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EVALUATION OF THE TEMPERATURE DEPENDENCE OF VAPOUR PRESSURE FOR SILICON AND GERMANIUM

M.M. STEVANOVIĆ

Materials Department, Boris Kidrich Institute of Nuclear Sciences, Vinča, Belgrade (Yugoslavia)

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ABSTRACT

Coefficients of the Rankin–Kirchoff (RK) equation are evaluated for Si, Ge, Sn and Pb using two procedures. In the temperature range 1700–2500 K the sums of partial pressures of E_i species present in the saturated vapour are used as issued values of vapour pressure. In the Sn and Pb saturated vapours the clusterization is not pronounced and the coefficients of the RK equation evaluated by a least-squares optimisation give rise to the successful predictability of the RK equation. It is not the case for Si and Ge. In their saturated vapours the presence of E_i molecular species is important. For Si and Ge a new procedure for the evaluation of the coefficients of the RK equation is proposed. With coefficients optimised by the proposed procedure the vapour pressure predictability of the RK equation for Si and Ge is improved. With thus optimised coefficients the RK equation may be applied for the temperature range of liquid state, i.e., from melting point up to temperatures at which the volumetric behaviour of saturated vapour cannot be described successfully by a truncated form of the virial equation.

INTRODUCTION

The Rankin–Kirchoff vapour pressure equation

$$\ln P = \alpha - \frac{\beta}{T} + \gamma T + D \ln T \tag{1}$$

which represents the temperature dependence of the vapour pressure of a pure solid or liquid, is based theoretically on the integration of a form of the Clausius–Clapeyron equation

$$\frac{\mathrm{d} \ln P}{\mathrm{d}T} = \frac{L}{RT^2} \tag{2}$$

which is accurate when the vapour is perfect and the molar volume of the condensed phase is negligible compared to that of the vapour, i.e., at not too high values of the vapour pressures.

The values of the coefficients in eqn. (1) can be evaluated from numerical (experimental) values of vapour pressure for a set of temperatures, via the

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least-squares method. However, for the fourth group elements, the coefficients α, β, γ and D obtained by the linear regression method applied to eqn. (1) show that a least-squares optimisation gives limited accuracy in predicting the vapour pressure of Si and Ge, in the temperature range 1700–2500 K and at relatively low vapour pressures (0.07–530 Pa for Si and 28–5600 Pa for Ge). In the same temperature range, but at much higher saturation pressures (19000–16000 Pa for Sn and 13000–780000 Pa for Pb), the predictability of eqn. (1) with coefficients optimised by the least-squares method for Sn and Pb is quite satisfactory.

In order to improve the unsatisfactory correlation between vapour pressure and temperature when the coefficients of eqn. (1) optimised via the least-squares method are used, attention was focussed to the fact that the saturated vapour of these elements, as a mixture of atoms E_1 and molecular species E_i, presents the behaviour of a nonideal gas.

The saturated vapour of all the fourth group elements consists of atoms and molecular species with a different number of atoms [1–8]. Clusterization of atoms decreases with increasing atomic number; i.e., from C and Si up to Pb. Clusterization is highest in C saturated vapour [9]; the contribution to the vapour pressure by the species under C_6 is not negligible up to 4000 K. In the temperature range 1700–2500 K, for the above saturation pressures, the presence of Si_2 and Si_3 species in Si saturated vapour is important [1,2]. At these temperatures, the contribution of Ge_3 to the total vapour pressure is negligible [7,8] and in spite of vapour pressures being higher than those of Si and Ge, dimer content in the saturated vapours of lead and tin is low [3,5–8]. Taking all this into account, it should be noted that the vapour pressure in the temperature range 1700–2500 K for silicon is a sum of Si_1, Si_2 and Si_3 species' partial pressures and for germanium, tin and lead the sum of monomer and dimer partial pressures.

During the thermodynamic characterization of the vaporization of the fourth group elements [10] the method of evaluation of coefficients in eqn. (1) was derived. With these coefficients the issued vapour pressure values can be predicted with much better accuracy than if coefficients obtained by the least-squares method are used.

The main contribution to the established procedure for the optimization of coefficients of the temperature dependence of vapour pressure is the inclusion in the computations of two thermodynamically consistent relations. Both these expressions are developed from rigorous thermodynamic expressions (third- and second-law expressions for $\Delta_v H_0^0$) on the basis of the same statements. In developing these expressions, the Woolley approach was used [11] which implies a description of the volumetric behaviour of a mixture consisting of atoms E_1 and molecular species E_i, by a virial equation for a real monatomic gas. For low vapour pressures, the Woolley statements suggest the use of a virial equation truncated at the second term. Moreover, the vapour pressure values used, as the sum of the partial pressure of the species present, are theoretically constrained to fulfil in the physical sense any one of the particular equations in the set of equations included in the computation.

The procedure is reliable as CODATA-recommended values for standard vaporization enthalpy, spectroscopic values for the standard enthalpy of the molecular species E_i dissociation, as well as table values for the thermodynamic functions ($\Phi = [-(G_T^0 - H_0^0)/T]$; $H_T^0 - H_0^0$) of the condensed and ideal gas state of E_1 atoms and the molecular species E_i are used. For vapour pressure values the sums of the partial pressures of the species present in the saturated vapours of these elements were taken

$$P = \sum_{i=1}^{n} p_i \tag{3}$$

with $n = 3$ for silicon and $n = 2$ for other elements. p_1 was calculated using the expression

$$p_1 = P^0 \exp \frac{T\Delta_v\Phi(E_1) - \Delta_v H_0^0(E_1)}{RT} \tag{4}$$

deduced from the third-law expression (eqn. 12) and $p_i (i \neq 1)$ through the expression

$$p_i = \frac{p_1^i}{Kp_i} \tag{5}$$

where Kp_i represents the constant of equilibrium

$$E_i \rightleftarrows iE_1 \tag{6}$$

Kp_i was calculated with values for thermodynamic functions of the E_i species through the expression

$$Kp_i = P^0 \exp \frac{\Delta T_d\Phi(E_i) - \Delta_d H_0^0(E_i)}{RT} \tag{7}$$

EVALUATION ON THE COEFFICIENTS OF EQUATION (1)

First, the coefficients of eqn. (1) were evaluated for Si, Ge, Sn and Pb, by applying the linear regression method directly to eqn. (1), with P (eqn. 3) values as issued vapour pressure values, at temperatures 1700, 1800,...,2500 K. Optimised values of α, β, γ and D coefficients, for all the elements studied are given in Table 1, together with the values for the corresponding correlation coefficient of the eqn. (1) linear regression that was calculated using the expression

$$r(1) = \frac{\beta\sigma\left(-\frac{1}{T}\right) + \gamma\sigma(T) + D\sigma(\ln T)}{\sigma(\ln P)}$$

where $\sigma^2(x)$ represents the variance of $x[-1/T, T, \ln T, \ln P]$. In Table 1

TABLE 1

Values of coefficients in the equation[a] $\ln P = \alpha - \beta/T + \gamma T + D \ln T$ optimised by the least-squares method

Element	α	$\beta \times 10^{-4}$ (K)	$\gamma \times 10^5$ (K^{-1})	D	$1-\lvert 1-r(1)\rvert$
Si	59.2150	5.3834	14.0	−5.9218	0.996
Ge	2.7443	3.9051	−3.0	1.3874	0.995
Sn	6.4572	3.4756	−1.0	0.7529	0.998
Pb	26.9946	2.3778	5.0	−2.1363	0.998

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

$r(1)$ values are given through the degree of correlation defined as $1 - |1 - r(1)|$.

The same coefficients from the same issued, P (eqn. 3) values were derived using the following procedure.

The saturated vapour of any of the elements analysed, as a mixture of atoms E_1 and molecular species E_i, is treated as a monatomic-particle real gas, whose volumetric behaviour is described by a truncated form of virial equation

$$v = \frac{RT}{P} + B \tag{8}$$

From Woolley's statements for this case [11] it follows that the temperature dependence of B has to be represented by equation

$$B = -aT \exp\frac{b}{T} \tag{9}$$

where the parameter b is defined by the relation

$$bR = \Delta_d H_T^0(E_2) \tag{10}$$

where $\Delta_d H_T^0(E_2)$ is the standard enthalpy of dimer dissociation.

On the basis of eqn. (7), the fugacity coefficient of the saturated vapour is given by

$$\ln\frac{f}{P} = \frac{BP}{RT} \tag{11}$$

so the developed third-law expression for $\Delta_v H_0^0(E_1)$ has the following form

$$\Delta_v H_0^0(\mathrm{III}) = T\Delta_v\Phi - RT\ln\frac{P}{P^0} - BP \tag{12}$$

The developed $\Delta_v H_0^0(E_1)$ second-law expression

$$\Delta_v H_0^0(\mathrm{II}) = -\Delta_v\left(H_T^0 - H_0^0\right) + \left(\frac{B}{T} + \gamma T + D\right)(RT + BP) - \frac{bBP}{T} \tag{13}$$

is obtained with the aid of eqns. (1), (10), (11) and (13).

On the basis of eqns. (1), (9), (12) and (13) the numerical procedure for the evaluation of the coefficients in eqn. (1) was established. The procedure has included following steps:

(1) calculation of issued vapour pressure values, P (eqn. 3) values, by means of eqns. (3)–(7);

(2) calculation, for a set of temperatures, with P (eqn. 3) values, the absolute values of the second virial coefficient, through the following expression

$$|B| = \frac{\Delta_v H_0^0 - T\Delta_v \Phi + RT \ln \dfrac{P}{P^0}}{P} \tag{14}$$

(3) evaluation of the values of the parameters a and b, by applying the linear regression method to the logarithmic form of eqn. (9)

$$\ln \frac{|B|}{T} = \ln a + \frac{b}{T} \tag{15}$$

(4) calculation, for all the temperatures, of the values of the function M

$$M = \frac{\Delta_v H_0^0 + \Delta_v\left(H_T^0 - H_0^0\right) - \dfrac{bBP}{T}}{RT + BP} \tag{16}$$

that is related, through eqn. (13), to the coefficients β, γ and D by the linear equation

$$M = \frac{\beta}{T} + \gamma T + D \tag{17}$$

(5) evaluation of the parameters β, γ and D, by applying the linear regression method to eqn. (17), M (eqn. 16) values being used;

(6) calculation of the α parameter mean value from thus obtained β, γ and D values and P (eqn. 3) values, via eqn. (1).

The described procedure was applied to Si, Ge, Sn and Pb, for five temperatures in the range 1700–2500 K. For this purpose thermodynamic

TABLE 2

Values of coefficients in the equation[a] $\ln P = \alpha - \beta/T + \gamma T + D \ln T$ optimised in the new procedure

Element	α	$\beta \times 10^{-4}$ (K)	$\gamma \times 10^{6}$ (K^{-1})	D	$1-\lvert 1-r(1)\rvert$
Si	25.93735	4.75569	7.8	−0.0857	0.9982
Ge	24.55975	4.03523	6.0	0.0263	0.9998
Sn	21.63072	3.52430	0.2	0.2746	0.9999
Pb	22.98408	2.17124	17.8	−0.0986	0.9990

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

function data from ref. 12, that include CODATA recommended values for $\Delta_v H_0^0$ [13], were used. Obtained values for eqn. (1) coefficients, as well as corresponding degrees of correlations for all the treated elements are summarised in Table 2.

The vapour pressure predictability of eqn. (1) with coefficients optimised

TABLE 3

Deviations between P (eqn. 1) and P (eqn. 3) values for silicon

Temperature (K)	Vapour pressure (Pa)	SiO_2 content (%)	$\overline{\delta P}_M$ [a] $\pm s(\delta P_M)$ or δP_M (%)	δP_D [a] $\pm s(\delta P_D)$ or δP_D (%)
1690	5.91×10^{-2}	2.69	0.11	6.95
1700–2500	6.98×10^{-2}–5.25×10^{2}	2.75–9.01	0.11 ± 0.09	9.72 ± 1.57
3000	1.23×10^{4}	12.94	0.17	17.90
3500	1.17×10^{5}	16.26	0.50	30.06
4000	6.32×10^{5}	18.88	2.47	50.70

[a] $\delta P = [P$ (eqn. 1)$-P$ (eqn. 3)$]/P$ (eqn. 3)$\times 100$ the index M denotes P (eqn. 1) values calculated with coefficients optimised by the new procedure, and the index D denotes P (eqn. 1) values calculated with coefficients optimised by the least-squares method.

TABLE 4

Deviations between P (eqn. 1) and P (eqn. 3) values for germanium

Temperature (K)	Vapour pressure (Pa)	Ge_2 content (%)	$\overline{\delta P}_M \pm s(\delta P_M)$ or δP_M (%)	$\overline{\delta P}_D \pm s(\delta P_D)$ or δP_D (%)
1210	1.8×10^{-4}	0.52	1.57	9.76
1700–2500	2.80×10^{0}–5.64×10^{3}	3.01–9.80	0.07 ± 0.06	10.42 ± 1.42
3000	8.31×10^{4}	13.75	1.04	14.35
3500	5.63×10^{5}	17.78	2.50	15.41
4000	2.35×10^{6}	19.25	4.57	15.67

TABLE 5

Deviations between P (eqn. 1) and P (eqn. 3) values for tin

Temperature (K)	Vapour pressure (Pa)	Sn_2 content (%)	$\overline{\delta P}_M \pm s(\delta P_M)$ or δP_M (%)	$\overline{\delta P}_D \pm s(\delta P_D)$ or δP_D (%)
1000	8.48×10^{-6}	0.004	3.68	0.60
1700–2500	18.97–1.60×10^{4}	0.46–3.11	0.06 ± 0.04	3.29 ± 0.44
3000	1.76×10^{5}	5.60	0.55	5.05
3500	9.69×10^{5}	8.12	1.90	6.51
4000	3.46×10^{6}	10.33	4.19	8.46

TABLE 6

Deviation between P (eqn. 1) and P (eqn. 3) values for lead

Temperature (K)	Vapour pressure (Pa)	Pb_2 content (%)	$\overline{\delta P_M} \pm s(\delta P_M)$ or δP_M (%)	$\overline{\delta P_D} \pm s(\delta P_D)$ or δP_D (%)
1200	64.32	0.04	4.96	0.47
1700–2500	1.35×10^4–7.83×10^5	0.56–3.86	0.15 ± 0.06	2.12 ± 0.27
3000	3.34×10^6	7.02	1.26	3.16
3500	9.60×10^6	10.23	3.92	3.35

by the two methods described was estimated through calculated (relative) deviations between P (eqn. 1) and P (eqn. 3) values (Tables 3–6).

DISCUSSION

In the optimisation temperature range (1700–2500 K) the average established deviations between calculated vapour pressure values P (eqn. 1) and original values P (eqn. 3) for lead and tin are 2 and 3%, respectively (Tables 5 and 6), while δP values for silicon and germanium are about 10% (Tables 3 and 4), provided the parameters of eqn. (1) are optimised by the least-squares method. From these results it follows that the predictability of eqn. (1), with coefficients optimised by the linear regression method for Sn and Pb can be accepted as satisfactory. This is not the case for Ge and Si.

When in computations of P (eqn. 1) values the coefficients obtained in our procedure are used, deviations in vapour pressure values in the optimisation temperature range are lower than 1% (Table 3 and 4). It was noted that the values of the degree of correlation $(1 - |1 - r(1)|)$ for our procedure (Table 2) were higher than corresponding values obtained using coefficients of eqn. (1) optimised by the least-squares method (Table 1).

Improvement of vapour pressure predictability, in the optimisation temperature range, obtained by our procedure in relation to that of linear regression optimisation, is evident, in spite of the fact that in our procedure the number of points used (five temperatures) was lower than in the case of the linear regression (nine temperatures). However, the practical meaning of this improvement is important only for silicon and germanium.

Also the vapour pressure predictability of eqn. (1) was considered with coefficients optimised by both methods outside the optimisation temperature range, by calculating the deviations between P (eqn. 1) and P (eqn. 3) values (Tables 3–6). From results obtained the same could be concluded as for the optimisation temperature range. The predictability of eqn. (1) with coefficients optimised by our procedure is higher than with coefficients optimised by the least-squares method. Even when the departure from the optimisation temperature range is higher, the reliability of P (eqn. 1) values with coefficients optimised by the linear regression method decreases progressively, especially for Si and Ge. On the other hand, the range of applicability of eqn. (1) with our coefficients can be extended up to 1210 and 4000 K for Ge (the range of liquid Ge from its melting point to 4000 K) and to 4000 K for Si. Since the melting point of Si lies at 1690 K, the extension of applicability of eqn. (1) toward lower temperatures is not possible.

From the calculated deviations in vapour pressure values it is possible to evaluate the essential difference concerning the extension of the temperature range of applicability of eqn. (1) depending on the method of coefficients' optimisation. When the least-squares-optimisation coefficients are used, deviations between P (eqn. 1) and P (eqn. 3) values gradually increase especially at higher temperatures, with a departure from the optimisation temperature range. This is not the case with coefficients evaluated in our procedure. Deviations $\overline{\delta P}_{\mathrm{M}}$ are slightly worse outside the optimisation temperature range than inside it; this rise is not connected with the departure from the optimisation temperature range, but with the conditions under which the truncated form of the virial equation (eqn. 8) and the Woolley model [1] are no longer appropriate for saturated vapour.

Relating the parameters of saturated vapour (E_2 content, vapour pressure) and vapour pressure predictability of eqn. (1) with parameters optimised by our procedure or by the linear regression method, we can conclude that for a higher dimer content, predictability with coefficients optimised by the least-squares method is low (Tables 3 and 4). If, under these conditions, coefficients optimised in our new procedure are used, deviations in vapour pressure values are remarkably lower. Improvement in the predictability of eqn. (1) with our coefficients for high E_2 content diminishes only at high vapour pressures. Therefore, the new procedure was proposed for the evaluation of coefficients of vapour-pressure temperature dependence for liquid silicon and germanium.

When clusterization is insignificant in a saturated vapour, as in the saturated vapour of tin and lead at low vapour pressures (lower than 0.5 MPa), the application of the proposed procedure for the improvement of the predictability of eqn. (1) is unjustifiable and inefficient.

CONCLUSION

With vapour pressure values given as sums of partial pressures of E_i species present in a saturated vapour in the temperature range 1700–2500 K, the coefficients of Rankin–Kirchoff equations for Si, Ge, Sn and Pb are derived using the least-squares method.

On the basis of deviations in vapour pressure values, the optimised coefficients for Sn and Pb can be accepted as reliable while the predictability of the Rankin–Kirchoff equation for Si and Ge with coefficients optimised through the linear regression method is not satisfactory.

A new, efficient, procedure for optimisation of coefficients in the Rankin–Kirchoff equation, representing vapour-pressure temperature dependencies, is developed by introducing into the computation two thermodynamically consistent equations. Both of these equations are developed from rigorous thermodynamic expressions (third- and second-law expressions for $\Delta_v H_0^0$) on the basis of the approach in which the volumetric behaviour of a gas mixture, consisting of atoms E_1 and molecular species E_i, has to be described by a virial equation of a real monatomic gas.

With the coefficients optimised during this procedure the equations of Rankin–Kirchoff type for silicon

$$\ln P = 25.9374 - \frac{47556 \times 9}{T} + 0.0000078T - 0.0857 \ln P$$

and for germanium

$$\ln P = 24.5598 - \frac{40352 \times 3}{T} + 0.000006T + 0.0263 \ln P$$

where P is in Pa and T in K, possess very good vapour pressure predictability for the whole temperature range of the liquid state, from the melting point up to temperatures at which the vapour pressure reaches values of 0.5 MPa.

LIST OF SYMBOLS

P	pressure
p_i	partial pressure
f	fugacity
v	molar volume
T	temperature
R	gas constant
B	second virial coefficient
H	enthalpy
L	latent enthalpy of vaporization
Φ	free energy function, $-G_T^0 - H_0^0/T$
M	mathematical function
α, β, γ, D	vapour pressure temperature dependence coefficients
a, b	parameters of virial coefficient temperature dependence
Kp_i	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

Superscript

0	standard state

Subscripts

d	dissociation
i	molecular species
0	reference temperature
v	vaporization
m	melting point
M	results obtained with coefficients optimised in new procedure
D	results obtained with coefficients optimised by the least-squares method

REFERENCES

1 R.E. Honing, J. Chem. Phys., 22 (1954) 1610.
2 J. Drowart, G. De Maria and M.G. Inghram, J. Chem. Phys., 26 (1958) 1015.
3 R.E. Honing, J. Chem. Phys., 21 (1953) 573.
4 A.W. Searcy and R.D. Freeman, J. Chem. Phys., 23 (1955) 88.
5 A.W. Searcy and R.D. Freeman, J. Am. Chem. Soc., 76 (1954) 5229.
6 L. Brewer and R.F. Porter, J. Chem. Phys., 21 (1953) 2012.
7 A.T. Aldred and J.M. Pratt, Trans. Faraday Soc., 57 (1961) 611.
8 J.R. Hawkins and R. Hultgren, Trans. AIME, 239 (1967) 1046.
9 M.M. Stevanović, Int. J. Thermophys., 4 (1983) 127.
10 M.M. Stevanović, Int. J. Thermophys., in press.
11 H. Woolley, J. Chem. Phys., 21 (1953) 236.
12 V.P. Gluško, L.V. Gurvič, G.A. Bergman, I.V. Veyc, V.A. Medvedev, G.A. Hačkunuzov and B.C. Yungman, Termodinamičeskie Svoistva Individualnyh Veščestv, Nauka, Moscow, 1979, Vol. 2.
13 CODATA Recommended Key Values for Thermodynamics, 1977, J. Chem. Thermodyn., 10 (1978) 903.