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BRIEF COMMUNICATIONS

Critical Parameters of Chlorinated Tetramethyl- and Tetraethylgermane

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Abstract—The critical parameters of chlorinated tetramethyl- and tetraethylgermane were determined by calculational methods. The reliability of calculated data was confirmed by several independent methods.

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Organoelemental compounds find ever widening application, in particular, in such important chemical technologies as organic synthesis and preparation of metal coatings, plastics, semiconductor materials, etc. [1, 2]. The critical parameters of chlorinated tetraethylsilane [3] and tetraethyl tin [4] were determined earlier.

Here, we determined the critical parameters of chlorinated tetramethyl- and tetraethylgermane.

The critical parameters were calculated by equations whose reliability was confirmed [3, 4] for similar organometallic compounds of Group IV elements. The critical temperature T_c, K, and critical volume V_c, cm^3 mol^{-1}, were calculated by the formulas

$$T_c = T_b/\theta, \quad (1)$$

$$V_c = 80\Pi - 1,$$

where θ is the reduced temperature at the boiling point (T_b/T_c), which was calculated as

$$\theta = 0.092 \ln \Pi + 0.515,$$

where Π is the parachor, J$^{1/4}$ cm$^{5/2}$ mol^{-1}, whose values were taken from [5, 6].

The critical pressure P_c, MPa, was calculated by the formula

$$P_c = 1.039T_c/b, \quad (1)$$

where b is the Van der Waals constant, cm^3 mol^{-1}, which was calculated using the molar volume of a liquid at the boiling point by the equation [5]

$$b = 1.27V_b - 6.$$

Table 1 lists the initial data (boiling point parameters) [7–10] and the calculated critical parameters of chlorinated tetramethyl- and tetraethylgermane.

The reliability of the calculated data was assessed by the following methods. At the present time, the properties of molecular liquids (density, saturated vapor pressure) can be predicted with a high reliability by thermodynamic similarity theory methods [5] utilizing critical parameters of a substance as the initial data. Chlorinated tetramethyl- and tetraethylgermane belong to little studied compounds, but some of them were characterized by experimental density in the liquid state and saturated vapor pressure [9, 10].

Here, we calculated these characteristics by the thermodynamic similarity theory equations with the use of the T_c, P_c, and V_c values obtained. By comparing the calculated values of these characteristics with the corresponding experimental data it is possible to assess the reliability of the critical parameters determined.

To this end, we calculated the density of the liquid ρ, g cm^{-3}, by the Mathias equation [5]

$$\rho = (M/V_c)[2(2 - T/T_c)]$$

Table 1. Initial [7–10] and calculated data

Substance	Π, $J^{1/4}$ $cm^{5/2}$ mol^{-1}	T_b, K	V_b, cm^3 mol^{-1}	T_c, K	V_c, cm^3 mol^{-1}	P_c, MPa
$Ge(CH_3)_4$	4.89	316.6	142.4	476.0	380.0	2.81
$Ge(CH_3)_3Cl$	4.79	372.1	138.0	564.0	372.0	3.47
$Ge(CH_3)_2Cl_2$	4.69	397.0	131.0	604.0	364.0	3.91
$Ge(CH_3)Cl_3$	4.59	385.5	126.2	588.0	356.0	3.96
$Ge(C_2H_5)_4$	7.65	436.6	220.4	615.0	596.2	2.18
$Ge(C_2H_5)_3Cl$	6.86	449.2	193.4	649.0	538.0	2.81
$Ge(C_2H_5)_2Cl_2$	6.07	448.2	167.7	658.0	475.0	3.30
$Ge(C_2H_5)Cl_3$	5.28	414.8	147.4	621.0	411.0	3.56

Table 2. Accuracy of calculation of the density of the liquid, using the values of the critical parameters, determined in this study

Substance	Density (T = 293 K), g cm^{-3}		Divergence, %
	calculation	experiment	
$Ge(CH_3)_3Cl$	1.222	1.249	–2.1
$Ge(CH_3)_2Cl_2$	1.445	1.492	–3.1
$GeCH_3Cl_3$	1.637	1.703	–3.9
$Ge(C_6H_5)_3Cl$	1.124	1.166	–3.6
$Ge(C_6H_5)_2Cl_2$	1.320	1.374	–3.9
$GeC_6H_5Cl_3$	1.547	1.599	–3.3

Table 3. Accuracy of calculation of the saturated vapor pressure, using the values of the critical parameters, determined in this study

Vapor pressure, MPa	Relative error, %		
	$Ge(CH_3)_3Cl$	$GeCH_3Cl_3$	$GeC_6H_5Cl_3$
0.006	7.7	–5.1	–5.6
0.008	6.9	–4.5	–4.9
0.01	6.2	–4.0	–4.3
0.02	4.4	–2.6	–2.8
0.04	2.5	–1.3	–1.5
0.06	1.4	–0.7	–1.0
0.08	0.6	–0.3	–0.7
0.1	0.1	–0.1	–0.5
Absolute value of the average	3.7	2.3	2.7

and saturated vapor pressure P, MPa, by the Riedel-Planck-Miller equation [11]

$$\ln P_{red} = -\frac{g}{T_{red}}[1 - T_{red}^2 + K(3 + T_{red})(1 - T_{red})^3],$$

where $g = 0.4835 + 0.4605h$,

$$K = \frac{h/g - 1 - \theta}{(3 + \theta)(1 - \theta)^2},$$

$$h = \theta\frac{(\ln P_c + C)}{1 - \theta}, \quad P_{red} = P/P_c, \quad \theta = T_b/T_c.$$

Table 4. Correlation coefficient r and rms error s of the dependences obtained by the comparative calculation method (version 1)

Critical constant checked	Compounds compared	Characteristic compared	r	s, %
Chlorinated tetraethylgermanes				
T_c	Si-Ge	T_c	0.9006	2.9
	Sn-Ge		0.9251	2.6
V_c	Si-Ge		0.9991	0.9
	Sn-Ge		0.9999	0.1
P_c	Si-Ge		0.9651	5.0
	Sn-Ge		0.9908	2.4
Chlorinated tetramethylgermanes[a]				
T_c	Si-Ge	T_c	0.9006	2.9
V_c	Si-Ge	V_c	0.9462	1.5
P_c	Si-Ge	P_c	0.9291	4.6

[a] For the methyl compounds, checking utilized the data for the corresponding silicon compounds only, since there are no published data on the critical parameters of chlorinated tin compounds.

Table 5. Correlation coefficient r and rms error s for the dependences obtained by the comparative calculation method (version 2)

Critical constant checked	Compounds compared	Characteristic compared	r	s, %
T_c	Chlorinated	T_c–T_b	0.9725	1.5
V_c	tetraethylger	$V_c - \Pi$	0.9985	1.5
P_c	manes	P_c–T_b/V_b	0.9910	2.3
T_c	Chlorinated	T_c–T_b	0.9945	0.9
V_c	tetramethylge	$V_c - \Pi$	0.9544	1.7
P_c	rmanes	P_c–T_b/V_b	0.9981	0.7

Tables 2 and 3 compare the calculated and experimental data.

Also, the reliability of the calculated values of the critical parameters can be validated by the comparative calculation method [3–5]. The latter is underlain by the fact that similar substances should exhibit linear variation of one property in two different series of compounds (version 1) or linear variation of two different properties in one series of compounds (version 2). For examples of such plots, see [3, 4].

For version 1 we examined the patterns of variation of each of the critical parameters in two series of similar substances. The first member in each series was a tetraethyl (or tetramethyl) compound, and the last member, a tetra-chloride compound: ER_4–ER_3Cl–ER_2Cl_2–$ERCl_3$–ECl_4, where E is the element (Ge, Si, or Sn); R, radical; Et, ethyl radical (C_2H_5); and M, methyl radical (CH_3). The abscissa was the critical parameter of a silicon or tin compound, and the ordinate, the corresponding critical parameter of a germanium compound.

For version 2 we examined how the critical parameters varied in relation to a different property in a series of germanium compounds GeR_4–GeR_3Cl–GeR_2Cl_2–$GeRCl_3$–$GeCl_4$. For each of the dependences we determined the correlation coefficient r and the rms error s by least-squares procedure. The results are listed in Tables 4 and 5.

Tables 4 and 5 show that all the correlations exhibit fairly high linearities and comparatively small rms errors.

CONCLUSION

All the data considered confirm reliability of the values of the critical parameters, obtained for chlorinated tetramethyl- and tetraethylgermane.

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