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Thermodynamic Characterization of Vaporization of the Fourth Group Elements

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Thermodynamic characterization of silicon, germanium, tin, and lead vaporization is performed by the method applied earlier to alkali metals and carbon, i.e., by evaluation of analytical expressions representing dependence of the second virial coefficient and vapor pressure on temperature. Starting from saturation pressure values given as a sum of partial pressure of present species, through a modified procedure applied before to carbon, the parameters of anticipated forms of $B=f(T)$ and $P=f(T)$ are optimized with very high degree of correlation. A new, simple, and efficient procedure for optimization of $P=f(T)$ parameters from particular P data is derived. The values of $\Delta_v H_0^0(\mathrm{III})$ and $\Delta_v H_0^0(\mathrm{II})$, calculated for all the elements from the evaluated relations $B=f(T)$ and $P=f(T)$, agree mutually as well as with the CODATA recommended values. Applicability and efficiency of this method when applied to thermodynamic characterization of vaporization of the fourth group elements is justified through comparison of the obtained vapor pressure and saturated vapor molar volume values with the corresponding values deduced from the published data.

KEY WORDS: dissociation; enthalpy; germanium; lead; molar volume; saturated vapor; silicon; tin; vapor pressure; vaporization; virial equation.

1. INTRODUCTION

As silicon saturated vapor is a mixture of molecular species with different numbers of Si atoms [1, 2], for thermodynamic characterization of silicon vaporization we used the approach given in ref. [3], the same as for alkali metals [4] and carbon [5, 6] vaporization. In this approach saturated vapor is treated as a real gas of monatomic particles whose volumetric behavior is

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described by a truncated form of the virial equation. Using the same numerical procedure as for carbon [5], we derived also for silicon analytical forms of temperature dependences of the second virial coefficient and vapor pressure. The established relation for $P = f(T)$ [3] gave Si vapor pressure values in the temperature range 1700–2500 K, which coincide with the values calculated as a sum of partial pressures[2]

$$P^* = \sum_{1}^{3} p_{\mathrm{Si}_i} \tag{1}$$

from Si_1, Si_2, and Si_3 species published data [8]. The mean value of a relative deviation, $\delta(P)$[3] of two P values for nine temperatures, is

$$\overline{\delta(P)} = 0.525\%$$

with the $\delta(P)$ standard deviation for nine points,

$$s_\delta(P) = 0.353\%$$

The saturated vapor molar volume for silicon for the temperature range 1700–2500 K was calculated by the virial equation

$$v = \frac{RT}{P} + B \tag{2}$$

applying B and P values computed by means of derived relations $B = f(T)$ and $P = f(T)$ [3]. These values fully agree with the values obtained by the ideal gas equation for the Si_1, Si_2, and Si_3 species mixture, taking for P_{Si_i} the values deduced from table data [8]. The mean value of the relative deviation of two calculated v values for 9 temperatures is 1.19%, while its standard deviation is 0.99%.

Encouraged by the results of these calculations, we applied the same numerical procedure, but without iterations, to a thermodynamic characterization of vaporization of the other elements of the fourth group, Ge, Sn, and Pb, and also obtained good results.

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[2] For an explanation of symbols, see nomenclature at the end of this article.

[3] $\delta(P) = |P - P^*|/P^* \times 100\%$.

2. DETERMINATION OF THERMODYNAMIC PROPERTIES

Saturated vapor of a fourth group element consists of molecular species with different numbers of atoms of the element [1, 2, 9–14]. Clusterization of atoms decreases with increasing atomic number, i.e., from C and Si up to Pb. Clusterization is highest in C saturated vapor: the contribution to the vapor pressure by the species under C_6 is not negligible up to 4000 K [6]. In the temperature range 1700–2500 K, for saturation pressures from 5×10^{-2} to 5×10^{2} Pa, the presence of Si_2 and Si_3 species in Si saturated vapor is important [1, 2]. At these temperatures, for Ge saturated vapor with the pressure ranging from 3 to 5000 Pa, contribution of P_{Ge_3} to the total vapor pressure is negligible [9, 10]. Although not high, clusterization is present in saturated vapor of tin in the investigated temperature range, at vapor pressures from 20 to 20,000 Pa. Under these conditions Sn_2 content is $1 - 3\%$ [9, 11, 12], while at the same temperatures, dimer content in the saturated vapor of lead is lower [9, 13, 14] in spite of vapor pressure (2×10^4 to 8×10^5 Pa) being higher than that of tin. Taking all these into account we express the total saturation pressure in the temperature range 1700–2500 K for silicon as a sum of Si_1, Si_2, and Si_3 species partial pressure and for germanium, tin, and lead as a sum of monomer and dimer partial pressures.

The thermodynamic characteristics of vaporization (second virial coefficient, vapor pressure, saturated vapor molar volume, third and second law values of vaporization standard enthalpy) have been calculated from equations for the dependences of the total vapor pressure and second virial coefficient on temperature, evaluated by a modified procedure applied for carbon [5]. Anticipated forms for temperature dependences of B,

$$B = -aT \exp \frac{b}{T} \tag{3}$$

and P

$$\ln P = \alpha - \frac{\beta}{T} + \gamma + D \ln T \tag{4}$$

and some steps of the algorithm, previous to the work reported in ref. [5], remained unchanged. Here we started with the vapor pressure values given as a sum of partial pressure of present molecular species,

$$P = \sum_{i=1}^{n} p_{E_i} \tag{5}$$

where $i = 1,2,3$ for Si and $i = 1,2$ for Ge, Sn, and Pb. Partial pressure values have been calculated from the published data for corresponding molecular species through the following relations:

$$p_{E_1} = \exp \frac{T\Delta_v \Phi_{E_1} - \Delta_v H^0_{0,E_1}}{RT}$$

$$p_{E_i} = \frac{p^i_{E_1}}{Kp_i} \qquad i = 2,3 \tag{6}$$

$$Kp_i = \exp \frac{T\Delta_d \Phi_{E_i} - \Delta_d H^0_{0,E_i}}{RT}$$

For five temperatures in the range 1700–2500 K, with P (Eq. 5) values, we have calculated absolute values of the second virial coefficient through the expression[4]

$$|B| = \frac{\Delta_v H^0_{0,E_1} - T\Delta_v \Phi_{E_1} + RT\ln(P/P^0)}{P} \tag{7}$$

which represents a rearranged third law expression for $\Delta_v H^0_{0,E_1}$. From the obtained B values, applying the linear regression method to the following equation,

$$\ln \frac{|B|}{T} = \ln a + \frac{b}{T} \tag{8}$$

we obtained, with a high degree of correlation, the values of the parameters $\underline{a}$ and $\underline{b}$ for all the treated elements (Table I).

Table I. Evaluated Values of $\underline{a}$ and $\underline{b}$ Parameters of the Virial Coefficient Temperature Dependence

Element	$a \times 10^{10}$ ($m^3 \cdot K^{-1} \cdot mol^{-1}$)	$b \times 10^{-4}$ (K)	$\lvert 1 - r(8) \rvert^a$
Si	2.658037883	3.927070996	1.01×10^{-3}
Ge	1.927480881	3.398755379	1.2×10^{-5}
Sn	5.210239075	2.568466885	3.4×10^{-4}
Pb	4.629339504	1.129944427	1.7×10^{-4}

[a] $r(8)$ is the correlation coefficient of Eq. (8) linear regression.

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[4] In these calculations we used published data [8] for thermodynamic functions of the condensed state and monatomic species of given elements.

Table II. Optimized Values of the Coefficients of the Equation[a] $\ln P = \alpha - \beta/T + \gamma T + D \ln T$

Elements	α	$\beta \times 10^{-4}$	$\gamma \times 10^{5}$	D	$\lvert 1 - r(4) \rvert$[b]
Si	23.42508728	4.701930398	1.539557915	0.2068800927	1.01×10^{-3}
Ge	24.64485003	4.035229570	0.599311980	0.0263244206	1.6×10^{-3}
Sn	21.63071696	3.524302600	0.019900573	0.2746527754	5.0×10^{-5}
Pb	23.00289795	2.171244403	1.778558994	− 0.098647935	9.1×10^{-3}

[a] Where P is in Pa and T is in K.

[b] $r(4)$ is the correlation coefficient of the linear regression given in Eq. (4).

Parameters of the anticipated form of the vapor pressure temperature dependence (Eq. 4) have been evaluated through the second law expression for $\Delta_v H^0_{0,E_1}$, developed on the basis of the anticipated general expressions for temperature dependence of B (Eq. 3) and P (Eq. 4),

$$\Delta_v H^0_{0,E_1} = -\Delta_v(H^0_T - H^0_0) + \left(\frac{\beta}{T} + \gamma T + D\right)(RT + BP) - \frac{bBP}{T} \tag{9}$$

In the procedure used, the values of the function M,

$$M = \frac{\Delta_v H^0_0 + \Delta_v(H^0_T - H^0_0) - (bBP/T)}{RT + BP} \tag{10}$$

for five temperatures in the range 1700–2500 K, were calculated first, and then the parameters β, γ, and D were evaluated from these values by applying the linear regression method to the expression

$$M = \frac{\beta}{T} + \gamma T + D \tag{11}$$

Using β, γ, and D values thus obtained, we calculated the mean value of the parameter α, from P (Eq. 5) values, via Eq. (4) (Table II). Computed with optimized parameters, the values of B (Eq. 3) and P (Eq. 4) were used as the basis for calculation of saturated vapor molar volume and third and second law values of standard enthalpy of vaporization, performed for the temperatures 1700, 1800, . . . , 2500 K. Mean $\Delta_v H^0_0$(III) and $\Delta_v H^0_0$(II) values, with standard deviations from 9 points calculations, are given in Table III.

Table III. Third and Second Law Values of Standard Enthalpy of Vaporization

	$\Delta_v H_0^0$(III) (kJ · mol^{-1})		$\Delta_v H_0^0$(II) (kJ · mol^{-1})		CODATA value
Element	Mean value	s	Mean value	s	(kJ · mol^{-1})
Si	445.666	0.019	445.602	0.295	445.667
Ge	369.036	0.006	369.037	0.090	336.037[a]
Sn	301.308	0.002	301.311	0.035	301.308
Pb	195.871	0.027	195.796	0.397	195.873

[a] Value from ref. [8].

3. DISCUSSION

Efficiency of evaluation of the parameters from Eqs. (3) and (4), performed according to the above described procedure, was estimated by calculation of the correlation coefficients of linear regression of Eqs. (8) and (4):

$$r(8) = \frac{\sigma(1/T)b}{\sigma(\ln(|B|/T))} \tag{12}$$

$$r(4) = \frac{\beta\sigma(-1/T) + \gamma\sigma(T) + D\sigma(\ln T)}{\sigma(\ln P)} \tag{13}$$

where $\sigma(x)^2$ represents variance of $x[1/T, \ln[|B|/T), \ln P, -1/T, T, \ln T]$ values. The correlation is better when the $|1 - r|$ value approaches zero. As we have mentioned above, the degree of correlation ($|1 - r|$) for Eq. (8) for all the treated elements is very high (Table I).

Evaluation of the parameters in Eq. (4) was not performed by the direct linear regression method of Eq. (4), but via Eqs. (10) and (11) derived from the developed, thermodynamically rigorous, second law expression (9) for standard enthalpy of vaporization. The obtained results prove the derived procedure to be simple, reliable, and more efficient than direct linear regression of Eq. (4). The degree of performed correlation of the vapor pressure temperature dependences, given as $|1 - r(4)|$, is satisfactory, for all the treated elements (Table II).

The efficiency of the mathematical procedure in evaluation of the analytical expressions $B = f(T)$ and $P = f(T)$ and reliability of the approach when applied to all considered elements have been justified by analyzing all other obtained results. Here we have calculated the third and second law values of the standard enthalpy of vaporization and found them to be in agreement, both mutually and with the CODATA recommended values [15], for all the treated elements (Table III). In the case of germanium, where the CODATA value for $\Delta_v H_0^0$ is not stated, the obtained value agrees with the value from ref. [8]. Standard deviations of $\Delta_v H_0^0$ values from 9 calculations, for all elements, are smaller for the third than for the second law value, for which they are also very small (Table III). Vapor pressure calculated by Eq. (4) with optimized parameters, given in Table II, are compared with the corresponding values computed by Eq. (5), using for partial pressures the values evaluated from published data [8], via Eqs. (6). The deviations between P values, calculated by Eqs. (4) and (5), as mean values with their standard deviations from 9 point calculations, summarized in Table IV, for all the treated elements are lower than 1%.

Saturated vapor molar volume values, calculated by the virial equation (2), applying B (Eq. 3) and P (Eq. 4) values, have been compared with those computed by the ideal gas equation for the mixture, using partial pressures evaluated from published data [8], via Eqs. (6). Molar volume is then given by the expression

$$v = \frac{RT}{\sum_{i=1}^{2(3)} i p_{E_i}} \tag{14}$$

Table IV. Deviations of Vapor Pressure Values and Saturated Vapor Molar Volume Values Calculated in Two Ways

Element	$\overline{\delta(P)}$ (%)	$s_{\delta(P)}$ (%)	$\overline{\delta(v)}$ (%)	$s_{\delta(v)}$ (%)
Si	0.53	0.35	1.30	0.93
Ge	0.07	0.06	0.63	0.57
Sn	0.0309	0.0305	0.03	0.02
Pb	0.14	0.06	0.21	0.13

Note to Table IV. The relative deviation of $x[v, P]$ values are calculated in two ways:

$$\delta(v) = \left|1 - \frac{v(\text{Eq. }2)}{v(\text{Eq. }14)}\right| \times 100\% \qquad \delta(P) = \left|1 - \frac{P(\text{Eq. }4)}{P(\text{Eq. }5)}\right| \times 100\%$$

Thus the mean value of the relative deviation is

$$\overline{\delta(x)} = \frac{1}{N}\sum_{i=1}^{N} \delta(x)_i$$

The standard deviation of $\delta(x)$ is

$$s_{\delta(x)} = \left[\frac{\sum_{i=1}^{N} [\delta(x)_i - \overline{\delta(x)}]^2}{N-1}\right]^{1/2}$$

Table V. Enthalpies of Dimer Dissociation and bR Values

Element	Temperature range (K)	Saturation pressure range (Pa)	bR (kJ · mol^{-1})	$\Delta_d H^0_{T,E_2}$ (kJ · mol^{-1})
Si	1700–2500	6.9×10^{-2}–5.3×10^{2}	326.51	335.55 ± 0.32
Ge	1700–2500	2.8×10^{0}–5.6×10^{3}	282.58	277.95 ± 2.65
Sn	1700–2500	1.9×10^{1}–1.6×10^{4}	213.55	211.32 ± 5.30
Pb	1700–2500	1.3×10^{4}–7.8×10^{5}	93.95	91.84 ± 3.37

Deviation between v values calculated by Eqs. (2) and (14) for all the treated elements, given in Table IV as the mean values with standard deviations from 9 point calculations, is slightly higher than that of vapor pressure values, but still shows excellent agreement between calculations in two ways. In spite of the fact that optimization of the parameters of the expression (3) for the second virial coefficient temperature dependence is performed by a one step operation, the obtained values of the subexponential parameter $\underline{b}$ for all the considered elements correspond to the anticipated Woolley's theoretical model [7], i.e. the bR product is approximately equal to the standard enthalpy of the corresponding dimer dissociation (Table V).

The obtained results fully justify description by a virial equation truncated on the second term of saturated vapor volumetric behavior, for all cited elements, in the given temperature range. In silicon and germanium saturated vapor, contribution of E_i $(i \neq 1)$ species to the total pressure is more important, while saturation pressure is relatively low (Table V). On the other hand, in tin and lead saturated vapor the pressure is higher, but clusterization is low. All the established agreements of computed thermodynamic properties values justify validity and efficiency of this procedure when applied to saturated vapor of treated elements, in the given temperature range. The fact that the discussed agreements are obtained without taking into account the species above E_3 and E_2, for silicon and the other elements, respectively, proves that their contribution to the vapor pressure is quite negligible.

4. CONCLUSIONS

In thermodynamic characterization of vaporization of the fourth group elements (Si, Ge, Sn, and Pb), the same approach is applied as for alkali metals and carbon. Saturated vapor, the mixture of molecular species with different numbers of atoms, is treated as a monatomic species real gas, whose volumetric behavior is described by the virial equation truncated at the second term. By modifying the numerical procedure applied in thermodynamic characterization of carbon vaporization, the parameters of anticipated expressions for temperature dependence of the second virial coefficient,

$$B = -aT \exp \frac{b}{T}$$

and of the vapor pressure,

$$\ln P = \alpha - \frac{\beta}{T} + \gamma T + D \ln T$$

are evaluated with a very high degree of correlation, from published thermodynamic data for molecular species present in saturated vapor of given elements. Temperature dependences of B and P, valid in the temperature range 1700–2500 K, have been established for all the cited elements and used as the basis for calculation of the third and second law values of standard enthalpy of vaporization, vapor pressure, and saturated vapor molar volume.

For all the considered elements the obtained values for the $\underline{b}$ subexponential parameter correspond to the statements of the anticipated Woolley's model, i.e., bR products are close to the corresponding standard enthalpy of dimer dissociation. In all analyzed cases, the third and second law values of $\Delta_v H_0^0$, with small deviations around the mean values, are in mutual agreement, and with exception of germanium, coincide with the CODATA values.

The values of vapor pressure and of saturated vapor molar volume computed by the applied procedure are compared with the corresponding values calculated for saturated vapor as a gas mixture, through the ideal gas equation, from published data of the present molecular species. The vapor pressure values computed in two ways agree within the limits 0.1, 0.2, 0.3, and 1.2% for tin, germanium, lead, and silicon, respectively. The deviations between saturated molar volume values calculated by the two cited procedures do not surpass 0.15, 0.20, 0.42, and 3.35% for tin, germanium, lead, and silicon, respectively. The obtained results justify an exposed approach in thermodynamic characterization of the fourth group elements vaporization. Within the thermodynamic characterization we have derived a very simple and efficient procedure for evaluation of the analytical expression of vapor pressure temperature dependence.

NOMENCLATURE

P	pressure
p_i	partial pressure

v	molar volume
T	temperature
R	gas constant
H	enthalpy
ϕ	free energy function, $-(G_T^0 - H_0^0)/T$
α, β, γ, D	vapor pressure temperature dependence coefficients
a, b	parameters of virial coefficient temperature dependence
K_p	equilibrium constant
E	element, E[Si, Ge, Sn, Pb]
$\delta(x)$	relative deviation
$s(x)$	standard deviation
$\sigma^2(x)$	variance
r	correlation coefficient of linear regression

Superscripts

0	standard state
*	ideal gas state

Subscripts

d	dissociation
i	molecular species
0	reference temperature
v	vaporization

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