

Prediction of the enthalpy of vaporization of metals and metalloids

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Abstract

A simple correlation equation without adjustable parameters is used to obtain the enthalpy of vaporization of 10 metals and 2 metalloids as a function of the temperature. Besides the critical temperature, this equation requires knowing of the enthalpy of vaporization at two reference temperatures: the lowest available temperature and the normal boiling temperature. Average relative deviations are less than 0.75% for the available ranges of temperature. A comparison is made with three other well-known empirical equations based only on the normal boiling point.

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1. Introduction

A plethora of correlation equations has been proposed in order to express the enthalpy of vaporization (ΔH) of pure substances as a function of the temperature. The choice of a specific equation depends on several factors, mainly, the available number of experimental data, the temperature range over which one wants to apply the correlation, and the set of substances chosen for testing the equation.

Because the enthalpy of vaporization is zero at the critical temperature, T_c , most correlation equations are given in terms of the variable $1 - (T/T_c)$ and include a certain number of adjustable coefficients. Svoboda and Basarova [1] have tested the ability to express the temperature dependence of the enthalpy of vaporization of pure substances in sixteen of these equations. Of these, the only one with a semi-theoretical basis is that proposed by Torquato and Stell [2] in 1981 from an extended scaling expression consistent with renormalization-group (RG) theory. This equation contains six system-dependent (adjustable) parameters and three fixed exponents given by the RG theory. In

1997, Xiang [3] proposed an equation able to correlate accurately the enthalpy of vaporization data for thirty substances, covering the entire range from the triple point to the critical point. Xiang's equation has three system-dependent parameters and two fixed exponents chosen to conform the near-critical behavior prescribed by the RG theory.

If the set of available experimental data is large enough, then correlation equations with three or more system-dependent parameters, such as the Torquato and Stell or the Xiang equations, should be applied in preference. However, if one has only a very few experimental data available, correlation equations with one or two system-dependent parameters are recommended. This is the case for metals and metalloids (or semimetals), for which usually a very few values of ΔH are available, including the one at the normal boiling temperature T_b .

In the literature there are three empirical equations for the enthalpy of vaporization of a pure substance that require as input data the critical temperature and ΔH at one reference point, usually the normal boiling point. The first, and the simplest, of these equations was proposed by Watson [4] in 1943 in order to estimate the enthalpy of vaporization of several compounds at any temperature without experimental determinations. The second was proposed by Fish and Lielmezs [5] in 1975, and includes two parameters with values reported for three groups of substances. The third was proposed by Meyra et al. [6] in

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2004 on the basis of T_c , the triple-point temperature, T_t , and the critical compressibility factor Z_c . By choosing the value $Z_c = 0.292$, the universal critical ratio suggested by Guggenheim [7], these authors are able to correlate ΔH for several substances, suggesting that the enthalpy of vaporization of a wide class of fluids shows a universal behavior over the whole coexistence curve.

In order to understand the apparent universal behavior suggested by Meyra et al. on a semi-theoretical basis, in a recent work Román et al. [8] proposed an equation that interpolates the temperature dependence of a given thermodynamic property (in particular, ΔH) both near the triple point and near the critical point. Under certain conditions, they find that the proposed equation can be reduced to a simple expression containing only two parameters, the corresponding critical point exponent and the slope at the triple point.

The aim of the present work is to apply the Watson, Fish and Lielmezs, Meyra et al., and Román et al. equations to predict the enthalpy of vaporization of a set of 10 metals and 2 metalloids, and to compare the results with the available data. In the first three models one needs to know the critical temperature, T_c , and the enthalpy of vaporization at a reference temperature. In the fourth model an additional value of the enthalpy of vaporization at a different reference temperature is required. In metals and metalloids the enthalpy of vaporization, ΔH_b , at the normal boiling temperature, T_b is usually available and, thus, in order to compare the four mentioned models, it will be used as a common reference in all of them. The enthalpy of vaporization, ΔH_0 , at the lowest available temperature, T_0 , will be used as the additional reference required by the Román et al. model.

2. Equations

We shall consider four different equations to predict the enthalpy of vaporization of metals. The equations are:

(1) Watson [4,9,10]:

$$\Delta H = \Delta H_1 \left(\frac{T_c - T}{T_c - T_1} \right)^{0.38}, \quad (1)$$

where ΔH_1 is the enthalpy of vaporization at a reference temperature T_1 . Taking as reference the normal boiling point, Eq. (1) was used by Watson [4] for the estimation of the enthalpy of vaporization of several liquids. With this choice, currently, the DIPPR data bank [11] includes results calculated from Eq. (1) as predicted values for ΔH of some metals (aluminium, calcium, iron, lithium, mercury, potassium, vanadium, and zinc) and metalloids (silicon). In the present paper we use Eq. (1) with $T_1 = T_b$ and $\Delta H_1 = \Delta H_b$.

(2) Fish and Lielmezs [5]:

$$\Delta H = \Delta H_b \frac{T X + X^n}{T_b (1 + X^m)}, \quad (2)$$

where

$$X = \frac{T_b}{T} \frac{T_c - T}{T_c - T_b}. \quad (3)$$

Three families of substances were considered by Fish and Lielmezs: organic and inorganic liquids, liquid metals, and quantum liquids, leading to three different values of the exponents n and m . In particular, by fitting 51 experimental data for five metals (Na, K, Rb, Cs, and Hg) and one metalloid (Te), Fish and Lielmezs report the values $n = 0.20957$ and $m = -0.17464$ with errors less than 3%.

(3) Meyra et al. [6]:

$$\Delta H = \Delta H_t \left(\frac{T_c - T}{T_c - T_t} \right)^{Z_c^2 (T - T_t) / (T_c - T_t) + Z_c}, \quad (4)$$

where ΔH_t is the enthalpy of vaporization at the triple point temperature T_t , and $Z_c = 0.292$ is the universal critical ratio suggested by Guggenheim. By using Eq. (4) Meyra et al. [6] correlate the experimental data for five simple substances (nitrogen, argon, methane, propylene, and water) with a standard deviation less than that of the Watson or Fish and Lielmezs equations. Furthermore, by choosing the lowest available temperature as reference, they check that Eq. (4) provides acceptable results for the enthalpy of vaporization of mercury and, using the normal boiling point as reference, they predict a reasonable value for the enthalpy of vaporization of iron at the triple point temperature. More recently, Malagoni et al. [12] have used the Watson, Fish and Lielmezs, and Meyra et al. equations to correlate the enthalpy of vaporization experimental data of fourteen substances (including some alcohols, acetates, acids, chlorinated, and water) and find that the distribution of absolute deviations in the enthalpy of vaporization is similar for the three equations.

In order to compare with the other models we use the Meyra et al. Eq. (4) considering the normal boiling point as a reference instead of the triple point, i.e.:

$$\Delta H = \Delta H_b \left(\frac{T_c - T}{T_c - T_b} \right)^{Z_c^2 (T - T_b) / (T_c - T_b) + Z_c}. \quad (5)$$

(4) Román et al. [8]:

$$\Delta H = \Delta H_b e^{(\lambda - b)(T - T_b) / (T_c - T_b)} \left(\frac{T_c - T}{T_c - T_b} \right)^\lambda, \quad (6)$$

where λ is an effective critical exponent and b is related to the slope of the enthalpy of vaporization at the normal boiling point:

$$b = - \frac{T_c - T_b}{\Delta H_b} \left(\frac{d\Delta H}{dT} \right)_{T=T_b}. \quad (7)$$

Since for $\lambda = b$ Eq. (6) reduces to the Watson form (1), we shall take $\lambda = 0.38$. Equation (6) was proposed by Román et al. using the triple point as reference, in order to understand the apparent universal behavior over the entire coexistence curve observed by Torquato et al. [13,14] and by Meyra et al. [6] for the enthalpy of vaporization of a wide class of fluids when both ΔH and T are reduced by using critical and triple point values.

Comparing with Eqs. (1), (2), and (5), one notes that Eq. (6) requires the slope of ΔH at the normal boiling point as

additional datum. If this slope is not known, an alternative way to calculate the parameter b requires as input ΔH at a second reference temperature T_0 . In this case, by applying Eq. (6) to T_0 , one obtains:

$$b = \lambda - \frac{T_c - T_b}{T_0 - T_b} \ln \left[\frac{\Delta H_0}{\Delta H_b} \left(\frac{T_c - T_0}{T_c - T_b} \right)^\lambda \right], \quad (8)$$

where ΔH_0 is the value of the enthalpy of vaporization at the temperature T_0 .

It should also be noted that Eq. (6) coincides with that proposed by Svoboda et al. [15],

$$\Delta H = A \exp(-\alpha T/T_c) \left(1 - \frac{T}{T_c} \right)^\beta, \quad (9)$$

where A , β , and α are system-dependent parameters obtained by a fitting procedure. Our result (6) becomes Eq. (9) with the obvious identification $\lambda = \beta$ and

$$A = \frac{\Delta H_b e^{(\lambda-b)/(1-T_b/T_c)}}{(1 - (T_b/T_c))^\lambda}, \quad (10)$$

$$\alpha = \frac{\lambda - b}{(1 - (T_b/T_c))}, \quad (11)$$

which give the parameters A and α of Eq. (9) in terms of our parameters λ and b , and normal boiling and critical point data.

3. Results and discussion

The normal boiling temperature, T_b , and the corresponding enthalpy of vaporization, ΔH_b , are available in the literature for most metals and metalloids [16,17]. Values for T_b and ΔH_b range from 629.8 K and ~ 59 kJ/mol for mercury to ~ 5900 K and ~ 800 kJ/mol for tungsten. The critical temperatures T_c of metals are usually estimated from theoretical models or by applying correlation methods to the coexistence densities or the vapor pressure curves. Values for T_c range from ~ 1750 K for mercury to $\sim 18,500$ K for tungsten [17,18]. However, literature values of enthalpy of vaporization at other temperatures are very scarce, except for alkali metals and mercury. In general, these values correspond to temperatures below the normal boiling temperature, and they are obtained from vapor–pressure data and subsequent substitution into the Clapeyron equation. In this work we shall use the available data for 10 metals (silver, beryllium, bismuth, caesium, iron, mercury, potassium, lithium, manganese, and sodium) and 2 metalloids (germanium and tellurium), as specified in Table 1. In this table, T_0 denotes the lowest temperature for which the corresponding enthalpy of vaporization, ΔH_0 , is available.

Fig. 1 presents the behavior of Eqs. (1) (Fig. 1a), (2) (Fig. 1b), (5) (Fig. 1c), and (6) (Fig. 1d) and the corresponding available data for the 10 metals and 2 metalloids. For each substance, the parameter b in Eq. (6) was calculated from Eq. (8) with $\lambda = 0.38$,

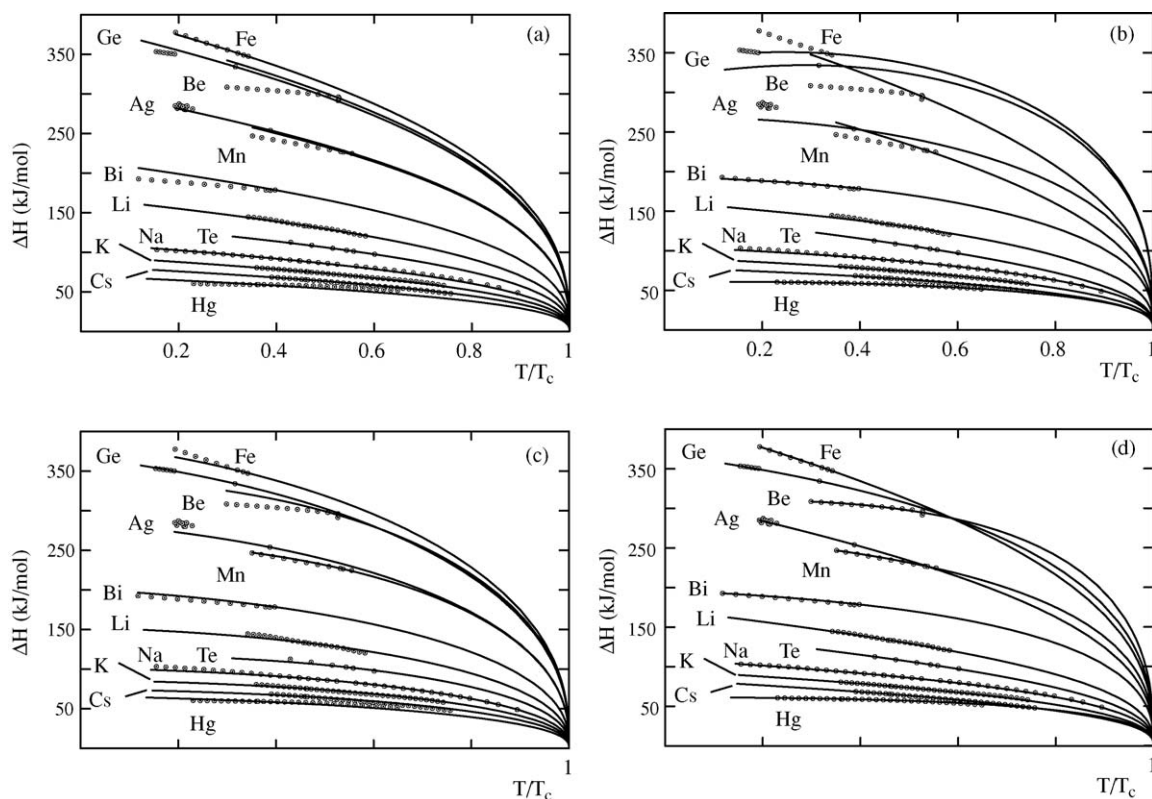


Fig. 1. Comparison between predictions (solid lines) and available data for the enthalpy of vaporization of the 10 metals and 2 metalloids listed in Table 1. The predictions range from the triple point to the critical point and correspond to: (a) Watson's Eq. (1); (b) Fish and Lielmezs' Eq. (2); (c) Meyra et al.'s Eq. (5); and (d) Román et al.'s Eq. (6). The data points have been taken from: Ref. [11] for Be, B, Na, and Ge; Ref. [19] for Ag; Ref. [20] for Cs; Ref. [21] for Li, K, Hg, and also for Cs; Ref. [22] for Fe; Ref. [23] also for K; Ref. [24] for Mn; Ref. [25] for Te.

Table 1
Substances and values for the system-dependent parameters used in this work

Substance	T_c (K)	T_i (K)	T_0 (K)	T_b (K)	ΔH_0 (kJ/mol)	ΔH_b (kJ/mol)	b
Ag	6410	1234	1237.00	2485.15	285.01	254.05	0.41165
Be	5205	1556	1556.00	2750.15	308.57	294.55	0.16594
Bi	4620	544	544.54	1837.15	192.68	178.63	0.23089
Cs	2048	302	800.00	942.05	68.61	65.40	0.39555
Fe	9340	1811	1811.00	3110.15	377.80	349.21	0.41225
Hg	1735	234	400.00	629.85	60.56	59.27	0.13830
K	2223	336	800.00	1029.83	80.57	75.42	0.37541
Li	3503	454	1200.00	1614.40	144.57	133.42	0.40223
Mn	4325	1519	1519.00	2324.15	246.85	226.55	0.27394
Na	2573	371	400.00	1154.55	103.30	89.03	0.35477
Ge	9803	1210	1510.00	3100.00	353.42	334.30	0.27348
Te	2329	723	1000.00	1266.00	112.63	102.58	0.41436

Values of the parameter b were calculated from Eq. (8). The following sources of data have been used: Ref. [11] for Be, B, Na, and Ge; Ref. [19] for Ag; Ref. [20] for Cs; Ref. [21] for Li, K, Hg, and also for Cs; Ref. [22] for Fe; Ref. [23] also for K; Ref. [24] for Mn; Ref. [25] for Te.

and T_0 and ΔH_0 given in Table 1. The resulting values are given in the last column of this table.

Fig. 1a shows that the Watson equation (1) can be useful to estimate the enthalpy of vaporization of metals and metalloids for which the parameter b has a value close to $\lambda = 0.38$ (Ag, Cs, Fe, K, Li, Na, and Te). Fig. 1b shows that the Fish and Lielmezs Eq. (2) can be recommended to correlate data for Bi, Hg, K, Li, Na, and Te. Fig. 1c shows that the Meyra et al. Eq. (5) can be used to predict ΔH values for Bi, K, Mn, and Ge. Fig. 1d shows that the Román et al. Eq. (6) provides a very reasonable estimate of the enthalpy of vaporization for the 10 metals and 2 metalloids considered.

Table 2 gives the average absolute relative deviation:

$$\bar{\Delta} = \frac{1}{N} \sum_{i=1}^N \left[\left| 1 - \frac{\Delta H_{i,\text{cal}}}{\Delta H_{i,\text{ava}}} \right| \times 100 \right], \quad (12)$$

and the maximum absolute relative deviation

$$\Delta_{\text{max}} = \max \left[\left| 1 - \frac{\Delta H_{i,\text{cal}}}{\Delta H_{i,\text{ava}}} \right| \times 100 \right] \quad (i = 1, \dots, N), \quad (13)$$

where $\Delta H_{i,\text{cal}}$ denotes the value calculated from the correlation equation, $\Delta H_{i,\text{ava}}$ the corresponding available value, and N is the number of data points. One observes that only the Román et al.

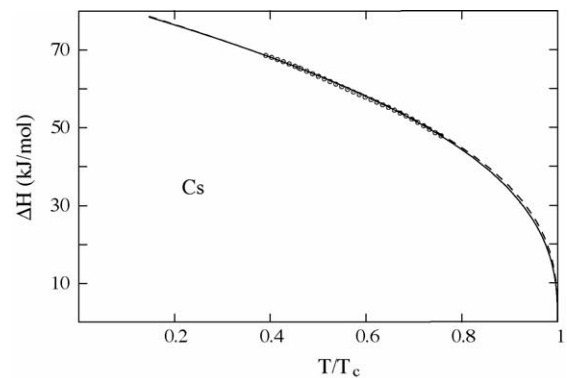


Fig. 2. Comparison between predictions of Eq. (6) and available data for the enthalpy of vaporization of caesium [20,21]. Solid line corresponds to $\lambda = 0.38$ and $b = 0.39555$. Dashed line corresponds to $\lambda = 0.354$ and $b = 0.39402$.

Eq. (6) provides an average absolute relative deviation less than 0.75% for the 10 metals and the 2 metalloids in the available temperature ranges.

A remark is in order about the role played in the Román et al. Eq. (6) by the parameter λ as an effective critical exponent. The choice of the value $\lambda = 0.38$ is the same as in the Watson Eq. (1), and very close to the one obtained from the Meyra et al. Eq.

Table 2
Absolute relative deviations for the enthalpy of vaporization

Substance	Temperature range (K)	N	Watson		Fish and Lielmezs		Meyra et al.		Román et al.	
			Δ_{max} (%)	$\bar{\Delta}$ (%)	Δ_{max} (%)	$\bar{\Delta}$ (%)	Δ_{max} (%)	$\bar{\Delta}$ (%)	Δ_{max} (%)	$\bar{\Delta}$ (%)
Ag	1237–2485	13	2.12	1.15	7.58	5.97	5.06	3.72	1.22	0.69
Be	1556–2750	14	11.0	4.78	12.7	5.55	5.42	2.55	1.08	0.24
Bi	544–1790	13	7.17	3.61	0.84	0.41	2.15	1.48	0.71	0.45
Cs	800–1550	32	1.00	0.59	3.30	1.64	4.30	2.27	0.64	0.24
Fe	1811–3200	9	0.67	0.18	7.23	2.97	2.63	0.99	0.25	0.13
Hg	400–1125	31	8.59	4.18	0.63	0.30	5.85	2.80	1.87	0.37
K	800–1650	36	2.50	0.72	0.83	0.46	1.74	0.92	2.30	0.67
Li	1200–2040	23	0.91	0.41	1.78	0.74	2.62	1.16	0.81	0.32
Mn	1519–2400	11	4.36	2.14	6.17	2.94	0.66	0.38	0.45	0.24
Na	400–2300	37	3.44	1.27	2.69	0.87	4.25	1.19	1.75	0.73
Ge	1510–3100	7	2.56	1.82	6.45	4.94	0.22	0.09	0.27	0.11
Te	1000–1400	6	0.85	0.25	0.79	0.33	3.24	1.17	0.53	0.14

N is the number of available data points.

(5), $\lambda = Z_c + Z_c^2 = 0.377$. Other choices for the value of λ are possible. For example, Viswanath and Kulor [26] recommend a system-dependent value for λ , given by

$$\lambda = \left(0.00264 \frac{\Delta H_b}{RT_b} + 0.8794 \right)^{10}, \quad (14)$$

where R is the perfect gas constant. For the cases considered here, Eq. (6) gives values ranging from $\lambda = 0.354$ for caesium to $\lambda = 0.412$ for iron. A comparison between the predictions of Eq. (6) with $\lambda = 0.38$ ($b = 0.39555$) and $\lambda = 0.354$ ($b = 0.39402$) for caesium is shown in Fig. 2. One can see that there are practically no differences between the two predictions except for the high temperature region ($T/T_c \geq 0.8$) for which experimental data are not available. Therefore, Eq. (14) with $\lambda = 0.38$ can be used for reasonable predictions of the enthalpy of vaporization of metals and metalloids over the whole coexistence curve, from the triple point to the critical point.

4. Conclusions

Four correlation equations to estimate the enthalpy of vaporization, ΔH , of metals and metalloids were tested according to the available data for 10 metals and 2 metalloids. Three of these equations (Watson, Fish and Lielmezs, and Meyra et al.) use as inputs the critical temperature and the value of ΔH at the normal boiling point, while the fourth (Román et al.) also needs the value of ΔH at another reference point. In the present paper we have considered the lowest available temperature. The results support the conclusion that, in general, the three equations based only on the normal boiling temperature cannot be recommended a priori to estimate the enthalpy of vaporization of metals over the whole coexistence curve, while the fourth equation can be used reasonably to this end.

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