

Full Paper

Static Vapor Pressure Measurement of Low Volatility Precursors for Molecular Vapor Deposition Below Ambient Temperature**

By Taisuke Ohta, Fabio Ciccoira, Pascal Doppelt, Lionel Beitone, and Patrik Hoffmann*

Static vapor pressure measurements of volatile metal precursors, in the pressure range 10^{-1} Pa to 10^3 Pa, are described. The vapor pressures and the sublimation or evaporation enthalpies, in the range 265 K–300 K, of $\text{Mo}(\text{CO})_6$ (77.7 kJ mol^{-1}), two dimethyl(β -diketonato)gold(III) complexes, $\text{Me}_2\text{Au}(\text{tfa})$ (83.5 kJ mol^{-1}) and $\text{Me}_2\text{Au}(\text{hfa})$ (68.1 kJ mol^{-1}), and an inorganic Rh precursor, $[(\text{PF}_3)_2\text{RhCl}]_2$ (90.8 kJ mol^{-1}), were determined. The sublimation enthalpy for $\text{Mo}(\text{CO})_6$ was larger by more than 10% in the measured temperature range than reported values measured at higher temperatures. At ambient temperatures, partial decomposition was observed only for the gold precursors.

Keywords: CAS 107-46-0 (HMDSO), CAS 13939-06-5 ($\text{Mo}(\text{CO})_6$), CAS 14876-98-3 ($[(\text{PF}_3)_2\text{RhCl}]_2$), CAS 63470-53-1 ($\text{Me}_2\text{Au}(\text{tfa})$), CAS 63470-54-2 ($\text{Me}_2\text{Au}(\text{hfa})$), Electron beam induced deposition (EBID), Sublimation enthalpy, Vapor pressure

1. Introduction

The vapor pressure of the precursor as a function of its temperature is one of the key parameters influencing the choice of precursor in CVD and related processes. There are different ways of determining the vapor pressure of chemical compounds, with mass or torsion effusion methods being the most commonly employed. These methods allow the measurement of vapor pressures of transition metal halide and organic compounds^[1,2] down to 10^{-4} Pa. These methods are described in the literature.^[3] Vapor pressure measurements of organic compounds were carried out by Griffiths et al., using an ultrasonic monitor.^[4] A general review of transpiration, ebulliometric, vibrating fiber, thermistor, and mass or torsion effusion methods is given by Carson.^[5]

Static vapor pressure measuring methods have also been developed, and have been in use for some time. Methods employing a manometer,^[5] or capacitance gauge with a membrane null gauge^[6–9] are also widely applied. The membrane is used to insulate the pressure gauge from the vapor of the chemical compound in order to avoid corrosion, etching or deposition. Spee and Mackor recently applied another static method involving the precursor vapor being in contact with mercury.^[10] However, this limits application of the method to nonreactive chemicals, and

makes the lowest measurable pressure that of the vapor pressure of mercury (0.1 torr).

In this work, a simple method for the static vapor pressure measurement of small sample quantities is described. We show the results for the vapor pressures of four precursors used for EBID.^[11] The vapor pressures are measured directly by means of a capacitance gauge, with results in the range 10^{-1} – 10^3 Pa. The system also allows the sample to be observed so that, for example, color changes, phase transitions, or decomposition under low pressure conditions, as well as the presence of impurities in the precursor sample, may be detected.

2. Results and Discussion

Vapor pressure measurements were carried out for molybdenum hexacarbonyl ($\text{Mo}(\text{CO})_6$), dimethyl-gold-trifluoroacetylacetonate $\text{Me}_2\text{Au}(\text{tfa})$, dimethyl-gold-hexafluoroacetylacetonate $\text{Me}_2\text{Au}(\text{hfa})$, and tetrakis-trifluorophosphine-dichloro-dirhodium $[(\text{PF}_3)_2\text{RhCl}]_2$.

2.1. Measurement of the Vapor Pressure of $\text{Mo}(\text{CO})_6$

$\text{Mo}(\text{CO})_6$ (Aldrich), a white solid at room temperature, has been used for vapor deposition experiments for several decades. The vapor pressure has been reported by Boxhoorn et al.,^[12] Lander and Germer,^[13] Monchamp and Cotton,^[14] and Hieber and Romberg.^[15]

Figure 1 shows that there is good agreement between our measurements and the reported values.^[13,15] The lines in Figure 1 are fitted according to Equation 1 (which is given in the Experimental section below). With this fit, the sublimation enthalpy of the compound is determined, from Equation 2 (also in the Experimental section), to be

[*] Dr. P. Hoffmann, T. Ohta, F. Ciccoira
Institute of Applied Optics
Swiss Federal Institute of Technology Lausanne
CH-1015 Lausanne EPFL (Switzerland)
E-mail patrik.hoffmann@epfl.ch

Dr. P. Doppelt, L. Beitone
Ecole Supérieure de Physique et Chimie Industrielle, C.N.R.S
10, Rue Vauquelin, F-75005 Paris (France)

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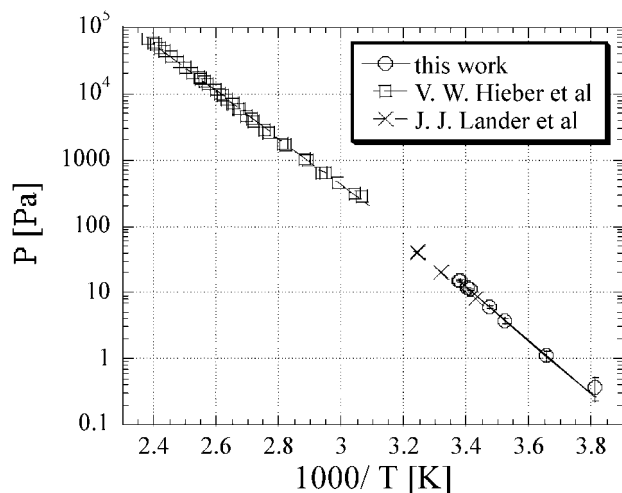


Fig. 1. Vapor pressure of $\text{Mo}(\text{CO})_6$.

77.7 kJ mol^{-1} . This figure, together with the literature values,^[12–15] is listed in Table 1. The data in Table 1 show a clear tendency for the lower sublimation enthalpy values to be found in the higher temperature range. It is assumed that vibrational excitation of the molecules, inducing or accompanying a solid–vapor phase transition, results in an increase of lattice energy and, therefore, a decrease in the sublimation enthalpy. With six degrees of freedom for a solid and a temperature difference ΔT of 150 K, the increase in kinetic energy, $(6/2)k_B\Delta T = 6.21 \times 10^{-21} \text{ [J]}$ (where k_B is the Boltzmann constant), corresponds to 3.7 kJ mol^{-1} . This value is approximately 39 % of the 9.5 kJ mol^{-1} difference in sublimation enthalpies between this study and that by Hieber and Romberg. The maximum temperature difference between the two studies was 150 K.

Table 1. Fitting constants, A and B , sublimation enthalpy, and measured temperature range obtained for $\text{Mo}(\text{CO})_6$ from the values measured by the authors and those reported earlier.

Reference	Fitting constants for Equation 1		Sublimation enthalpy ΔH_s , [kJ mol ⁻¹]	Temperature range [K]
	$\log_{10} p = A + B/T$			
	A	B [K]		
[12]	14.8	-4018 ± 46	76.9 ± 0.9	240–285
This work	14.9	-4058	77.7	262.5–296.1
[13]	13.919	-3800	72.7 [a]	291.6–308.4
[14]	13.298	-3561.3	69.8	343.1–383.2
[15]	13.298	-3561.3	68.2	326.4–419.9

[a] Calculated from reported fitting constants for Equation 1.

2.2. Measurement of $\text{Me}_2\text{Au}(\text{tfa})$

Dimethyl gold trifluoroacetylacetonate, $\text{Me}_2\text{Au}(\text{tfa})$, has been used as a gold precursor for various CVD processes.^[16] It is a white solid at room temperature.

Figure 2 shows the vapor pressure values of $\text{Me}_2\text{Au}(\text{tfa})$ measured at 297.0 K (23.8 °C), 293.8 K (20.6 °C), 293.1 K (19.9 °C), 292.8 K (19.6 °C), 291.3 K (18.1 °C), 289.0 K

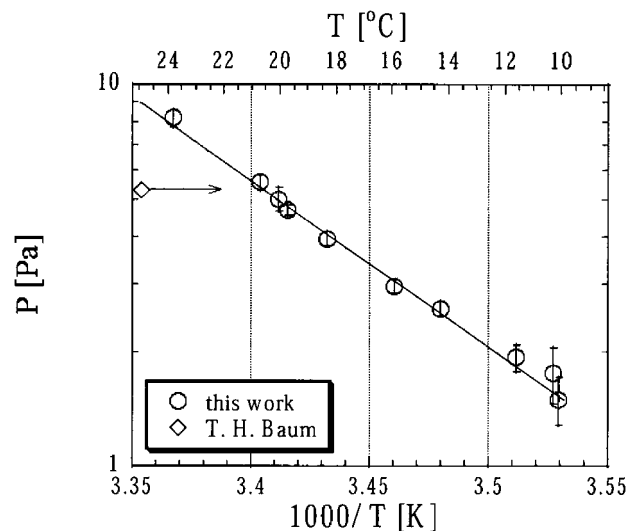


Fig. 2. Vapor pressure of $\text{Me}_2\text{Au}(\text{tfa})$.

(15.8 °C), 287.3 K (14.1 °C), 284.8 K (11.6 °C), 283.6 K (10.4 °C), and 283.3 K (10.1 °C), together with a value (also measured with a capacitance pressure gauge) reported in the literature.^[17] According to the author, the relevant temperature for this value should be 295–296 K (22–23 °C) rather than 298 K (25 °C).^[18] When taking this correction factor (indicated by the arrow in Fig. 2) into account, good agreement is obtained. The sublimation enthalpy, ΔH_s , of the compound is found to be 83.5 kJ mol^{-1} . This result is listed in Table 2.

A change in the color of the solid precursor, and a blue-violet deposit on the Cu gasket exposed to the precursor vapor at room temperature, were observed. X-ray photoelectron spectroscopy (XPS) of the latter deposit detected the presence of Au, C, and F. No deposit was observed on the stainless steel tubes of the vacuum system.

During the vapor pressure measurement, the pressure increases continuously over time, probably due to ongoing decomposition at ambient temperature of the $\text{Me}_2\text{Au}(\text{tfa})$ on the Cu gasket. The rate of increase of pressure over time is about $3\text{--}6 \times 10^{-4} \text{ Pa per second}$. No strong variation of the slope with varying precursor partial pressure is observed. According to XPS results, the pressure increase could be a consequence of a Cu surface-catalyzed decomposition of the precursor compound. Assuming the precursor has a constant vapor pressure of 7.1 Pa at 296 K (23 °C), the measured rate of decomposition corresponds to 1 % of precursor over 3 min.

2.3. Measurement of the Vapor Pressure of $\text{Me}_2\text{Au}(\text{hfa})$

Dimethyl gold hexafluoroacetylacetonate, $\text{Me}_2\text{Au}(\text{hfa})$, is also widely used in the molecular vapor deposition of gold.^[16–19] The complex is a yellow liquid at room temperature.

Figure 3 shows our measured vapor pressure values of $\text{Me}_2\text{Au}(\text{hfa})$ at 296.9 K (23.7 °C), 296.7 K (23.5 °C), 283.4 K

(10.2 °C), 273.7 K (0.5 °C), and 262.7 K (−10.5 °C), together with one reported value, also measured with a capacitance pressure gauge.^[17] A similar correction of the literature value to that in Section 2.2 is indicated by the arrow.^[18] From the fitting parameters (see Table 2), the enthalpy of evaporation, ΔH_e , of the compound was found to be 68.1 kJ mol^{−1}. This value is smaller than the one obtained for Me₂Au(tfa), indicating a strong decrease of intermolecular interaction forces due to further fluorination.

During measurement, the sample underwent a color change from yellow to black, but this did not influence the vapor pressure measurement. As before, there were blue-violet deposits on the Cu gasket and XPS showed these to contain Au, C, and F.

As in the case of Me₂Au(tfa), we can interpret these results as a Cu surface-catalyzed decomposition of the precursor compound. For Me₂Au(hfa), the pressure increase grows linearly with precursor partial pressure. The rate of increase, about 1.4 % per minute, is several times higher than that of the Me₂Au(tfa) compound.

2.4. Measurement of the Vapor Pressure of [(PF₃)₂RhCl]₂

The trifluorophosphine rhodium chloride complex is an inorganic precursor for Rh deposition.^[20,21] The compound was synthesized according to the literature.^[22]

The vapor pressure values of [(PF₃)₂RhCl]₂ measured between 23 °C and 0.5 °C are shown in Figure 4. It can be seen that these values are higher than those previously determined, using an infrared transmission detection method, and assuming that the optical absorption cross sections for both free PF₃ and PF₃ ligands in the complex were identical.^[22] From Equation 1, with the fitting values listed in Table 2, the enthalpy of sublimation of [(PF₃)₂RhCl]₂ was found to be 90.8 kJ mol^{−1}. Neither a color change of the sample, nor a pressure increase with time, was observed during the measurements.

3. Summary

The fitting constants of the Clausius–Clapeyron equation, *A* and *B*, the correlation coefficient, *R*, the sublimation or evaporation enthalpy, ΔH_s or ΔH_e , and the fitted

Table 2. Fitting constants, *A* and *B*, correlation coefficient *R*, sublimation (ΔH_s) or evaporation (ΔH_e) enthalpy, and the fitted vapor pressure value at 23 °C for the Mo carbonyl, the two gold, and the Rh precursors in the temperature range −10 °C to 24 °C.

Compounds	Fitting constants for Equation 1		Correlation coefficient <i>R</i>	Sublimation or evaporation enthalpy ΔH_s^* or ΔH_e [kJ mol ^{−1}]	Fitted vapor pressure value at 23 °C [Pa]
	$\log_{10} p = A + \frac{B}{T}$				
	<i>A</i>	<i>B</i> [K]			
Mo(CO) ₆	14.9±0.35	−4058±102.0	0.998	77.7 ± 1.95*	14.9
Me ₂ Au(tfa)	15.6±0.44	−4362±127.5	0.997	83.5 ± 2.44*	7.11
Me ₂ Au(hfa)	13.9±0.37	−3559±105.2	0.999	68.1 ± 2.01	73.2
[(PF ₃) ₂ RhCl] ₂	16.9±0.41	−4745±121.5	0.998	90.8 ± 2.32*	7.47

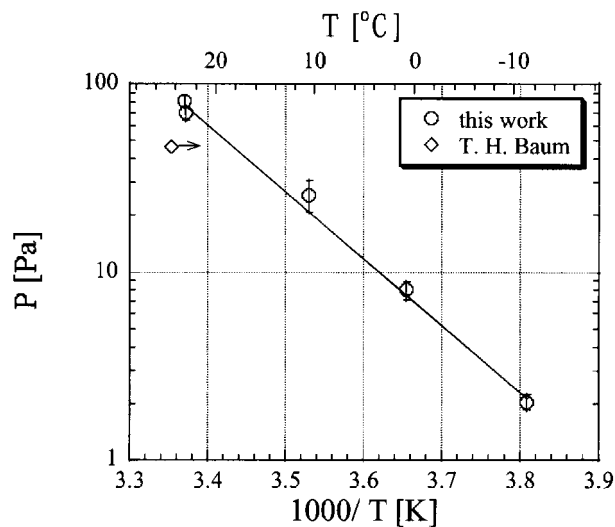


Fig. 3. Vapor pressure of Me₂Au(hfa).

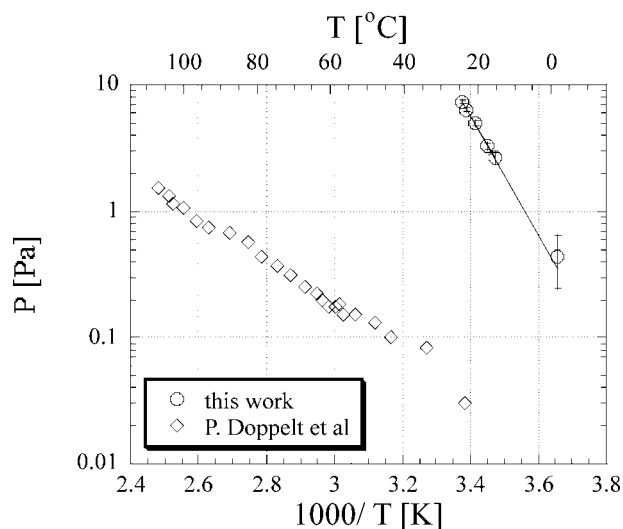


Fig. 4. Vapor pressure of [(PF₃)₂RhCl]₂ with reported FTIR values [22].

vapor pressure value at 23 °C for each precursor, are listed in Table 2. The lower value of sublimation enthalpy of Me₂Au(hfa), compared to Me₂Au(tfa), confirms the increased volatility caused by higher fluorination of the diketonato ligand.

4. Conclusions

Vapor pressure measurements were performed for Mo(CO)₆, Me₂Au(tfa), Me₂Au(hfa), and [(PF₃)₂RhCl]₂ between 263 K and 298 K (−10 °C and 24 °C). The sublimation enthalpies were found to be 77.7 kJ mol^{−1}, 83.5 kJ mol^{−1}, 68.1 kJ mol^{−1}, and 90.8 kJ mol^{−1}, respectively. For Mo(CO)₆, this value is 10 % higher than the reported value (measured at a higher

temperature). Partial decomposition of $\text{Me}_2\text{Au}(\text{tfa})$ and $\text{Me}_2\text{Au}(\text{hfa})$ was observed at ambient temperature, whereas $\text{Mo}(\text{CO})_6$ and $[(\text{PF}_3)_2\text{RhCl}]_2$ showed no decomposition in the observed temperature range.

5. Experimental

Experimental Setup: The system used for vapor pressure measurements of precursor compounds is shown schematically in Figure 5. All the components are made with 304L stainless steel ultra high vacuum (UHV) material and equipped with Conflat (CF) flanges.

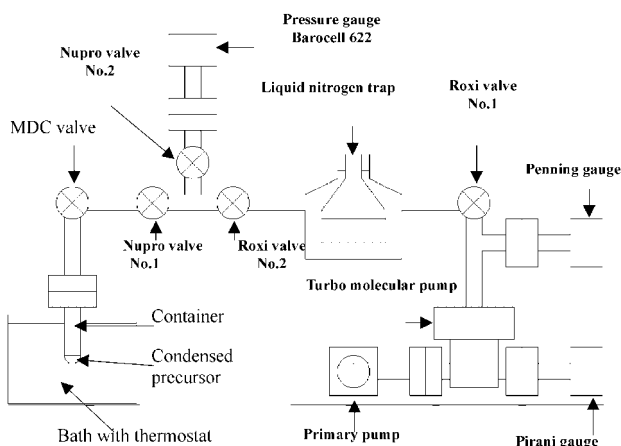


Fig. 5. Schematic view of the vapor pressure measurement setup.

The sample is loaded into a glass container welded to a stainless steel flange. The latter is connected to a bellow valve, the function of which is to both introduce the precursor vapor into the measuring chamber, and to avoid the precursor coming into contact with ambient gases during mounting. To minimize outgassing, silylation treatment [23] of the glass containers is carried out prior to precursor loading.

Pumping is achieved by a turbomolecular pumping station with a 100 L s^{-1} nominal pumping speed for N_2 . To protect the pumping system from the precursor vapors, a liquid nitrogen trap is mounted between the measuring chamber and the turbomolecular pump. The ultimate pressure in the measuring chamber is measured by a Penning gauge, mounted close to the turbomolecular pump.

Vapor pressure measurements are carried out by means of a capacitance gauge (Edwards BAROCELL 622), working in the pressure range 10^{-1} Pa to 10^3 Pa (0.001–10 mbar) with an accuracy of 0.15 %.

Temperature Control: To measure the vapor pressure as a function of temperature, during the experiments over a range of temperatures, the temperature of the precursor container is regulated by a thermostat with an accuracy of $\pm 0.1^\circ\text{C}$. Between 241 K and 283 K (-29°C and 10°C), the sample container is immersed in a Dewar containing a substance at its melting point. Decane (m.p. = -32.1°C), dodecane (m.p. = -10.6°C), pentadecane (m.p. = 10.6°C), and deionized water (m.p. = 0.3°C), were employed as cooling substances. The melting point temperatures measured with calibrated thermometers (Normschliff Gerätebau Wertheim, Germany) differ slightly from the literature values [24] probably due to the presence of impurities. In the temperature range 288 K to 296 K (15°C to 23°C), the sample is kept at a constant temperature using a circulating water thermostat (Haake 001-1407, Germany).

Precursor Loading: Precursor loading is carried out in a dry nitrogen-purged glove box to reduce contact between the precursors and water vapor. After mounting onto the vacuum system, the precursor container is evacuated to a rough vacuum; further evacuation is carried out by applying several freeze-pump-thaw cycles.

To guarantee the purity of the precursor, several measurements were collected for each load until reproducible pressure values were obtained. After each measurement, the whole measuring volume, except the cooled container, was evacuated to about 10^{-5} Pa .

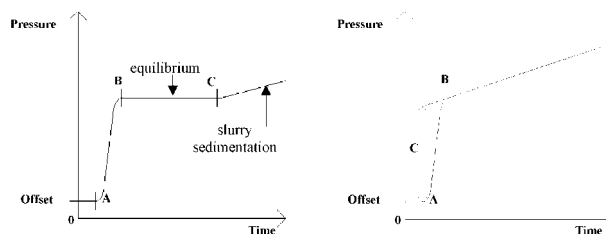


Fig. 6. Schematic drawing of the temporal pressure evolution of stable (left) and partially decomposing (right) compounds.

Data Acquisition: The pressure versus time evolution can vary depending on the precursors. Typical curves for stable compounds (left) and partially decomposing compounds (right) are shown in Figure 6.

Stable compounds Figure 6 (left), need several minutes to reach an equilibrium pressure (B) which then remains constant for about 40 min. The slight pressure increase that occurs at point (C) is due to a temperature gradient following sedimentation of solid onto the bottom of the Dewar. Only the equilibrium values were taken into account when calculating the mean value and standard deviation of the vapor pressure.

Partially decomposing precursors show a continuous pressure increase with time, as shown schematically in Figure 6 (right). After reaching thermal equilibrium (B), the pressure increases at a constant rate. Because leaks and degassing from the walls of the system can be discounted, the pressure increase probably results from partial decomposition of the precursor. We assume that the intercept of the measured pressure data (the length C in Fig. 6 right) represents the vapor pressure of the precursor, P_{VR} , as proposed in the literature [8]. In the case of precursor decomposition, the slope of the temporal pressure increase after (B) is assumed to be the decomposition rate of the precursor compound.

The pressure values were acquired over a period of 2000 s to 8000 s. At least three consecutive measurements were carried out at each temperature. All measurements show good reproducibility.

Data Processing: Because the temperature of the pressure gauge differs from that of the precursor container, the vapor pressure measurements can be influenced by thermal transpiration. The detected pressures are corrected to the temperature of the precursor compounds with an empirical thermal transpiration correction factor [25,26]. The corrections are always smaller than 5 % of the measured values, thus resulting in a smaller than 5 % correction of the sublimation/evaporation enthalpy.

The mean values of the vapor pressure of a compound at each temperature are represented in a logarithmic pressure [Pa] versus $1/T$ [K] plot. The error bars on the ordinate (pressure) indicate two times the standard deviation, whereas the error bars for the abscissa are smaller than the symbols. The data was fitted to an integrated form of the Clausius–Clapeyron equation.

$$\log_{10} p = A + B/T \quad (1)$$

The fitting was weighted by the ratio of the standard deviation to the mean value. The errors for the fitting constants A and B indicate the standard error for the fitting calculation.

Determination of the Sublimation Enthalpy: With a negligible condensed phase molar volume compared to the gas phase molar volume and an application of the ideal gas law, the sublimation/evaporation enthalpy, ΔH , of solids or liquids can be obtained, as in Equation 2 [27].

$$\Delta H = -R \frac{d \ln p}{d(1/T)} = -2.303 R B \quad (2)$$

R [$\text{J mol}^{-1} \text{K}^{-1}$] is the gas constant, and B [K] is the fitting constant for Equation 1. The error for ΔH is derived from the error for the fitting constant, B .

Precision Limit of the System: Background pressure measurements at room temperature resulted in a stabilized constant pressure of $0.3 \pm 0.15 \text{ Pa}$ after two outgassing cycles, with the statistical fluctuation corresponding to the smallest measurable value of the pressure gauge controller. Measurement of vapor pressures larger than 1 Pa is, therefore, reasonably reliable.

Calibration Measurement: The system was calibrated using hexamethyl disiloxane (HMDSO), a standard for which several vapor pressure data are available [28–32]. Our measured vapor pressure at 241.1 K (-32.1°C) and

262.6 K (-10.6°C) are in good agreement with the extrapolated fitting curve of these reported values, especially with the results of Reuther and Reichel [28], and Grinberg et al. [29].

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- [1] G. Bardi, B. Brunetti, V. Piacente, *J. Chem. Eng. Data* **1996**, *41*, 14.
- [2] V. Piacente, D. Fontana, P. Scardala, *J. Chem. Eng. Data* **1994**, *39*, 231.
- [3] A. S. Carson, in *Thermochemistry and Its Applications to Chemical and Biochemical Systems* (Ed: M. A. V. Ribeiro da Silva), Reidel, Dordrecht, The Netherlands **1984**, p. 127.
- [4] C. L. Griffiths, A. Stafford, S. J. C. Irvine, N. Maung, A. C. Jones, L. M. Smith, S. A. Rushworth, *Appl. Phys. Lett.* **1996**, *68*, 1294.
- [5] F. Daniels, *Phys. Laboratory McGill Univ.* **1928**, *50*, 1114.
- [6] P. O'Brien, J. R. Walsh, A. C. Jones, S. A. Rushworth, C. Meaton, *J. Mater. Chem.* **1993**, *3*, 739.
- [7] C. G. De Kruif, T. Kuipers, J. C. Van Miltenburg, R. C. F. Schaake, G. Stevens, *J. Chem. Thermodyn.* **1981**, *13*, 1081.
- [8] P. Tobaly, *Rev. Sci. Instrum.* **1991**, *62*, 2011.
- [9] P. Tobaly, G. Lanchei, *J. Chem. Thermodyn.* **1993**, *25*, 503.
- [10] C. I. M. A. Spee, A. Mackor, *Conf. Proc. Sci. Technol. Thin Film Supercond.* **1989**, *xiv557*, 281.
- [11] I. Utke, B. Dwir, K. Leifer, F. Cicoira, P. Doppelt, P. Hoffmann, E. Kapon, *Microelectron. Eng.* **2000**, *53*, 261.
- [12] G. Boxhoorn, J. M. Ernstuing, D. J. Stufkens, A. Oskam, *Thermochim. Acta* **1980**, *42*, 315.
- [13] J. J. Lander, L. H. Germer, *Trans. Am. Inst. Min., Metall., Pet. Eng.* **1947**, *October*, 648.
- [14] R. R. Monchamp, F. A. Cotton, *J. Chem. Soc.* **1960**, 1438.
- [15] V. W. Hieber, E. Romberg, *Z. Anorg. Allg. Chem.* **1935**, *221*, 332.
- [16] T. T. Kodas, T. H. Baum, P. B. Comita, *J. Appl. Phys.* **1987**, *62*, 281.
- [17] T. H. Baum, *J. Electrochem. Soc.* **1987**, *134*, 2616.
- [18] T. H. Baum, personal communication **1999**.
- [19] A. D. Dubner, A. Wagner, *J. Appl. Phys.* **1989**, *65*, 3636.
- [20] P. Doppelt, V. Weigel, P. Guinot, *Mater. Sci. Eng. B* **1993**, *17*, 143.
- [21] F. Marchi, D. Tonneau, R. Pierrisnard, V. Bouchiat, V. Safarov, H. Dalaporta, P. Doppelt, R. Even, *J. Phys. IV* **1999**, *9*, 733.
- [22] P. Doppelt, L. Ricard, V. Weigel, *Inorg. Chem.* **1993**, *32*, 1039.
- [23] P. W. Hoffmann, M. Stelzle, J. F. Rabolt, *Langmuir* **1997**, *13*, 1877.
- [24] K. P. C. Vollhardt, *Organic Chemistry*, 5th ed., W. H. Freeman & Co., New York, NY **1987**.
- [25] K. F. Poulter, M. J. Rodgers, P. J. Nash, T. J. Thompson, M. P. Perkin, *Vacuum* **1983**, *33*, 311.
- [26] T. Takaishi, Y. Sensui, *Trans. Faraday Soc.* **1963**, *59*, 2503.
- [27] P. W. Atkins, *Physical Chemistry*, 6th ed., Oxford University Press, Oxford **1978**.
- [28] V. H. Reuther, G. Reichel, *Chem. Tech.* **1954**, *6*, 479.
- [29] E. E. Grinberg, N. G. Chernaya, A. M. Bershetskii, G. Y. Nechaeva, Y. M. Abuzin, A. A. Efremov, *Russ. J. Phys. Chem. (Engl. Transl.)* **1986**, *60*, 779.
- [30] I. I. Skorokhodov, V. E. Ditsent, N. A. Terent'eva, M. M. N. Zolotar-ev, *Russ. J. Phys. Chem. (Engl. Transl.)* **1971**, *45*, 902.
- [31] O. L. Flaningam, *J. Chem. Eng. Data* **1986**, *31*, 266.
- [32] D. W. Scott, J. F. Messerly, D. D. Todd, G. B. Guthrie, I. A. Hosselopp, R. T. Moore, A. Osborn, W. T. Berg, J. P. McCullough, *J. Phys. Chem.* **1961**, *65*, 1320.