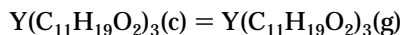


Figure 1. Schematic diagram of the torsion effusion-weight loss apparatus.

during vaporization. No such effects were detected in this work. Also included in the tables are the least-squares coefficients A and B of the vapor pressure/temperature relation $\log(P/\text{Pa}) = A - BK/T$ along with second law slope enthalpies for each cell. The total vapor pressures are plotted as $\log P$ vs $1/T$ in Figures 2 and 3. The measured average molecular weights, M , of (469 and 422 and 667 and 627) g mol^{-1} are close to the theoretical molecular weights of 430 g mol^{-1} for Cu(TMHD)_2 and 639 g mol^{-1} for Y(TMHD)_3 , respectively, indicating that the saturated vapors of both species are monomeric. From the measured values of M , one can be assured that the processes



and



correctly represent the equilibrium vaporization reactions of the copper and yttrium precursors studied here.

As seen for Cu(TMHD)_2 in Figure 2, a small orifice-size effect was noted, with the smaller orifice cell, P-2, yielding pressures about 15% higher than those of P-1, but the magnitude is such that the P-2 pressures are essentially equilibrium values. The total vapor pressures of Y(TMHD)_3 from P-1 and P-2 are essentially identical, as seen in Figure 3. Second law slope enthalpies obtained with the two cells for both compounds are also nearly identical as given in Tables 1 and 2. For use in representing the vapor pressures from these studies, and for subsequent comparison with literature data, we adopt the P-2 cell data for both substances. From past experience with accurate thermodynamic studies, we are confident that these vapor pres-

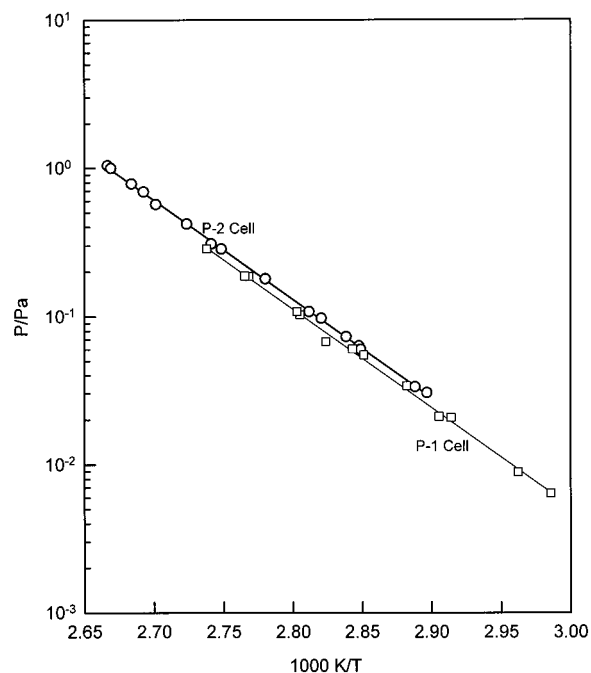


Figure 2. Total vapor pressure over $\text{Cu}(\text{C}_{11}\text{H}_{19}\text{O}_2)_2(\text{c})$ measured with two platinum rhodium effusion cells for the sublimation process $\text{Cu}(\text{C}_{11}\text{H}_{19}\text{O}_2)_2(\text{c}) = \text{Cu}(\text{C}_{11}\text{H}_{19}\text{O}_2)_2(\text{g})$.

sure data can be reliably extrapolated to higher temperatures.

Discussion

Earlier determinations of the vapor pressures of Cu(TMHD)_2 and Y(TMHD)_3 were obtained by mass-loss

Table 1. Total Vapor Pressure of Cu(C₁₁H₁₉O₂)₂(c) Measured by the Torsion-Effusion Method (Pt–Rh Effusion Cell)

<i>T</i>	<i>P</i>	<i>M</i>
K	Pa	g mol ⁻¹
P-2 Cell: 0.06-cm Orifice Diameter ^a		
372.6	7.84 × 10 ⁻¹	471
363.9	2.87 × 10 ⁻¹	
346.2	3.34 × 10 ⁻²	481
351.2	6.31 × 10 ⁻²	496
345.2	3.04 × 10 ⁻²	464
359.7	1.80 × 10 ⁻¹	465
352.3	7.30 × 10 ⁻²	456
367.2	4.19 × 10 ⁻¹	469
371.4	6.90 × 10 ⁻¹	459
375.0	1.04	462
374.7	9.98 × 10 ⁻¹	460
351.0	5.99 × 10 ⁻²	506
355.7	1.08 × 10 ⁻¹	484
364.8	3.08 × 10 ⁻¹	468
370.2	5.67 × 10 ⁻¹	456
354.6	9.73 × 10 ⁻²	443
	<i>M</i> _{average} =	469
P-1 Cell: 0.11-cm Orifice Diameter ^b		
361.2	1.86 × 10 ⁻¹	432
343.2	2.08 × 10 ⁻²	437
351.7	6.03 × 10 ⁻²	422
347.0	3.39 × 10 ⁻²	416
350.7	5.49 × 10 ⁻²	421
356.5	1.03 × 10 ⁻¹	406
356.8	1.07 × 10 ⁻¹	427
361.6	1.87 × 10 ⁻¹	430
365.2	2.86 × 10 ⁻¹	423
334.9	6.41 × 10 ⁻³	
337.6	8.90 × 10 ⁻³	421
344.2	2.11 × 10 ⁻²	413
354.1	6.77 × 10 ⁻²	423
	<i>M</i> _{average} =	422

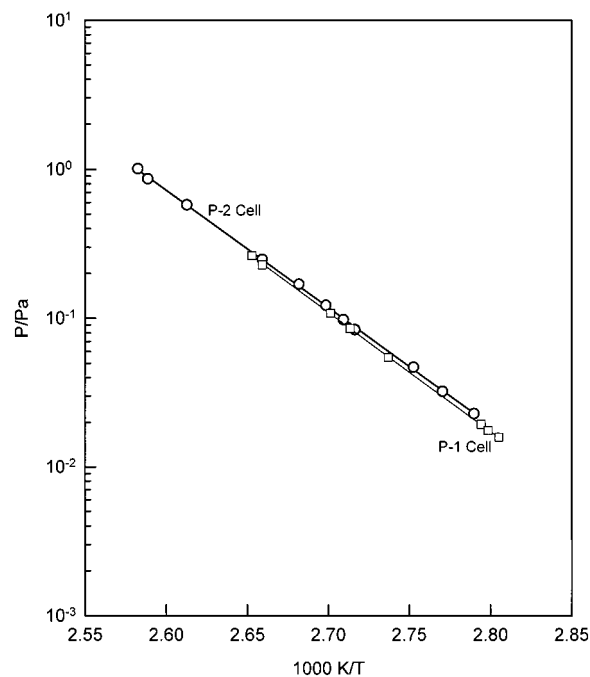
^a A: 17.789 ± 0.121; B: -6669 ± 33. Δ_{sub}*H*_m(361 K) = (127.6 ± 0.4) kJ mol⁻¹. ^b A: 17.677 ± 0.366; B: -6653 ± 92. Δ_{sub}*H*_m(351 K) = (127.2 ± 1.7) kJ mol⁻¹.

effusion³ and transpiration^{5,6} methods; one method⁴ was not clearly stated. Comparisons of the present results with literature values^{3–6} are shown in Figures 4 and 5; extrapolation of our data up to the vicinity of the melting point (denoted “MP”; 198 °C for Cu(TMHD)₂; 170 °C for Y(TMHD)₃) is shown by the dotted line. As can be seen, there is a considerable spread among the various determinations. In Table 3, the pressure ratios *P*/*P*_{This_work} give a more quantitative indication of the comparison of literature values with the present work at two temperatures. Clearly, the transport results of Yuhya et al.⁵ are in closest accord with our new measurements, with the vapor pressures agreeing within a factor of 2 or better at each temperature, and the slopes are compatible as well. The Cu(TMHD)₂ vapor pressures of Waffenschmidt et al.⁶ are about a factor of 4 lower than our results, while the data for Y(TMHD)₃ show a markedly lower temperature dependence. For Y(TMHD)₃, the effusion pressures of Amano et al.³ are a factor of 4 or more lower than our results, although the slopes are compatible. The single points reported by Erbil et al.⁴ are about a factor of 2 higher than the present results, while similar points listed in the Strem Chemicals, Inc. catalog¹¹ are higher by factors of 32 and 76 for Cu(TMHD)₂ and Y(TMHD)₃, respectively. Clearly, those interested in MOCVD applications should use caution in selecting the proper data sets for predicting optimum process conditions. We are confident that, for use in MOCVD process applications, the vapor pressure expressions

Table 2. Total Vapor Pressure of Y(C₁₁H₁₉O₂)₃(c) Measured by the Torsion-Effusion Method (Pt–Rh Effusion Cell)

<i>T</i>	<i>P</i>	<i>M</i>
K	Pa	g mol ⁻¹
P-2 Cell: 0.06-cm Orifice Diameter ^a		
382.8	5.77 × 10 ⁻¹	672
368.1	8.39 × 10 ⁻²	661
358.4	2.29 × 10 ⁻²	
372.9	1.69 × 10 ⁻¹	675
363.3	4.71 × 10 ⁻²	667
376.1	2.48 × 10 ⁻¹	673
360.9	3.23 × 10 ⁻²	
370.6	1.22 × 10 ⁻¹	
369.1	9.78 × 10 ⁻²	696
386.3	8.62 × 10 ⁻¹	656
387.2	1.01	633
	<i>M</i> _{average} =	667
P-1 Cell: 0.11-cm Orifice Diameter ^b		
376.1	2.28 × 10 ⁻¹	607
377.0	2.64 × 10 ⁻¹	624
368.5	8.56 × 10 ⁻²	630
370.2	1.08 × 10 ⁻¹	621
356.5	1.59 × 10 ⁻²	639
357.9	1.95 × 10 ⁻²	655
365.4	5.49 × 10 ⁻²	613
357.3	1.76 × 10 ⁻²	625
	<i>M</i> _{average} =	627

^a A: 20.359 ± 0.159; B: -7885 ± 44. Δ_{sub}*H*_m(372 K) = (151.0 ± 0.8) kJ mol⁻¹. ^b A: 20.636 ± 0.095; B: -7999 ± 26. Δ_{sub}*H*_m(366 K) = (153.1 ± 0.4) kJ mol⁻¹.

**Figure 3.** Total vapor pressure over Y(C₁₁H₁₉O₂)₃(c) measured with two platinum rhodium effusion cells for the sublimation process Y(C₁₁H₁₉O₂)₃(c) = Y(C₁₁H₁₉O₂)₃(g).

$$\text{for Cu(TMHD)}_2: \log(P/\text{Pa}) = 17.789 - 6669K/T$$

$$\text{for Y(TMHD)}_3: \log(P/\text{Pa}) = 20.359 - 7885K/T$$

can be used reliably for predicting copper and yttrium transport rates in the temperature ranges of interest. In this context, we note that the value obtained here for the enthalpy of sublimation of Cu(TMHD)₂, Table 1, agrees well with a value for the standard molar enthalpy of sublima-

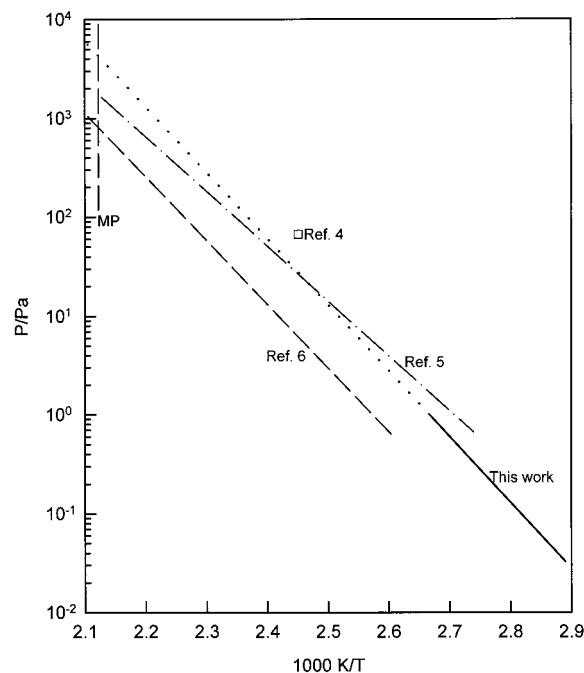


Figure 4. Comparison of the total vapor pressure over $\text{Cu}(\text{C}_{11}\text{H}_{19}\text{O}_2)_2(\text{c})$ from the present work with literature data.

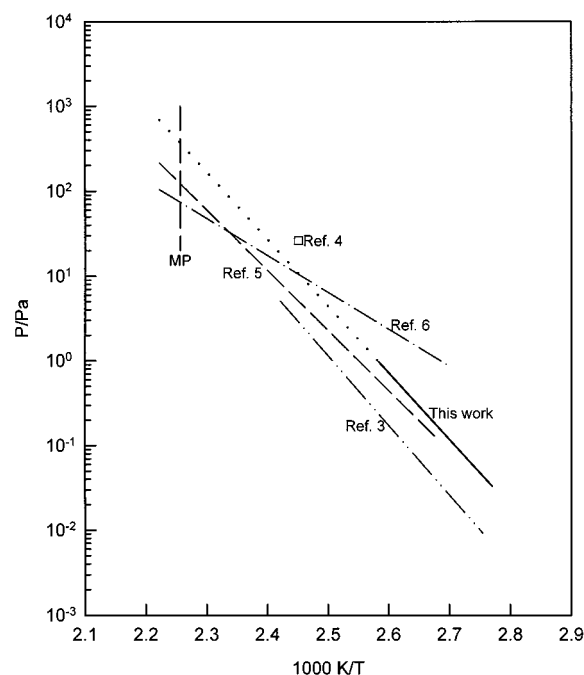


Figure 5. Comparison of the total vapor pressure over $\text{Y}(\text{C}_{11}\text{H}_{19}\text{O}_2)_3(\text{c})$ from the present work with literature data.

tion at room temperature, $(123 \pm 7) \text{ kJ mol}^{-1}$, obtained calorimetrically.¹²

In extrapolating our measured data as shown in Figures 4 and 5, we recognize that there is probably a relatively small downward curvature to the $\log P$ vs $1/T$ plots at the higher temperatures; however, a reliable estimated heat capacity correction is impractical for these complex molecular species. More importantly, the amount by which our data need to be extrapolated to reach sample pressures of interest for efficient CVD application (say, 50 Pa) is small, and we consider a linear extrapolation to be sufficient over the narrow range required (for a vapor pressure of 50 Pa, to about 150 °C in both cases).

Table 3. Comparison of $\text{Cu}(\text{TMHD})_2$ and $\text{Y}(\text{TMHD})_3$ Vapor Pressures (Pa) at Selected Temperatures

$\text{Cu}(\text{TMHD})_2$				
ref	$P(380 \text{ K})$	$P/P_{\text{This work}}$	$P(408 \text{ K})$	$P/P_{\text{This work}}$
2			66.9	2.4
3	2.63	1.5	26.3	0.94
4	0.43	0.25	6.18	0.22
this work	1.75	1.0	28.1	1.0
$\text{Y}(\text{TMHD})_3$				
ref	$P(373 \text{ K})$	$P/P_{\text{This work}}$	$P(408 \text{ K})$	$P/P_{\text{This work}}$
1	0.04	0.24	2.94	0.27
2			26.3	2.4
3	0.12	0.71	5.07	0.46
4	1.01	5.9	10.1	0.92
this work	0.17	1.0	11.0	1.0

For process applications, it is important to bear in mind that the molecularity of the precursor vapors must be clearly established since metal transport and deposition rates are directly proportional to the number of metal atoms in the vapor molecule. This is not a trivial issue, and simple assumptions about vapor composition should not be taken for granted. For example, we have encountered several metalcarbonyl vapors that are shown to be dimeric or trimeric in nature, as determined from torsion/mass-loss studies.¹³ Similarly, recent mass spectrometric studies in our laboratory¹⁴ have shown $\text{Ba}(\text{TMHD})_2(\text{c})$ to vaporize primarily as the dimeric species $[\text{Ba}(\text{TMHD})_2]_2$. The vapor molecular weight data presented here show conclusively that the saturated vapors of both $\text{Cu}(\text{TMHD})_2$ and $\text{Y}(\text{TMHD})_3$ are highly monomeric.

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International Superconductivity Technology Center (ISTEC) as collaborative research and development of fundamental technologies for superconductivity applications under the Agency of Industrial Science and Technology (AIST) of the Ministry of International Trade and Industry of Japan.

Received for review October 18, 2000. Accepted December 21, 2000.
This work is supported by the New Energy and Industrial
Technology Development Organization (NEDO) through the

JE0003445