

Evaluation of correlations for prediction of the normal boiling enthalpy

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Abstract

Ten analytical models were used to calculate the enthalpy of vaporization of fluids at the boiling temperature. The correlations considered were six specific expressions valid only at that temperature, and four general correlations valid for any temperature. Most of these models require as inputs the critical properties and the acentric factor, but one of the specific models requires only the molecular weight (and, obviously, the boiling temperature). One of the models is a correlation requiring a molecular Lennard–Jones parameter and the acentric factor as inputs. Results for 290 fluids are compared with the values given by the DIPPR project.

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1. Introduction

The enthalpy of vaporization of a pure fluid at its normal boiling temperature (atmospheric pressure) is a very important thermodynamic property. It is required in the design of every process that involves a liquid–vapor change of phase such as distillation, evaporation, drying, etc. Moreover this property is sometimes used in the prediction or correlation of other thermodynamic properties. There is thus engineering and theoretical interest in the measurement and correlation of values of this property [1–9].

The normal boiling enthalpy can be calculated using either equations of state applied to the liquid and vapor phases, or more simply by means of empirical correlations [5–9]. There are many empirical correlations that allow one to calculate the enthalpy of vaporization of pure fluids [8,10–26]. Some of them are general analytical expressions that only require as input parameters certain properties of the fluid, such as the critical temperature, critical pressure, acentric factor, triple-point temperature, etc., while others are specific correlations that also require a knowledge of certain constants for each substance. The enthalpy of vaporization may also be calculated by means of group contribution models [27–31], in which it is necessary to know the chemical groups in the molecule as well as its chemical struc-

ture. Some of them [30,31] have been specifically developed to give the boiling enthalpy.

As an alternative, there has been proposed a molecular model for non-polar fluids [32,33] that includes two parameters related to the shape of the molecule and to the intensity of the attractive intermolecular Lennard–Jones interactions, respectively.

In this work we compare 10 different methods that use critical properties as their main inputs, some of them also requiring the acentric factor. We also include an analytical model that uses molecular parameters as input [32,33]. The results given by all these models are compared with the values for the boiling enthalpy given by the DIPPR project [34–37] for 290 substances [37].

2. Correlations

We shall here only consider those analytical expressions that do not require specific adjustable coefficients for each substance, but rather are based on a knowledge of some properties of the liquid–vapor equilibrium (critical properties mainly) or on molecular properties.

In particular, we selected six specific expressions that are valid only for the calculation of the normal boiling enthalpy. Three of them are well known [7,9], corresponding to the work of Riedel [11], Chen [12] and Vetere [14]. We also include two more proposals of Vetere [15,16] and a more recent proposal of Liu [23]. Their analytical expressions are the following:

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- Riedel [11]:

$$\Delta H_{vb} = 1.093 RT_b \frac{\ln P_c - 1.013}{0.93 - T_b/T_c} \quad (1)$$

- Chen [12]:

$$\Delta H_{vb} = RT_b \frac{3.978(T_b/T_c) - 3.958 + 1.555 \ln P_c}{1.07 - T_b/T_c} \quad (2)$$

- Vetere (V-73) [14]:

$$\Delta H_{vb} = RT_b \frac{0.89584(T_b/T_c) - 0.69431 + 0.4343 \ln P_c}{0.37961 - 0.37306T_b/T_c + 0.15075P_c^{-1}(T_b/T_c)^{-2}} \quad (3)$$

- Vetere (V-79) [9,15]:

$$\Delta H_{vb} = RT_b \frac{(1 - T_b/T_c)^{0.38} [\ln P_c - 0.513 + 0.5066T_c^2/(P_c T_b^2)]}{1 - T_b/T_c + [1 - (1 - T_b/T_c)^{0.38}] \ln(T_b/T_c)} \quad (4)$$

- Vetere (V-95) [16]:

- Hydrocarbons and CCl₄:

$$\Delta H_{vb} = 4.1868T_b \left(8.27 + 4.20 \log_{10} T_b + \frac{0.0068T_b}{M} + \frac{0.0009T_b^2}{M} \right) \quad (5)$$

- Alcohols:

$$\Delta H_{vb} = 4.1868T_b \left(18.82 + 3.34 \log_{10} T_b - \frac{6.37T_b}{M} + \frac{0.036T_b^2}{M} - \frac{5.2 \times 10^{-5} T_b^3}{M} \right) \quad (6)$$

- Other polar compounds:

$$\Delta H_{vb} = 4.1868T_b \left(6.87 + 4.71 \log_{10} T_b + \frac{0.16T_b}{M} + \frac{0.0009T_b^2}{M} \right) \quad (7)$$

(for esters, this expression must be multiplied by 1.06). In Eqs. (5)–(7) M is the molecular weight.

- Liu [23]:

$$\Delta H_{vb} = RT_b \left(\frac{T_b}{220} \right)^{0.0627} \times \frac{(1 - T_b/T_c)^{0.38} \ln(P_c/P_a)}{1 - T_b/T_c + 0.38(T_b/T_c) \ln(T_b/T_c)} \quad (8)$$

where P_a is the atmospheric pressure.

Poling et al. [9] compared the accuracies of the Riedel, Chen, and the V-79 [15] proposals. Results for 29 fluids of different kinds were shown, and the methods studied were generally accurate to 2%. Liu [23] shows that Eq. (8) reduces the average percentage absolute deviation (AAD) for 160 fluids from near 4% with the classical expressions (with the exception of the sec-

ond Vetere proposal, Eq. (4), not considered by Liu) to only 1.90%. For monohydric alcohols and acids an “adjustable boiling temperature” strategy is used to reduce the errors. In this work we extend the Liu study by including Eq. (4), general correlations, and a large number of fluids.

We also consider three general empirical equations, based on the three-parameter corresponding state principle, which were proposed by Carruth and Kobayashi [13], Sivaraman et al. [17], and Morgan and Kobayashi [21], and which require the acentric factor of each substance as input. Finally, we used a molecular model [32,33], which is a polynomial expression of the temperature with Lennard–Jones parameters and the acentric factor as inputs. The calculations presented here include a great number of fluids not considered in the fitting procedure to find these constants.

The analytical expressions for these general correlations are the following:

- Carruth and Kobayashi (CK) [7,13]:

$$\frac{\Delta H_V}{RT_c} = 7.08 \left(1 - \frac{T}{T_c} \right)^{0.354} + 10.95 \omega \left(1 - \frac{T}{T_c} \right)^{0.456} \quad (9)$$

- Sivaraman et al. (SMK) [17]:

$$\frac{\Delta H_V}{RT_c} = \left(\frac{\Delta H_V}{RT_c} \right)^{(R1)} + \left(\frac{\omega - \omega^{(R1)}}{\omega^{(R2)} - \omega^{(R1)}} \right) \times \left[\left(\frac{\Delta H_V}{RT_c} \right)^{(R2)} - \left(\frac{\Delta H_V}{RT_c} \right)^{(R1)} \right] \quad (10)$$

with $\omega^{R1} = 0.21$, and $\omega^{R2} = 0.46$, and

$$\begin{aligned} & \left(\frac{\Delta H_V}{RT_c} \right)^{(R1)} \\ &= 6.537 \left(1 - \frac{T}{T_c} \right)^{1/3} - 2.467 \left(1 - \frac{T}{T_c} \right)^{5/6} \\ & \quad - 77.251 \left(1 - \frac{T}{T_c} \right)^{1.208} + 59.634 \left(1 - \frac{T}{T_c} \right) \\ & \quad + 36.009 \left(1 - \frac{T}{T_c} \right)^2 - 14.606 \left(1 - \frac{T}{T_c} \right)^3 \end{aligned} \quad (11)$$

$$\begin{aligned} & \left(\frac{\Delta H_V}{RT_c} \right)^{(R2)} - \left(\frac{\Delta H_V}{RT_c} \right)^{(R1)} \\ &= -0.133 \left(1 - \frac{T}{T_c} \right)^{1/3} - 28.215 \left(1 - \frac{T}{T_c} \right)^{5/6} \\ & \quad - 82.958 \left(1 - \frac{T}{T_c} \right)^{1.208} + 99.000 \left(1 - \frac{T}{T_c} \right) \\ & \quad + 19.105 \left(1 - \frac{T}{T_c} \right)^2 - 2.796 \left(1 - \frac{T}{T_c} \right)^3 \end{aligned} \quad (12)$$

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