Vapor Pressure of Trimethylantimony and *tert*-Butyldimethylantimony

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Vapor pressures of trimethylantimony (CAS Registry Number 594-10-5) and *tert*-butyldimethylantimony (CAS Registry Number 138260-00-1) were measured using the static method in the temperature range of (248 to 308) K. The experimental data were fitted with the Clarke and Glew and Antoine equations and compared with the previously published values.

Introduction

Metalorganic vapor phase epitaxy (MOVPE) and other epitaxial techniques use a broad variety of organometallic precursors. The correct and exact knowledge of the essential physical and chemical parameters is necessary for precise technological application of these materials during technological processes. In particular, volatility data and a detailed vapor pressure equation are essential for controlled precursor dosimetry and thermodynamic analysis of MOVPE growth.[1−3] The vapor pressure of most precursors falls in the low pressure region (pressure below 1 kPa), where measurements are often subject to large systematic errors. Moreover, many precursors are pyrophoric, and some of them are also toxic. High-purity samples were not available in the past and became available in the past decade only. Vapor pressure data obtained using the static method may also systematically deviate due to insufficient degassing of samples. As a consequence, experimental vapor pressure data for these compounds either show significant scatter or are unavailable. Our laboratory has been involved in systematic measurement of vapor pressure of new as well as recently available high quality precursors used for MOVPE. The vapor pressure data of the precursors of Ga, Al, Sb (triethylantimony), Zn, Si, In, Y, Zr, and Ge were published in our previous works.[4−9] In this work we report the vapor pressure data for two antimony precursors, trimethylantimony $(CH_3)_3Sb$ and *tert*-butyldimethylantimony $C_4H_9(CH_3)_2Sb$, in the technologically important interval (248 to 308) K. $(CH_3)_3Sb$ is the conventional Sb source for MOVPE growth of Sb-containing materials. $C_4H_9(CH_3)_2Sb$ was shown to be an excellent replacement for $(CH_3)_3Sb$ for low temperature growth.[10]

Experimental Section

Materials. Both of the studied precursors, $(CH_3)_3Sb$ and $C_4H_9(CH_3)_2Sb$, were supplied by Alkyl (Moscow, Russia). They were synthesized by way of interaction between antimony trichloride and applicable alkyl magnesium halogenides. The purity of the materials after multistage purification was characterized by aggregate content of metal impurities, which was below 10 ppm according to inductively coupled plasma (ICP) spectrometry, and by that of organic impurities, which was below 30 ppm according to NMR. Prior to the measurement of vapor pressure, the samples were carefully degassed by multistage vacuum distillation as described in detail in ref 9.

Apparatus and Procedure. Vapor pressure measurements were performed using the static method with an apparatus internally denoted as STAT7. The apparatus and measuring procedure were previously described in detail.[9] Therefore, only short description is given.

The pressure was measured by a capacitance diaphragm absolute gage MKS Baratron 631A12TBEM (MKS Instruments Inc., USA). Its measuring upper limit is 13 332 Pa. The temperature of the pressure sensor was kept at $T = 398$ K by the self-controlling temperature system. The pressure gauge was calibrated at 398 K by the manufacturer at seven equally spaced pressures from (0 to 13332) Pa. Additional calibration focusing on the beginning of a pressure span was performed in the Czech Metrology Institute. The uncertainty of the pressure reading was less than 0.25 %. The sample temperature was measured by a platinum resistance thermometer Pt100 in a four-wire connection. The thermometer was calibrated at the ice point and/or by comparison to a standard platinum resistance thermometer (SPRT). This SPRT was calibrated to the ITS-90, and its calibration was traceable to the National Institute of Standards and Technology (NIST). The uncertainty of the temperature measurement was estimated to be less than 0.02 K. All temperatures reported here are based on the international temperature scale ITS-90. The apparatus STAT7 is fully automated.

Results and Discussion

The vapor pressure measurements of $(CH_3)_3Sb$ and $C_4H_9(CH_3)_2Sb$ were performed in the temperature interval (248 to 308) K by varying the temperature at random to detect systematic errors caused by possible decomposition or insufficient degassing of the sample. When the pressure at selected temperatures, at which the experiments were performed repeatedly, did not change with the number of measuring cycles, the sample was considered completely degassed, and the final set of data was recorded. At least two experimental points were

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obtained for each temperature. It is a common practice in our group to treat vapor pressure data using the simultaneous correlation with the related thermal data (ideal heat capacities, heat capacities of condensed phases, and calorimetrically determined sublimation and vaporization enthalpies).[7,11,12] This method serves as a sensitive test of the thermodynamic consistency and allows a reliable extrapolation from the vapor pressure equation to temperature regions where vapor pressures are not experimentally determined. However, both compounds under study are pyrophoric which makes it impossible to determine heat capacities of condensed phases with the calorimeters currently available in our laboratories. No thermal data were found in the literature either. Therefore, only data on vapor pressure were used in the development of the vapor pressure equation in this work. The experimental data on vapor pressure listed in Table 1 were fitted with the Clarke and Glew equation[13]

$$R\ln\left(\frac{p}{p^0}\right) = -\frac{\Delta_{\mathrm{cd}}^{\mathrm{g}}G_{\mathrm{m}}^{0}(\theta)}{\theta} + \Delta_{\mathrm{cd}}^{\mathrm{g}}H_{\mathrm{m}}^{0}(\theta)\left(\frac{1}{\theta} - \frac{1}{T}\right) + \Delta_{\mathrm{cd}}^{\mathrm{g}}C_{p,\mathrm{m}}^{0}(\theta)\left[\left(\frac{\theta}{T}\right) - 1 + \ln\left(\frac{T}{\theta}\right)\right] \quad (1)$$

where p is the vapor pressure, p^0 is a selected reference pressure, θ is a selected reference temperature, R is the molar gas constant ($R = 8.314472\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$), $\Delta_{\mathrm{cd}}^{\mathrm{g}}G_{\mathrm{m}}^{0}$ is the difference in molar Gibbs energy between the gaseous and the crystalline or liquid phases (condensed phase) at the selected reference pressure (the gaseous phase is supposed to have characteristics of ideal gas at the pressure p^0), $\Delta_{\mathrm{cd}}^{\mathrm{g}}H_{\mathrm{m}}^{0}$ is the difference in molar enthalpy between the gaseous and the condensed phase, and $\Delta_{\mathrm{cd}}^{\mathrm{g}}C_{p,\mathrm{m}}^{0}$ is the difference between the heat capacities of the ideal gas and of the condensed phase. Given the temperature range studied, the use of the Clarke and Glew eq 1 with three parameters is adequate. The advantage of this equation lies in a physical significance of the fitted parameters. The parameters of the Clarke and Glew eq 1 together with the standard deviation of the fit, σ, are presented in Table 2.

As the Antoine equation

$$\ln(p/\mathrm{Pa}) = A - \frac{B}{(T/\mathrm{K}) + C} \quad (2)$$

is widely used in common software packages and chemical engineering simulators, we also present the parameters of this equation in Table 3. Comparison of experimental vapor pressures with smoothed values obtained from the Clarke and Glew eq 1 is shown in Figures 1A and 2A. The overall uncertainty of the data obtained from the Clarke and Glew eq 1 is estimated to be less than 0.1 % and 0.4 % for $(CH_3)_3Sb$ and $C_4H_9(CH_3)_2Sb$, respectively, in the temperature range studied. The Antoine eq 2 yields the vapor pressure data with the same uncertainty.

Table 1. Experimental Data on the Vapor Pressure of $(CH_3)_3Sb$ and $C_4H_9(CH_3)_2Sb$[b]

$(CH_3)_3Sb$			$C_4H_9(CH_3)_2Sb$		
T K	p^a Pa	Δp Pa	T K	p^a Pa	Δp Pa
249.24	974.21	−0.90	Crystalline Phase		
249.24	974.37	−0.74	248.34	38.29	0.05
250.24	1042.1	0.1	248.34	38.17	−0.07
250.24	1041.8	−0.2	248.34	38.26	0.02
250.24	1041.9	−0.1	253.33	58.45	−0.05
251.23	1112.6	0.4	253.33	58.51	0.01
251.23	1112.4	0.3	253.33	58.54	0.04
251.23	1112.2	0.1	258.35	88.05	0.09
252.21	1186.4	0.8	258.35	87.84	−0.13
252.21	1186.3	0.7	258.35	88.07	0.10
252.21	1186.0	0.5	263.35	129.87	0.27
253.21	1264.6	−0.1	263.35	129.84	0.23
253.21	1264.5	−0.1	268.55	189.75	−0.65
253.21	1264.5	−0.2	268.55	189.76	−0.65
258.19	1730.2	0.2	268.55	189.99	−0.41
258.19	1730.1	0.1	273.40	268.68	0.44
258.19	1729.6	−0.3	273.40	268.48	0.25
263.24	2345.5	1.5	278.29	374.04	0.64
263.24	2344.8	0.7	278.29	374.12	0.72
263.24	2343.3	−0.7	278.29	373.97	0.57
268.3	3134.4	−2.1	283.32	516.67	−0.46
268.3	3136.1	−0.4	283.32	516.82	−0.32
268.3	3136.0	−0.5	283.32	516.43	−0.70
273.35	4143.4	0.8	Liquid Phase		
273.35	4142.7	0.1	288.32	702.32	−1.35
273.35	4143.4	0.8	288.32	702.22	−1.45
278.36	5398.4	1.7	288.32	702.29	−1.38
278.36	5398.9	2.2	293.29	942.18	1.09
278.36	5395.4	−1.4	293.29	942.08	0.99
283.33	6940.9	0.1	293.29	941.97	0.88
283.33	6940.4	−0.4	298.29	1250.8	2.2
283.33	6938.1	−2.6	298.29	1251.3	2.7
283.33	6940.2	−0.6	298.29	1251.2	2.7
288.27	8821.9	−2.2	303.28	1642.0	1.7
288.27	8820.9	−3.2	303.28	1641.8	1.5
288.27	8820.9	−3.2	303.28	1641.8	1.6
290.71	9900.0	−0.2	308.27	2131.3	−4.5
290.71	9899.8	−0.3	308.27	2131.4	−4.5
290.71	9899.3	−0.8	308.27	2131.6	−4.2
293.24	11128.5	0.4			
293.24	11127.4	−0.8			
293.24	11128.9	0.8			
296.22	12737.8	4.9			
296.22	12737.9	5.0			
296.22	12733.5	0.6			

[a] Values are reported with one digit more than is justified by the experimental uncertainty. This is to avoid round-off errors in calculations based on these results. [b] $\Delta p = p - p^{\mathrm{calcd}}$, where p^{calcd} is calculated from the Clarke and Glew eq 1 with parameters given in Table 2.

Figures 1B and 2B show the deviations of the literature results found from the present smoothed values for the entire temperature range studied. Rosenbaum and Sandberg[14] determined the vapor pressure of $(CH_3)_3Sb$ using the static method in the temperature range (248 to 298) K. The relative deviation of their data varies from (−1.2 to 7.8) %. The data for $(CH_3)_3Sb$ by Bamford et al.[15] obtained using the static method in the temperature interval (263 to 333) K are systematically higher than those from this work differing from (4.8 to 16.8) % in the temperature range studied. Long and Sackman[16] reported two vapor pressure points at (273.15 and 290.15) K after the synthesis of $(CH_3)_3Sb$. These values are lower by (1.5 and 1.2) %, respectively, than those of this research. Chen et al.[10] reported the vapor pressure for liquid $C_4H_9(CH_3)_2Sb$ in the temperature range (285 to 336) K. These data show high scatter and differ from the present smooth values from (−18.2 to 2.4) %. Extrapolating the vapor pressure equation far beyond the temperature for which its parameters are applicable should only be done with caution. Still, the normal boiling temperature of $(CH_3)_3Sb$, 353.51 K, calculated from the Clarke and Glew eq 1 is in good agreement with the published value of 353.75 K.[15]

The standard molar enthalpies of vaporization and sublimation $\Delta_{\mathrm{cd}}^{\mathrm{g}}H_{\mathrm{m}}^{0}(\theta)$ at reference temperatures θ are summarized in Table 2. As the Clarke and Glew eq 1 was used with three parameters only, the temperature dependence of $\Delta_{\mathrm{cd}}^{\mathrm{g}}H_{\mathrm{m}}^{0}(\theta)$ in the studied temperature interval results in a linear equation $\Delta_{\mathrm{cd}}^{\mathrm{g}}H_{\mathrm{m}}^{0}(T) = \Delta_{\mathrm{cd}}^{\mathrm{g}}H_{\mathrm{m}}^{0}(\theta) + \Delta_{\mathrm{cd}}^{\mathrm{g}}C_{p,\mathrm{m}}^{0}(T - \theta)$. Vaporization enthalpies calculated from the literature vapor pressure data are compared with values of this research in Table 4. Values of $\Delta_{\mathrm{cd}}^{\mathrm{g}}C_{p,\mathrm{m}}^{0} = C_{p,\mathrm{m}}^{\mathrm{g},0} - C_{p,\mathrm{m}}^{\mathrm{cd}}$

Table 2. Parameters of the Clarke and Glew Eq 1 at the Reference Temperatures θ K and Pressure $p^0 = 10^5$ Pa

compound	phase	θ K	$T_{\min}-T_{\max}$ K	$\Delta_{cd}^{g}G_{m}^{0}$ J·mol^{-1}	$\Delta_{cd}^{g}H_{m}^{0}$ J·mol^{-1}	$\Delta_{cd}^{g}C_{p,m}^{0}$ J·K^{-1}·mol^{-1}	σ^a Pa
$(CH_3)_3Sb$	liquid	298.15	249−296	4896.99 ± 0.37	32513.86 ± 9.70	−39.55 ± 0.34	1.6
$C_4H_9(CH_3)_2Sb$	crystalline	265.83[b]	248−283	14284.07 ± 1.33	43500.62 ± 19.17	−70.75 ± 3.91	0.4
$C_4H_9(CH_3)_2Sb$	crystalline	286.81[c]	248−283	12035.32 ± 2.90	42016.22 ± 87.02	−70.75 ± 3.91	0.4
$C_4H_9(CH_3)_2Sb$	liquid	298.15	288−308	10885.01 ± 1.17	41128.72 ± 49.29	0	2.7

[a] σ is the standard deviation of the fit defined as $\sigma = [(\sum_{i=1}^{n}(\Delta p)_i^2)/(n - m)]^{1/2}$ where Δp is the difference between the experimental and the smoothed values, n is the number of experimental points used in the fit, and m is the number of adjustable parameters of the Clarke and Glew eq 1. [b] Mean temperature of the interval in which vapor pressure was determined. [c] Triple point temperature.

Table 3. Parameters of Antoine Eq 2

compound	phase	$T_{\min}-T_{\max}$ K	A	B	C	σ Pa
$(CH_3)_3Sb$	liquid	249−296	21.0431	3000.32	−37.366	1.3
$C_4H_9(CH_3)_2Sb$	crystalline	248−283	21.2515	3547.46	−46.869	0.5
$C_4H_9(CH_3)_2Sb$	liquid	288−308	23.7131	4946.64	0	2.7

listed in Table 2 that were derived in this work from the vapor pressure data are in the same range as for other metal organic precursors.[7] Comparison with $\Delta_{cd}^{g}C_{p,m}^{0}$ calculated from calorimetric measurements cannot be performed as the calorimetrically determined heat capacities for condensed phases $C_{p,m}^{cd}$ are unavailable.

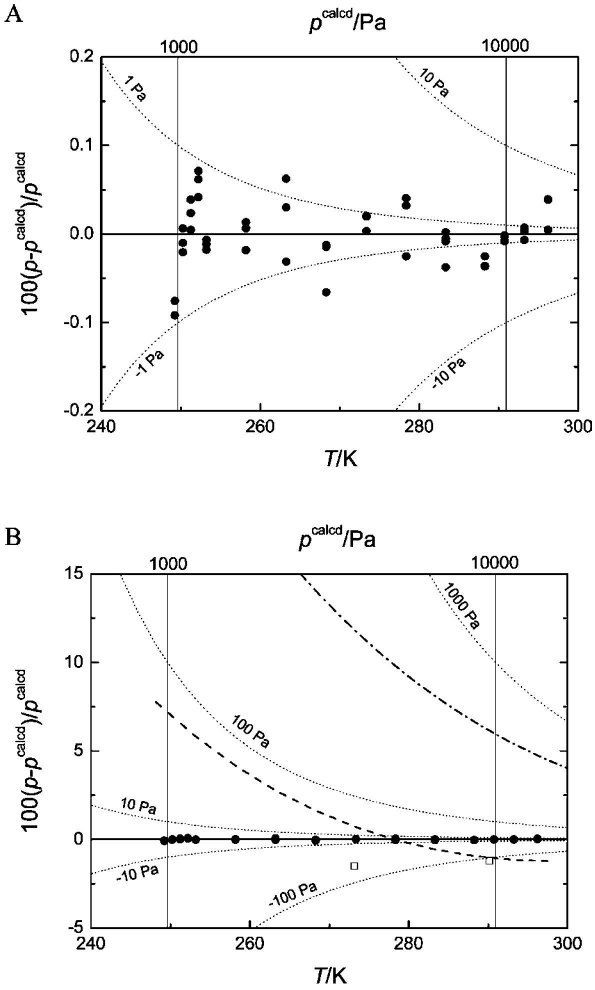

Figure 1. Comparison of experimental vapor pressures p for $(CH_3)_3Sb$ with smoothed values p^{calcd} obtained from the Clarke and Glew eq 1. (A) This work only. (B) This work and literature values. ●, this work; −−, Rosenbaum and Sandberg;[14] −·−, Bamford et al.;[15] □, Long and Sackman;[16] ·····, absolute errors (1 Pa, 10 Pa, 100 Pa, and 1000 Pa).

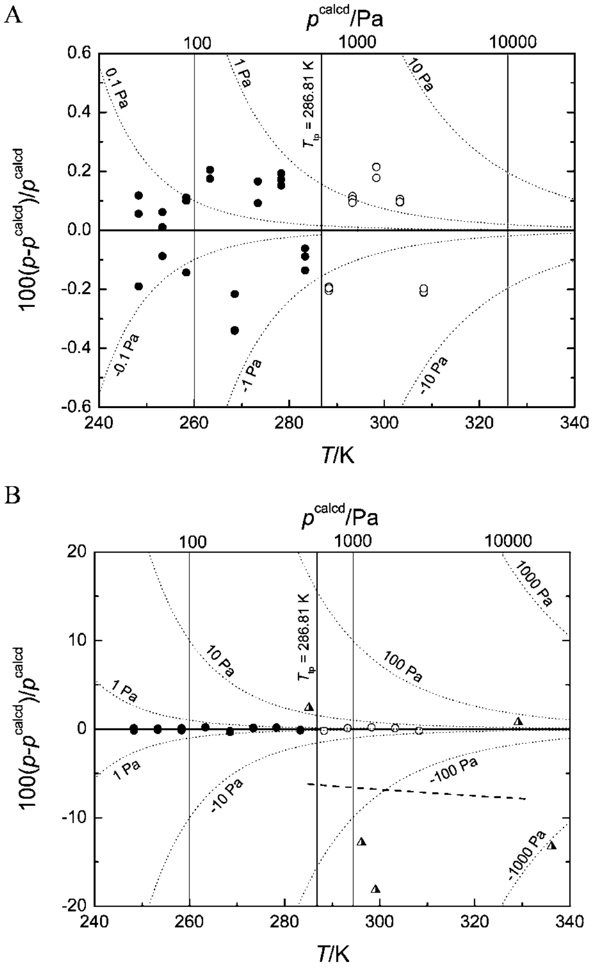

Figure 2. Comparison of experimental vapor pressures p for $C_4H_9(CH_3)_2Sb$ with smoothed values p^{calcd} obtained from Clarke and Glew eq 1. (A) This work only. (B) This work and literature values. ●, this work (crystalline phase); ○, this work (liquid phase); ▲, Chen et al.[10] (experimental data points); −−, Chen et al.[10] (smoothed values); ·····, absolute errors (0.1 Pa, 1 Pa, 10 Pa, 100 Pa, and 1000 Pa).

For $C_4H_9(CH_3)_2Sb$ the vapor pressure measurements were performed on both crystalline and liquid phases. This allowed us to calculate the triple point coordinates from the intersection of the vapor pressure equations for the crystalline and liquid phases, T_{tp} = (286.8 ± 0.5) K and p_{tp} = (643 ± 20) Pa. The triple point temperature is in good agreement with the fusion temperature T_{fus} = (286.7 ± 0.5) K determined in our lab by visual observation but differs significantly from the value T_{fus} = 281.15 K reported by Chen et al.[10] The enthalpy of fusion for $C_4H_9(CH_3)_2Sb$ calculated from the sublimation and vaporization enthalpies at the triple point is (0.9 ± 0.1) kJ·mol^{-1}. No calorimetrically determined values were found for comparison.

Table 4. Comparison of Vaporization Enthalpies for $(CH_3)_3Sb$ and $C_4H_9(CH_3)_2Sb$ Obtained in This Work with Literature Values

compound	T K	$\Delta_l^g H_m^0$ $kJ \cdot mol^{-1}$	reference
$(CH_3)_3Sb$	273.15[a]	32.5	Rosenbaum and Sandberg[14]
	273.15	33.5	this work
	298.15[a]	31.2	Bamford et al.[15]
	298.15	32.5	this work
$C_4H_9(CH_3)_2Sb$	310.65[a]	40.9	Chen et al.[10]
	298.30[a]	41.1	this work

[a] Mean temperature of the interval in which vapor pressure was determined.

Conclusions

New reliable data of vapor pressures for high purity $(CH_3)_3Sb$ and $C_4H_9(CH_3)_2Sb$ in the temperature range typically used in MOVPE were obtained. Vapor pressure data for crystalline $C_4H_9(CH_3)_2Sb$ are reported for the first time.

Literature Cited

(1) Jou, M. J.; Stringfellow, G. B. Organometallic vapor phase epitaxial growth studies of $GaP_{1-x}Sb_x$ and $InP_{1-x}Sb_x$. *J. Cryst. Growth* **1989**, *98*, 679–689.

(2) Seki, H.; Koukitu, A. Thermodynamic analysis of metalorganic vapor phase epitaxy of III-V alloy semiconductors. *J. Cryst. Growth* **1986**, *74*, 172–180.

(3) Wei, C. H.; Edgar, J. H. Thermodynamic analysis of $Ga_xB_{1-x}N$ grown by MOVPE. *J. Cryst. Growth* **2000**, *217*, 109–114.

(4) Fulem, M.; Růžička, K.; Růžička, V.; Hulicius, E.; Šimeček, T.; Melichar, K.; Pangrác, J.; Rushworth, S. A.; Smith, L. M. Vapor pressure of metal organic precursors. *J. Cryst. Growth* **2003**, *248*, 99–107.

(5) Fulem, M.; Růžička, K.; Růžička, V.; Hulicius, E.; Šimeček, T.; Pangrác, J.; Rushworth, S. A.; Smith, L. M. Measurement of vapour pressure of In-based metalorganics for MOVPE. *J. Cryst. Growth* **2004**, *272*, 42–46.

(6) Fulem, M.; Růžička, K.; Růžička, V.; Šimeček, T.; Hulicius, E.; Pangrác, J. Vapour pressure and heat capacities of metal organic precursors, $Y(thd)_3$ and $Zr(thd)_4$. *J. Cryst. Growth* **2004**, *264*, 192–200.

(7) Fulem, M.; Růžička, K.; Růžička, V.; Šimeček, T.; Hulicius, E.; Pangrác, J. Vapour pressure measurement of metal organic precursors used for MOVPE. *J. Chem. Thermodyn.* **2006**, *38*, 312–322.

(8) Fulem, M.; Růžička, K.; Růžička, V.; Šimeček, T.; Hulicius, E.; Pangrác, J.; Becker, J.; Koch, J.; Salzmann, A. Vapor pressure of di-*tert*-butylsilane. *J. Chem. Eng. Data* **2005**, *50*, 1613–1615.

(9) Pangrác, J.; Fulem, M.; Hulicius, E.; Melichar, K.; Šimeček, T.; Růžička, K.; Morávek, P.; Růžička, V.; Rushworth, S. A. Vapor pressure of germanium precursors. *J. Cryst. Growth* **2008**, *310*, 4720–4723.

(10) Chen, C. H.; Huang, K. T.; Drobeck, D. L.; Stringfellow, G. B. Tertiarybutyldimethylantimony for InSb growth. *J. Cryst. Growth* **1992**, *124*, 142–149.

(11) Růžička, K.; Majer, V. Simultaneous treatment of vapor pressures and related thermal data between the triple and normal boiling temperatures for *n*-alkanes C_5-C_{20}. *J. Phys. Chem. Ref. Data* **1994**, *23*, 1–39.

(12) Růžička, K.; Majer, V. Simple and controlled extrapolation of vapor pressures towards the triple point. *AIChE J.* **1996**, *42*, 1723–1740.

(13) Clarke, E. C. W.; Glew, D. N. Evaluation of thermodynamic functions from equilibrium constants. *Trans. Faraday Soc.* **1966**, *62*, 539–547.

(14) Rosenbaum, E. J.; Sandberg, C. R. Vapor pressures of trimethylphosphine, trimethylarsine and trimethylstibine. *J. Am. Chem. Soc.* **1940**, *62*, 1622–1623.

(15) Bamford, C. H.; Levi, D. L.; Newitt, D. M. Physical and chemical properties of organo-metallic compounds. Part I. The vapour pressures and freezing points of simple metal alkyls of groups II, III, and V. *J. Chem. Soc.* **1946**, *46*, 8–471.

(16) Long, L. H.; Sackman, J. F. The heat of formation of antimony trimethyl. *Trans. Faraday Soc.* **1955**, *51*, 1062–1064.

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