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Boiling enthalpy from correlations
Results for 83 families of fluids

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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 1591 polar and non-polar fluids, grouped into 83 families, 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–vapour 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 vapour 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 structure. 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 1591 substances [37]. Those are experimental data only for 292 fluids. The boiling enthalpy for the other fluids were obtained by using the DIPPR correlation, which has specific coefficients for each fluid, obtained by the DIPPR staff by using data available at other temperatures.

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

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Nomenclature

b_i	constant coefficients in Eq. (14)
F_i	constant coefficients in Eq. (15) (values given in Table 1).
H	enthalpy
k	Boltzmann constant
Ln	Neperian logarithm
M	molecular weight
P	pressure
P_a	atmospheric pressure
R	ideal gas constant
T	temperature

Greek letters

ε	Lennard-Jones parameter
ω	acentric factor

Subscripts and superscripts

b	boiling point
c	critical point
v	vaporization

the liquid–vapour 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:

Riedel [11]:

$$\Delta H_{vb} = 1.093 RT_b \frac{\mathrm{Ln}P_c - 1.013}{0.93 - T_b/T_c} \tag{1}$$

Chen [12]:

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

Vetere (V-73) [14]:

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

Vetere (V-75) [9,15]:

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

Vetere (V-95) [16]:

- Hydrocarbons and CCl_4:

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

- Alcohols:

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

- Other polar compounds:

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

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

Liu [23]:

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

where P_a is the atmospheric pressure

Poling et al. [9] compared the accuracies of the Riedel, Chen, and the V-75 [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 AAD for 160 fluids from near 4% with the classical expressions (with the exception of the second 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 [7,13]:

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

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

$$\left(\frac{\Delta H_V}{RT_c}\right)^{(R1)} = 6.537\left(1 - \frac{T}{T_c}\right)^{1/3} - 2.467\left(1 - \frac{T}{T_c}\right)^{5/6}$$

$$- 77.251\left(1 - \frac{T}{T_c}\right)^{1.208} + 59.634\left(1 - \frac{T}{T_c}\right)$$

$$+ 36.009\left(1 - \frac{T}{T_c}\right)^2 - 14.606\left(1 - \frac{T}{T_c}\right)^3 \quad (11)$$

$$\left(\frac{\Delta H_V}{RT_c}\right)^{(R2)} - \left(\frac{\Delta H_V}{RT_c}\right)^{(R1)} = -0.133\left(1 - \frac{T}{T_c}\right)^{1/3}$$

$$- 28.215\left(1 - \frac{T}{T_c}\right)^{5/6} - 82.958\left(1 - \frac{T}{T_c}\right)^{1.208}$$

$$+ 99.000\left(1 - \frac{T}{T_c}\right) + 19.105\left(1 - \frac{T}{T_c}\right)^2$$

$$- 2.796\left(1 - \frac{T}{T_c}\right)^3 \quad (12)$$

Morgan and Kobayashi (MK) [21,38]:

$$\Delta H_V = \Delta H_v^{(0)} + \omega \Delta H_v^{(1)} + \omega^2 \Delta H_v^{(2)} \quad (13)$$

$$\frac{\Delta H_V}{RT_c} = b_1^{(j)}\left(1 - \frac{T}{T_c}\right)^{0.3333} + b_2^{(j)}\left(1 - \frac{T}{T_c}\right)^{0.8333}$$

$$+ b_3^{(j)}\left(1 - \frac{T}{T_c}\right)^{1.2083} + b_4^{(j)}\left(1 - \frac{T}{T_c}\right)$$

$$+ b_5^{(j)}\left(1 - \frac{T}{T_c}\right)^2 + b_6^{(j)}\left(1 - \frac{T}{T_c}\right)^3 \quad (14)$$

The six coefficients, $b_i^{(j)}$ with $j = 0$, 1, 2 and $i = 1$–6, were obtained by a fitting procedure and are listed by Morgan and Kobayashi [21]. They found an AAD of 2.21% for the boiling enthalpy of 10 long n-alkanes (from C_{21} to C_{43}). Extrapolations for other kind of fluids were not made.

Faúndez et al. (FMC) [32,33]:

$$\Delta H_V = \left(\frac{\varepsilon}{k}\right) R \left[\sum_{i=0}^{4} F_i\left(\frac{kT}{\varepsilon}\right)^i + \omega\sum_{i=5}^{8} F_i\left(\frac{kT}{\varepsilon}\right)^{i-5}\right.$$

$$\left. + \omega^2\sum_{i=9}^{11} F_i\left(\frac{kT}{\varepsilon}\right)^{i-9}\right], \quad (15)$$

Table 1
Coefficients of the molecular model of Faúndez et al. [32], Eq. (15).

I	F_i	I	F_i
0	−7.071434	6	96.873695
1	68.842680	7	−124.019801
2	−118.404491	8	48.128476
3	87.974558	9	−22.806287
4	−25.417920	10	67.410156
5	−7.323657	11	−33.826117

where the input parameters are the Lennard-Jones parameter, ε, related to the intensity of the attractive intermolecular forces, and the acentric factor, ω, which is related to the shape of the molecules (its value increases for substances whose molecules have a shape that differs from the sphere assumed in the Lennard-Jones model). The coefficients F_i, whose values are listed in Table 1, are universal for non-polar fluids and were obtained by fitting the data provided by the DIPPR-1996 [36] project for 42 non-polar fluids over a wide range of temperatures, the absolute mean deviation being 0.8% and the maximum 2.8% [32]. Its validity for a larger number of fluids (polar fluids for example) has not been checked.

3. Results

We carried out calculations for 1591 fluids, 426 of them being non-polar, which were grouped into the 83 families listed in Tables 2–7. In these tables the AADs with respect to the values given by the DIPPR [37] project are given for each family of fluids and each of the models used. We would emphasize that Eq. (5) was used for all the non-polar fluids, and not just for hydrocarbons and CCl_4.

The values of the critical pressure, critical temperature, boiling point, molecular weight, and acentric factor were taken from the DIPPR project [37]. For the molecular model, the values of the parameter ε of the Lennard-Jones potential were obtained using the method given by Cuadros et al. [39].

3.1. Results for alkanes, alkenes, aromatics, and some other hydrocarbons

As can be seen in Table 2, the MK [21] correlation, Eqs. (13) and (14), is the one that reproduces best the boiling enthalpy for non-polar n-alkanes. This is an expected result because the model was constructed specifically for alkanes and long-chain hydrocarbons. In fact, the AAD found here is of the same order as that given by Morgan and Kobayashi [21] for only 10 long n-alkanes. The FMC model, Eq. (15), gives a clearly lower AAD than those obtained using the CK and SMK general models.

The good results reported by Reid et al. [7] for 22 saturated hydrocarbons (AAD less than 1%) for the Riedel, Chen, and V-79 models did not extend to the 32 n-alkanes considered here, as can be seen in Table 2. The AAD obtained using the V-95 model, Eq. (5), is clearly greater than that found by Vetere [16] which was only 0.75% for 29 hydrocarbons and CCl_4. None of

Table 2
Absolute average deviations (AAD) of the values obtained with the models studied from the values provided by DIPPR [37] for several families of fluids

FAMILY OF FLUIDS	N (NP)	AAD (%)									
		R	Chen	V-73	V-79	V-95	Liu	CK	SMK	MK	FMC
N-ALKANES	32 (0)	12.23	2.76	2.66	3.71	3.92	2.56	3.39	4.23	1.54	2.73
METHYLALKANES	17 (2)	0.67	0.97	2.75	1.49	1.91	1.76	2.93	1.31	0.80	0.56
DIMETHYLALKANES	21 (0)	0.36	0.87	2.66	1.18	1.00	1.22	2.62	0.85	0.64	0.43
OTHER ALKANES	25 (0)	1.60	1.03	2.46	1.06	1.67	0.82	2.71	1.35	1.14	1.05
CYCLOALKANES and MULTIRING CYCLOALKANES	9 (0)	0.86	0.76	2.01	0.72	1.62	1.03	1.49	1.33	0.88	0.79
ALKYLCYCLOPENTANES	11 (0)	0.81	0.84	1.87	0.93	0.64	0.74	1.46	1.42	0.89	0.90
ALKYLCYCLOHEXANES	16 (0)	1.82	2.54	4.27	2.62	2.82	1.53	4.29	1.75	2.67	2.40
1-ALKENES	20 (19)	4.45	1.26	2.06	1.08	2.18	2.03	2.50	2.53	1.22	2.09
2.3.4-ALKENES	24 (12)	1.36	1.46	2.74	1.70	2.33	1.95	2.79	2.05	1.42	1.17
METHYLALKENES	22 (4)	0.80	1.17	2.69	1.34	1.10	1.15	2.60	1.02	1.27	1.12
ETHYL and HIGHER ALKENES	11 (0)	1.03	1.30	3.00	1.40	0.88	0.94	2.84	0.98	1.43	1.36
CYCLOALKENES	10 (5)	0.58	0.57	1.98	0.86	1.67	0.95	1.61	1.43	0.77	0.68
DIALKENES	26 (14)	2.81	3.01	4.47	2.96	2.11	2.34	4.69	2.97	4.04	3.87
ALKYNES	17 (15)	2.28	1.87	2.52	1.71	1.95	1.43	2.55	2.61	2.72	2.72
N-ALKYLBENZENES	19 (4)	5.22	1.66	2.77	1.80	3.20	2.46	2.89	2.33	1.38	2.40
OTHER ALKYLBENZENES	44 (27)	1.97	1.45	2.47	2.01	2.08	1.65	2.85	1.65	1.49	1.52
OTHER MONOAROMATICS	16 (11)	0.74	1.22	2.73	1.94	1.62	1.03	2.91	0.97	1.12	0.99
NAPHTHALENES	17 (7)	1.57	1.25	2.29	1.92	2.16	1.94	2.68	1.90	1.20	1.02
OTHER CONDENSED RINGS	10 (5)	3.25	2.86	3.41	3.25	1.99	2.60	3.67	2.61	2.58	2.55
DIPHENYL/POLYAROMATICS	19 (8)	2.04	1.52	3.06	2.79	3.49	2.23	3.86	2.15	1.12	1.01
TERPENES	6 (3)	0.82	1.49	2.81	2.02	1.57	1.42	2.93	1.09	1.30	1.14
OTHER HYDROCARBON RINGS	17 (12)	1.16	1.45	2.95	1.70	4.40	1.76	2.84	1.48	1.59	1.45

The lowest AADs are highlighted. NF (NP)—number of fluids (number of polar fluids); R—Riedel [11], Eq. (1); Chen—Chen [12], Eq. (2); V-73—Vetere [14], Eq. (3); V-79—Vetere [15], Eq. (4); V-95—Vetere [16], Eqs. (5)–(7); L—Liu [23], Eq. (8); CK—Carruth and Kobayashi [13], Eq. (9); SMK—Sivaraman et al. [17], Eqs. (10)–(12); MK—Morgan and Kobayashi [21], Eqs. (13) and (14); FMC—Faúndez et al. [32], Eq. (15).

the specific correlations give an AAD less than 2.5%, with that proposed by Liu [23], Eq. (8), being the best choice (the AAD for n-alkanes given by the Liu model is similar to the value reported by that author for 160 fluids), and the Chen and V-73 models being adequate simple alternatives.

Finally, we would note that for some n-alkanes it is very important to choose the model appropriately. Thus, although the Liu, Chen, and V-73 models give similar AADs, there are important differences for some particular fluids. Thus, for example, for n-dotriacontane the deviations are −1.8%, −3.2%, and 8.3%, respectively.

For alkylcyclohexanes, AADs below 2% are found only for the general SMK model and the specific Riedel and Liu models. Moreover, we found that the choice of model for a specific fluid can lead to very different results.

For dialkenes, we found individual deviations greater than 2% for many fluids and models. Only the Liu and the V-95 models reproduce all the boiling enthalpies with deviations below 10%. All the other models give deviations greater than 11% for 1,4-pentadiene and greater than 8% for trans-1,3-pentadiene. Similarly, AADs for alkynes are influenced by the fact that for vinylacetylene only the V-95 and the Liu models lead to a deviation less than 5%.

For other condensed rings, we found that all the models give values for fluoranthene that deviate by more than 4.5% with respect to the value reported by the DIPPR [37] project (57.8 kJ/mol).

Taking the above specific comments into account, we can summarize the results given in Table 2 as follows. The specific Chen [12] and Liu [23] models can be used for all these

Table 3
Absolute average deviations (AAD) of the values obtained with the models studied from the values provided by DIPPR [37] for several families of fluids

FAMILY OF FLUIDS	N (NP)	AAD (%)									
		R	Chen	V-73	V-79	V-95	Liu	CK	SMK	MK	FMC
ALDEHYDES	32 (29)	2.04	1.44	2.11	2.12	3.91	2.18	2.94	1.78	1.43	1.58
KETONES	35 (32)	2.10	1.67	2.59	2.05	2.37	1.70	2.64	1.51	1.67	1.75
N-ALCOHOLS	20 (20)	9.25	7.07	6.48	7.31	4.18	6.68	6.14	5.55	6.74	7.37
CYCLOALIPHATIC ALCOHOLS	11 (11)	6.82	2.97	4.22	4.23	11.18	5.56	4.90	3.78	2.74	3.61
AROMATIC ALCOHOLS	33 (33)	5.34	2.56	3.02	3.04	10.14	3.17	3.35	2.73	2.63	3.51
OTHER ALIPHATIC ALCOHOLS	28 (23)	4.12	4.65	5.74	6.78	3.37	8.56	7.09	5.57	4.08	3.88
POLYOLS	36 (32)	12.98	4.96	5.16	5.03	34.13	6.55	4.92	5.12	4.40	9.81

The lowest AADs are highlighted. NF (NP)—number of fluids (number of polar fluids); R—Riedel [11], Eq. (1); Chen—Chen [12], Eq. (2); V-73—Vetere [14], Eq. (3); V-79—Vetere [15], Eq. (4); V-95—Vetere [16], Eqs. (5)–(7); L—Liu [23], Eq. (8); CK—Carruth and Kobayashi [13], Eq. (9); SMK—Sivaraman et al. [17], Eqs. (10)–(12); MK—Morgan and Kobayashi [21], Eqs. (13) and (14); FMC—Faúndez et al. [32], Eq. (15).

Table 4

Absolute average deviations (AAD) of the values obtained with the models studied from the values provided by DIPPR [37] for several families of fluids

FAMILY OF FLUIDS	N (NP)	AAD (%)									
		R	Chen	V-73	V-79	V-95	Liu	CK	SMK	MK	FMC
N-ALIPHATIC ACIDS	16 (16)	12.38	6.31	5.47	6.23	8.99	5.72	4.83	4.58	5.22	5.65
OTHER ALIPHATIC ACIDS	20 (16)	5.41	2.78	4.45	4.78	14.11	7.11	5.48	4.98	1.98	2.35
DICARBOXYLIC ACIDS	14 (12)	7.46	1.50	1.93	4.92	21.27	8.02	5.56	5.45	0.47	2.31
AROMATIC CARBOXYLIC ACIDS	10 (8)	7.73	2.40	2.74	5.49	21.38	8.32	6.11	6.02	1.60	5.90
ANHYDRIDES	9 (6)	9.18	6.06	4.84	3.57	7.72	3.76	4.31	5.02	7.07	8.36
FORMATES	15 (15)	2.30	1.25	2.16	1.79	4.75	2.07	2.65	0.99	1.33	1.66
ACETATES	22 (21)	2.62	1.25	2.10	2.10	5.71	2.84	2.98	1.57	1.10	1.48
PROPIONATES AND BUTYRATES	13 (11)	1.28	1.24	2.37	2.06	4.32	2.27	2.72	1.16	1.10	1.01
OTHER SATURATED ALIPHATIC ESTERS	21 (21)	10.14	4.49	4.01	4.17	4.97	4.53	3.81	3.94	3.54	4.61
UNSATURATED ALIPHATIC ESTERS	23 (15)	3.25	1.67	2.83	2.56	5.87	3.61	3.77	2.55	1.57	1.74
AROMATIC ESTERS	29 (26)	9.28	3.39	3.86	3.59	7.64	4.98	4.13	4.21	2.75	3.48
ALIPHATIC ETHERS	32 (28)	2.21	1.50	2.02	1.52	2.23	1.69	2.08	2.04	1.56	1.65
OTHER ETHERS/DIETHERS	23 (20)	3.58	1.61	1.88	1.99	5.72	2.34	2.67	1.83	1.49	2.12

The lowest AADs are highlighted. NF (NP)—number of fluids (number of polar fluids); R—Riedel [11], Eq. (1); Chen—Chen [12], Eq. (2); V-73—Vetere [14], Eq. (3); V-79—Vetere [15], Eq. (4); V-95—Vetere [16], Eqs. (5)–(7); L—Liu [23], Eq. (8); CK—Carruth and Kobayashi [13], Eq. (9); SMK—Sivaraman et al. [17], Eqs. (10)–(12); MK—Morgan and Kobayashi [21], Eqs. (13) and (14); FMC—Faúndez et al. [32], Eq. (15).

families. In particular, the Chen model, which is slightly simpler than the Liu model, gives clearly better results than the latter for methylalkanes, 1-alkenes, cycloalkenes, *n*-alkylbenzenes, and diphenyl/poly-aromatics. The contrary is the case only for alkyl-cyclohexanes and dialkenes.

The old and simple Riedel approach works surprisingly well for many of the families included in Table 2. It can generally be considered the best specific approach for methylalkanes, dimethylalkanes, methylalkenes, cycloalkenes, other monoaromatics, terpenes, and other hydrocarbon rings. Also it gives similar results to the Chen and Liu proposals for some other families. Nevertheless, although good or even excellent results can be found for some specific fluids, it is generally not adequate for *n*-alkanes, 1-alkenes, or *n*-alkylbenzenes.

The three specific models proposed by Vetere are not recommended for general use for the fluids included in Table 2 because they lead to irregular results. Moreover, it is always possible to find a simple specific model giving an equal or better AAD. Only for some particular fluids do the Vetere proposals represent a better approach. A clear example is the good result obtained using the V-95 model for ethyl and higher alkenes.

With respect to the general models, the oldest and simplest CK model seems to be the worst choice. Nevertheless, for some families, including alkynes, it gives similar results to the other general models, and the highest AAD found for the families included in Table 2 is only 4.7%. Hence, if great accuracy is not required it might be an appropriate choice because of its simplicity.

With respect to the SMK model, the most surprising result is the high AAD found for *n*-alkanes. For all the other families in Table 2 it gives similar results to the other general models,

Table 5

Absolute average deviations (AAD) of the values obtained with the models studied from the values provided by DIPPR [37] for several families of fluids

FAMILY OF FLUIDS	N (NP)	AAD (%)									
		R	Chen	V-73	V-79	V-95	Liu	CK	SMK	MK	FMC
EPOXIDES	14 (13)	0.69	0.56	2.31	1.36	2.55	0.91	1.88	1.04	0.97	0.82
PEROXIDES	11 (6)	6.95	4.22	5.08	6.46	16.10	8.24	4.67	3.50	0.51	1.69
C1/C2 ALIPHATIC CHLORIDES	18 (15)	1.56	1.59	3.05	1.74	3.35	1.13	2.82	2.27	2.46	2.32
C3 & HIGHER ALIPHATIC CHLORIDES	26 (23)	2.13	2.22	3.45	2.45	1.97	1.87	3.37	2.34	2.65	2.52
AROMATIC CHLORIDES	15 (14)	2.32	2.52	3.63	2.99	3.21	2.39	3.54	2.45	2.48	2.38
N-ALIPHATIC PRIMARY AMINES	13 (13)	5.01	2.22	1.88	1.58	4.47	1.82	2.42	1.10	1.96	2.83
OTHER ALIPHATIC AMINES	21 (19)	4.49	2.79	3.53	3.18	4.51	3.60	3.83	3.09	2.92	3.17
AROMATIC AMINES	37 (36)	2.55	1.45	2.28	2.57	4.62	2.05	2.72	1.66	1.43	1.89
OTHER AMINES. IMINES	36 (27)	3.54	2.21	3.42	3.14	6.77	3.07	3.75	2.47	2.45	2.62
NITRILES	29 (23)	3.77	2.73	2.58	3.12	5.67	3.52	3.31	3.74	2.82	3.15
ISOCYANATES/DIISOCYANATES	10 (6)	4.09	3.37	3.98	4.40	10.23	5.14	4.71	3.52	2.75	2.98
MERCAPTANS	23 (23)	1.58	0.82	2.13	1.19	1.49	1.07	2.17	1.31	0.75	1.00
SULFIDES/THIOPHENES	26 (25)	1.77	1.24	2.39	1.61	1.27	1.04	2.10	1.10	1.42	1.45
NITROAMINES	7 (6)	6.96	1.20	0.86	2.77	14.20	4.35	3.30	2.59	1.61	3.65

The lowest AADs are highlighted. NF (NP)—number of fluids (number of polar fluids); R—Riedel [11], Eq. (1); Chen—Chen [12], Eq. (2); V-73—Vetere [14], Eq. (3); V-79—Vetere [15], Eq. (4); V-95—Vetere [16], Eqs. (5)–(7); L—Liu [23], Eq. (8); CK—Carruth and Kobayashi [13], Eq. (9); SMK—Sivaraman et al. [17], Eqs. (10)–(12); MK—Morgan and Kobayashi [21], Eqs. (13) and (14); FMC—Faúndez et al. [32], Eq. (15).

Table 6
Absolute average deviations (AAD) of the values obtained with the models studied from the values provided by DIPPR [37] for several families of fluids

FAMILY OF FLUIDS	N (NP)	AAD (%)									
		R	Chen	V-73	V-79	V-95	Liu	CK	SMK	MK	FMC
C-H-BR COMPOUNDS	17 (17)	3.25	3.14	3.40	3.11	4.60	2.56	4.60	4.77	4.64	4.67
C-H-I COMPOUNDS	8 (8)	3.43	3.12	2.22	2.46	3.41	3.12	3.71	5.17	4.56	4.75
C-H-F COMPOUNDS	28 (20)	1.33	1.41	2.60	1.60	7.70	2.89	2.25	1.56	1.39	1.34
C-H-MULTIHALOGEN COMPOUNDS	37 (35)	0.93	1.16	2.62	1.32	5.00	1.38	2.13	1.61	1.31	1.19
C-H-NO₂ COMPOUNDS	21 (19)	11.94	7.84	6.95	5.79	4.42	5.39	4.72	5.95	7.52	8.92
POLYFUNCTIONAL ACIDS	20 (20)	9.37	1.60	1.78	4.79	24.83	8.71	5.48	5.78	1.36	11.21
POLYFUNCTIONAL ESTERS	23 (18)	16.27	4.47	3.51	4.45	12.34	4.54	3.66	3.58	4.18	16.23
OTHER POLYFUNCTIONAL C-H-O	50 (48)	10.92	5.09	4.99	4.86	12.23	5.10	4.56	4.55	4.45	7.82
POLYFUNCTIONAL NITRILES	7 (3)	3.94	1.70	2.50	3.25	10.05	3.58	3.24	2.19	1.69	2.92
POLYFUNCTIONAL AMIDES/AMINES	27 (18)	5.83	3.08	4.05	4.72	13.40	5.26	4.65	3.77	2.33	3.54
POLYFUNCTIONAL C-H-O-N	30 (28)	4.28	2.41	3.38	4.71	11.09	5.23	4.58	3.64	1.79	2.68
POLYFUNCTIONAL C-H-O-S	13 (9)	5.18	3.36	3.63	3.06	7.46	1.99	2.88	2.18	3.21	3.69
POLYFUNCTIONAL C-H-O-HALIDE	35 (32)	3.45	2.70	3.21	2.84	9.88	3.49	3.32	2.76	2.95	3.15
POLYFUNCTIONAL C-H-N-HALIDE-(O)	13 (10)	3.60	2.72	2.80	3.03	6.96	3.27	2.83	2.54	2.21	2.42
OTHER POLYFUNCTIONAL ORGANICS	5 (4)	0.84	1.22	2.89	2.64	5.51	1.40	2.83	1.12	1.41	1.29

The lowest AADs are highlighted. NF (NP)—number of fluids (number of polar fluids); R—Riedel [11], Eq. (1); Chen—Chen [12], Eq. (2); V-73—Vetere [14], Eq. (3); V-79—Vetere [15], Eq. (4); V-95—Vetere [16], Eqs. (5)–(7); L—Liu [23], Eq. (8); CK—Carruth and Kobayashi [13], Eq. (9); SMK—Sivaraman et al. [17], Eqs. (10)–(12); MK—Morgan and Kobayashi [21], Eqs. (13) and (14); FMC—Faúndez et al. [32], Eq. (15).

Table 7
Absolute average deviations (AAD) of the values obtained with the models studied from the values provided by DIPPR [37] for several families of fluids

FAMILY OF FLUIDS	N (NP)	AAD (%)									
		R	Chen	V-73	V-79	V-95	Liu	CK	SMK	MK	FMC
INORGANIC GASES	21 (15)	2.90	2.89	3.89	3.39	9.40	4.28	4.11	4.59	4.21	4.05
SILANES/SILOXANES	36 (31)	2.26	2.35	4.52	2.26	2.16	3.17	3.92	3.39	2.44	2.38
INORGANIC HALIDES	11 (9)	5.67	5.33	5.14	4.58	3.35	4.40	6.65	6.80	7.52	7.60
INORGANIC ACIDS	7 (5)	12.84	11.69	10.80	9.53	12.07	10.47	12.15	12.26	13.71	14.02
ORGANIC/INORGANIC COMPOUNDS	6 (5)	3.81	3.37	4.94	4.72	9.36	4.23	5.89	4.20	4.41	4.93
ORGANIC SALTS	15 (14)	6.62	5.31	4.59	4.33	9.13	4.92	5.27	6.34	6.48	6.99
SODIUM SALTS (SODIUM CHLORIDE)	1 (1)	7.36	9.19	2.82	5.17	---	20.01	15.78	18.11	16.12	16.12
OTHER INORGANICS	4 (4)	2.66	3.08	1.34	0.84	4.98	1.01	1.81	4.19	3.78	4.13
RARE GASES	3 (0)	1.00	0.92	1.36	2.92	4.21	1.15	1.13	4.02	0.98	0.67
HALOGENS	4 (0)	0.87	1.03	2.17	1.12	8.39	2.54	1.35	2.81	1.42	1.41
ALKALI METALS	3 (0)	8.68	9.85	6.76	7.86	---	22.22	10.31	10.36	10.59	11.27
OTHER ELEMENTS	9 (0)	5.03	7.68	3.20	4.59	---	17.70	13.97	14.42	14.61	14.05

Legend as in Tables 2–6. The entries "–" stand for very large deviations.

and it is the best general model only for dialkenes, and ethyl and higher alkenes.

The MK and the FMC models give similar results, and the choice of one or the other may be based on the use of the inputs needed (critical properties or Lennard-Jones parameter). In any case, it seems to generally be preferable to use the MK correlation for 1-alkenes and n-alkylbenzenes, and FMC (although with only a slight reduction in the AAD) for methylalkanes and 2,3,4-alkenes. The worst results with these two models are for dialkenes, reflecting the poor results obtained for just a few of these substances.

As can be seen in Table 2, it is always possible to use these two general models with a certain degree of accuracy. The use of specific models can only be justified to slightly reduce the AAD for alkylcyclohexanes, dialkenes, and alkynes (choosing the Liu correlation), and for terpenes and other hydrocarbon rings (choosing the Riedel correlation).

3.2. Results for aldehydes, ketones, and alcohols

The AADs for aldehydes, ketones, and several families of alcohols are listed in Table 3. In particular, we would note that the high AADs found for n-alcohols are mainly due to the irregular behaviour of the models. Thus, although the specific V-95 (using Eq. (6), which was specifically given for alcohols) and the general SMK correlations give the lowest AADs, the choice of one or the other model can lead to very different results for the same substance. As can be seen in Fig. 1, the V-95 model agrees very well with the DIPPR data for the n-alcohols with lower boiling temperatures. For the SMK model, one observes that it underestimates the boiling enthalpy for low boiling temperatures, and overestimates it when that temperature increases. For high boiling temperatures, it reproduces the DIPPR data slightly better than the V-95 model. In any case, it must be borne in mind that the V-95 model has 2 input parameters fewer.
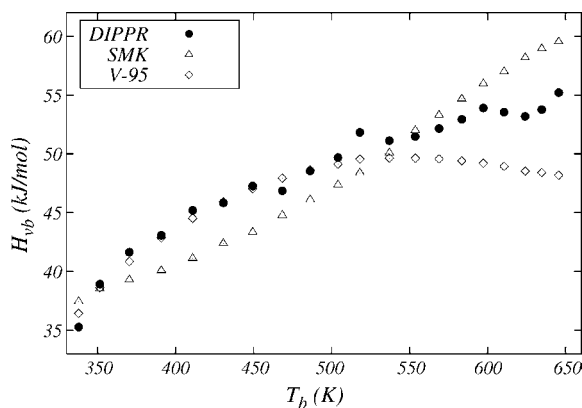
Fig. 1. Boiling enthalpy vs. boiling temperature for *n*-alcohols. Data are from DIPPR [37] and from the SMK [17], Eqs. (10)–(12), and V-95 [16], Eqs. (5)–(7), models.

Results for cycloaliphatic alcohols are influenced by the poor agreement found for cyclohexanol, which has the lowest boiling temperature in this family. The deviations given by the Chen and MK correlations are −10.6% and −12%, respectively (i.e., the values given for the correlations are similar but clearly different from that given by the DIPPR project). All the other correlations except V-95 give deviations that are negative and greater than 9% for this fluid. The V-95 models give a very high AAD due to the fact that deviations as large as 58%, 35%, and 19% are found for 3 of the 11 fluids studied. For the other 8 fluids the deviations given by this model are always below 2.7%.

For aromatic alcohols, the V-95 model gives deviations greater than 20% for 4 fluids. For other aliphatic alcohols (such as 2-butanol, 8-methyl-1-nonanol, and isopropanol) the V-95, MK, and FMC correlations give the lowest AADs. The greatest deviation for the V-95 model is for 3-methyl-3-pentanol (15.4%) for which the other two models mentioned are adequate (deviations below 2.8%). The contrary is the case for 2-methyl-1-pentanol, for which only V-95 (of all the others) gives adequate results. The Riedel and Chen models can also be used, although with less accuracy for some specific fluids.

As can be seen in Table 3, the specific Riedel and V-95 models seem to be clearly inadequate for polyols. Surprisingly, for V-95 we had to use Eq. (7) (valid for polar fluids) instead of Eq. (6) (valid for alcohols) because the latter gave excessively large deviations. In any case, Eq. (7) is also clearly inadequate. Also the general FMC model gives a high AAD. This is due to the fact that individual deviations for 10% to 69% are found for 8 fluids. In particular the FMC model does not work well when the boiling enthalpy is greater than 80 kJ/mol, which, according to the DIPPR data, occurs for 4 polyols.

All the other specific models except that proposed by Liu, and all the other general models give similar overall accuracies. Deviations greater than 10% are found for several fluids, which lead to AADs near 5%.

In sum, for the families included in Table 3, the greatest discrepancies between the values given by the models and that

given by the DIPPR project are for *n*-alcohols, other aliphatic alcohols, and polyols. In particular, for *n*-alcohols the choice of one or another model can lead to very different results for the same substance. The specific V-95 and MK models are recommended as a general choice for this family. The V-95 model also works well for aldehydes and ketones and other aliphatic alcohols, but is clearly not generally valid for the other families included in Table 3. This may be due to the fact that only one input parameter added to the boiling temperature is needed.

For the families included in Table 3, the general models give similar accuracies to the specific models. The specific Chen correlation and the general MK one are the best models, in a general sense. Only for *n*-alcohols and other aliphatic alcohols does the use of the V-95 model lead to clearly lower AADs. The SMK and FMC models behave similarly to the MK one, except when FMC is used for polyols with a boiling enthalpy greater than 80 kJ/mol. The CK correlation also behaves similarly, except for cycloaliphatic alcohols and other aliphatic alcohols. In any case, it is always possible to find a general model with better general agreement.

The Riedel correlation is adequate only for aldehydes, ketones, and other aliphatic alcohols, although it is possible always to find a model with a lower AAD. The V-73, V-79, and Liu correlations work well for aldehydes, ketones, aromatic alcohols, and polyols.

3.3. Results for some organic acids, anhydrides, formates, acetates, propionates, butyrates, esters, and ethers

The top four rows in Table 4 present the results for some organic acids. Although the DIPPR project gives data for 20 *n*-aliphatic acids and 25 other aliphatic acids, Table 4 includes only 16 and 20 of them, respectively. This is because there are some fluids for which all the selected models clearly disagree with the DIPPR data. In particular, there are 4 *n*-aliphatic acids (acetic acid, formic acid, *n*-propionic acid, and butyric acid) for which the DIPPR project gives boiling temperatures below 440 K and boiling enthalpies less than 36 kJ/mol. All the models
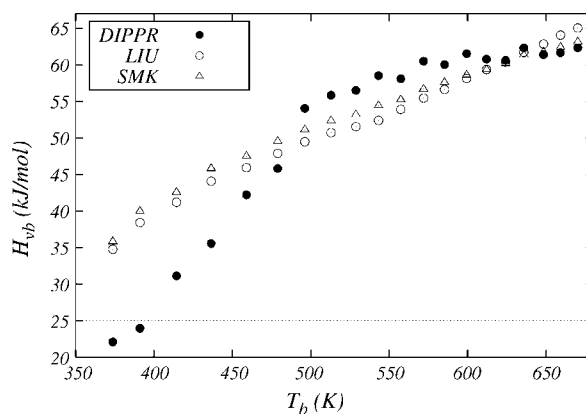

Fig. 2. Boiling enthalpy versus boiling temperature for *n*-aliphatic acids. Data are from DIPPR [37] and from the SMK [17], Eqs. (10)–(12), and Liu [23], Eq. (8), models.
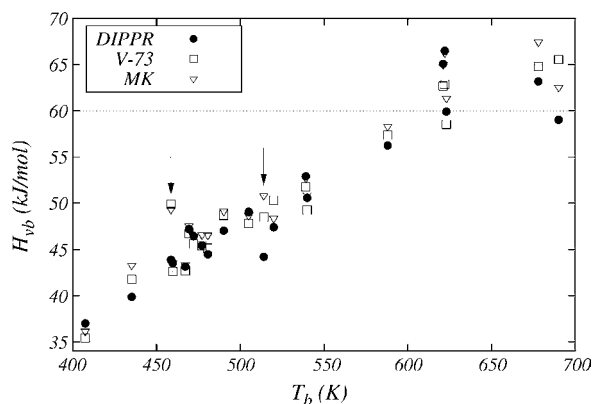
Fig. 3. Boiling enthalpy versus boiling temperature for other saturated aliphatic esters. Data are from DIPPR [37] and from the MK [21], Eqs. (13) and (14), and V-73 [14], Eqs. (5)–(7), models. Arrows indicate data for diethyl oxalate ($T_b = 458.61$ K) and epsilon-caprolactone ($T_b = 514$ K), respectively.

overestimate the latter property with respect to the DIPPR values. This is clearly seen in Fig. 2. One can also see that at intermediate boiling temperatures the models underestimate the DIPPR data (see Fig. 2).

As can be seen in Fig. 3, for other saturated aliphatic esters (including lactones, diesters, and higher paraffinic esters), the DIPPR boiling enthalpy data do not behave regularly as the boiling temperature increases. Thus, there are some fluids, such as diethyl oxalate ($T_b = 458.61$ K) and epsilon-caprolactone ($T_b = 514$ K), for which even the best models do not agree with the DIPPR values (arrows in Fig. 3).

We would note that within the aromatic esters all the models clearly disagree with the DIPPR values for dimethyl isophthalate and tri-*n*-heptyl trimellitate.

In sum, we can conclude that the specific Chen correlation and the general MK correlation are the models with the generally best agreement with the values given by the DIPPR project for the families listed in Table 4. They are particularly adequate, being clearly better than most of the other models, for other aliphatic acids, dicarboxylic acids, aromatic carboxylic acids, and unsaturated aliphatic esters. For anhydrides, however, other models lead to clearly better agreement.

The Riedel model should not be used for acids, anhydrides, aromatic esters, or other saturated aliphatic esters. The V-73 and V-79 models give similar results to each other, except for dicarboxylic acids or aromatic carboxylic acids, for which V-73 is clearly better.

The use of the V-95 model is not recommended in an overall sense. It gives adequate results only for a few families, being clearly not valid for dicarboxylic acids or aromatic carboxylic acids. The Liu model is not adequate for acids but it is for all the other families in Table 4.

For the general models, we recommend the use of the CK model especially for anhydrides. The SMK model gives AADs that are greater than or similar to the MK value, except for anhydrides for which SMK works better. The FMC model can be used for all these families except for anhydrides or for fluids for which the boiling enthalpy is greater than 100 kJ/mol (pyromellitic acid, for example).

3.4. Results for epoxides, peroxides, organic chlorides, amines, imines, nitriles, isocyanates and diisocyanates, mercaptans, sulfides and thiophenes, and nitroamines

As can be seen in Table 5, excellent results are found for epoxides by using even the simplest Riedel model. For peroxides, the MK model gives excellent results, with the FMC model generally being its only alternative. It is important to note that the Chen model works well (deviations below 2%) for all fluids of this kind except one − dicumyl peroxide − for which it deviates by 30.4%, which clearly leads to a high AAD. Only the SMK, MK, and FMC models agree with the DIPPR value for the boiling enthalpy of this fluid.

We found that the selected models do not agree with the DIPPR values for two aromatic chlorides − 1-chloronaphthalene and hexachlorobenzene − which have boiling temperatures higher than 530 K (they range from 400 to 500 K for all the other aromatic chlorides selected), and for which deviations greater than −6.5% and −9% are found. Any of the other models can be used for the rest of the fluids of this kind, although the three models proposed by Vetere and the CK model give the worst results.

Despite the good results obtained for most of the other aliphatic amines, aromatic amines, and other amines or imines, large deviations are found for some particular fluids. Thus, for tripropylamine, all the models except V-95 give deviations greater than 9.8%. Similarly, for tri-*n*-octylamine, the SMK model gives the lowest deviations, whereas the Chen, MK, and FMC models deviate by more than 9.6%. For 2,6-diethylaniline, the Liu, CK, and SMK models deviate by less than 1%, whereas deviations greater than 5.8% are found when the Chen, MK, or FMC models are used. The greatest deviations are found for pyrimidine, for which all the models disagree with the DIPPR value by more than −17.7%. For these fluids, the choice of one or another model clearly changes the results.

In sum, the specific Chen model and the general MK model give the best general agreement for the families of fluids included in Table 5. Only for peroxides must the Chen model be used with caution, with MK clearly giving better overall results. The FMC model also gives good results, although for peroxides, *n*-aliphatic primary amines, and nitroamines the MK model leads to clearly better results. In any case, for peroxides, the FMC model is the only clear alternative to MK. The SMK model has a general accuracy that is similar to the MK or FMC models, except for peroxides and perhaps for nitriles, isocyanates, and diisocyanates. With respect to the Liu model, our results indicate that its accuracy clearly depends on the family of fluids selected. It gives AAD values below 2.1% for 7 families, but clearly higher than those obtained with other simple specific models for other families. The Riedel model also behaves irregularly. Finally, we cannot generally recommend the use of the three models proposed by Vetere.

3.5. Results for other compounds containing carbon and hydrogen, and other polyfunctional substances

Results for different compounds containing carbon and hydrogen and other polyfunctional substances are given in

Table 6. We found large deviations for some C−H−Br compounds (1,1,2,2-tetrabromoethane, for example, for which all the models give values clearly below that proposed by the DIPPR project, the Liu model being the only one with a deviation less than 10%). The models must therefore be used with caution.

For C−H−NO$_2$ compounds, V-95 gives the lowest AAD, with individual deviations below 8.2% except for tetryl, which is the fluid with the highest boiling temperature (650 K) and for which the deviation is −27%. The V-79, Liu, and CK models give similar overall results to each other, being better than V-95 for tetryl although worse for some other fluids.

For polyfunctional acids, we found major differences between the models. In particular, the high deviation found for the FMC model is due in great part to the poor results obtained for only three fluids (ascorbic acid, citric acid, and tartaric acid), for which the boiling enthalpies are greater than 100 kJ/mol and the boiling temperature higher than 630 K. Although for these fluids the FMC model is clearly inadequate, it behaves similarly to the others for the rest of the fluids. The Riedel, Liu, SMK, and V-95 models are also inadequate for these three fluids.

The FMC model also gives a high AAD for polyfunctional esters and other polyfunctional C−H−O fluids (which include the following sub-families: alcohol-carbonyl, alcohol-ether, alcohol-aldehyde, aldehyde-ethers, aldehyde-acid, aldehyde-ether alcohol, and carbonyl-ether alcohol). As in the preceding case, this is due in great part to the poor results obtained for fluids with boiling enthalpies greater than 100 kJ/mol (diolein and dextrose, for example).

For other polyfunctional C−H−O fluids (which include the following sub-families: alcohol-carbonyl, alcohol-ether, alcohol-aldehyde, aldehyde-ethers, aldehyde-acid, aldehyde-ether alcohol, and carbonyl-ether alcohol), we observed that the choice of model can be important for some particular fluids because the distribution of individual deviations is arbitrary.

For the selected polyfunctional amides and amines, we observed that with the FMC model deviations greater than 10% are found for 3 fluids. One of them − ethylenediaminetetraacetic acid − has a boiling enthalpy greater than 91 kJ/mol, and the value given by the FMC model deviates by nearly −25% from that value.

In sum, our results show that for the families included in Table 6 the worst agreement between the models and the DIPPR values is found for C−H−NO$_2$ compounds, polyfunctional esters, and other polyfunctional C−H−O compounds. For the rest of the fluids, it is always possible to find a model with a low AAD. As can be observed in Table 6, the Riedel and FMC models can generally be used except for the aforementioned families and for polyfunctional acids. Moreover, the use of the V-95 model can be recommended only for C−H−NO$_2$ compounds. The Chen model can be regarded as generally the best specific model for the rest of the fluids, since it gives the lowest AAD for several families. The V-73 model is adequate for more families than V-79. The Liu model is adequate except for polyfunctional acids; for C−H−Br compounds, and even more clearly for polyfunctional C−H−O−S fluids, it gives bet-

ter agreement with the DIPPR values than the other specific models.

With respect to the general models, the CK model is the only one giving AADs below 5.6% for the families included in Table 6. Moreover it gives the lowest AADs of the general models when it is used for C−H−I or C−H−NO$_2$ compounds. The SMK and MK model lead to similar overall results, but for polyfunctional acids and polyfunctional C−H−O−N fluids, the MK gives clearly lower AADs. As mentioned above, the FMC model can be considered as adequate except for four families. Even then, the large mean deviations found for these families are due in great part to the large individual deviations found for some fluids for which the boiling enthalpy is greater than 90 kJ/mol.

Only for C−H−Br and C−H−I compounds are the specific models needed, in an overall sense, instead of the general ones. Indeed, for polyfunctional amines and amides, and for polyfunctional C−H−O−N fluids, the general models give better agreement with the DIPPR values than the specific ones.

3.6. Results for inorganic compounds and organic salts

The results for inorganic compounds and organic salts are listed in Table 7. We found great deviations between all the models and the DIPPR value for two inorganic gases (sulfur trioxide and tetrafluorohydrazyne), for two silanes and siloxanes (dichlorosilane and dimethyldimethoxysilane), and for two organic salts (dimethyl sulfate and di-*n*-butyl sulfate).

For inorganic acids, we found very high AADs, the lowest being that obtained using the V-79 correlation. In any case, there are four inorganic acids for which all the models agree (to a greater or lesser degree) with the DIPPR values, whereas there are three for which there are major discrepancies. This is clearly seen in Fig. 4, where the fluids are ordered from low to high values of the boiling enthalpy, and where one can see that the general models clearly disagree for sulfuric acid which has the highest value of the boiling enthalpy. Moreover, most of models give a value 2.5 or 3 times greater than that given by the DIPPR project for hydrogen fluoride. This fluid has therefore not been included in Table 7 or Fig. 4.
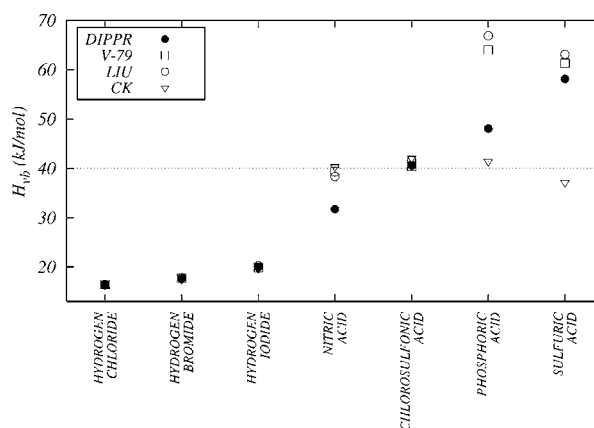

Fig. 4. Boiling enthalpy for inorganic acids. Data are from DIPPR [37] and from the V-79 [15], Eq. (4), Liu [23], Eq. (8), and CK [13], Eq. (9), models.

Table 8
Deviations of the values obtained with the studied models from the values provided by DIPPR [37] for three alkali metals and nine simple elements

SUBSTANCE	Deviations (%)									
	R	Chen	V-73	V-79	V-95	Liu	CK	SMK	MK	FMC
LITHIUM	4.56	6.37	-0.10	3.77	---	19.84	3.05	2.94	-3.24	-3.79
POTASSIUM	-2.66	-2.57	-6.73	-1.35	---	12.22	-11.70	-13.26	-22.10	-24.96
SODIUM	18.82	20.60	13.45	18.45	---	34.60	16.19	14.90	6.43	5.06
BERYLLIUM	5.14	6.86	0.53	2.12	---	18.89	5.37	7.67	6.27	6.40
BISMUTH	-1.09	1.23	-6.27	-1.79	57.49	15.43	-16.97	-23.16	-33.80	-39.03
CALCIUM	9.26	10.09	5.52	8.24	---	24.01	14.07	16.57	13.18	13.80
GERMANIUM	6.66	12.05	0.18	4.33	---	26.63	34.84	24.73	16.24	3.73
IRON	12.51	18.92	5.75	9.55	---	32.17	33.96	28.03	22.72	11.60
MERCURY	8.61	12.18	2.48	7.28	2.78	17.99	11.33	2.87	-8.59	-14.24
NITROGEN	0.04	0.13	-1.65	2.91	4.55	-2.99	0.40	3.84	-0.62	-0.17
OXYGEN	1.34	1.29	-0.90	3.14	-6.90	-1.46	1.45	4.47	-0.19	0.35
VANADIUM	0.61	6.33	-5.48	-1.98	---	19.70	-7.38	-18.46	-29.89	-37.08

Legend as in Tables 2–6. The entries "–" stand for very large deviations.

The DIPPR project includes a single sodium salt (sodium chloride), for which the V-73 models give the best agreement, and the V-95, Liu, and general models seem to be clearly inadequate.

A family of four other inorganics (deuterium oxide, hydrogen peroxide, water, and ammonia) is considered. As can be observed in Table 7, the specific V-73, V-79, and Liu models are very adequate, as is the general CK correlation.

Finally, we include some simple elements: three rare gases (argon, krypton, and xenon), four halogens (bromine, chlorine, fluorine, and iodine), three alkali metals (lithium, potassium, and sodium) and nine other elements. The mean deviations given in Table 7 for alkali metals are only indicative, because the results clearly change from one fluid to another. As can be observed in Table 8, for lithium all the other models work adequately, with V-73 giving the best agreement. All the models except MK and FMC disagree widely with the DIPPR value for sodium. For potassium, only the specific Riedel, Chen, and V-79 models seem to be adequate.

Table 8 also includes individual results for some nine other simple elements. In general, the V-73 model gives the lowest AAD (see Table 7), whereas the Liu and V-95 models are inadequate. The specific models generally give better results than the general ones. The general models are inadequate for bismuth, calcium, germanium (except FMC), iron, and vanadium. The FMC model is clearly inadequate also for mercury.

To summarize the results given in Table 7, it was shown that none of the selected models can be used for all the organic acids and alkali metals, although they may be adequate for some of them. The Liu and especially the V-95 correlations are inadequate for sodium chloride, alkali metals, and other simple elements. The Riedel and Chen correlations are especially adequate for inorganic gases, silanes and siloxanes, organic/inorganic compounds, rare gases, and halogens. The V-73 correlation gives the best agreement for sodium chloride and other simple elements, with clear differences with respect to the other models.

In a general sense, none of the general models give good agreement for inorganic acids, sodium chloride, alkali metals, and other simple elements. The SMK model also gives a higher AAD for rare gases than do the other general models. None of

these general models can be recommended for all the families of Table 7.

4. Conclusions

The validity of ten different methods, six being specific models and four being general models for the vaporization enthalpy, of obtaining the boiling enthalpy of 1591 substances grouped into 83 families was reviewed by comparing their predictions with the values given by the DIPPR project. The results obviously differed from one fluid to another in a given family, and from one family of fluids to another. Hence, in the previous section we analyzed all the results in detail. From that analysis, the following general conclusions and recommendations can be made.

No specific or general model gives the best agreement with the DIPPR values for all the selected families. Moreover, for some families, there is a clear disagreement between all the models and the DIPPR values for many of the substances involved. These families are n-alcohols, polyols, n-aliphatic acids, C−H−NO$_2$ compounds, other polyfunctional C−H−O compounds, inorganic halides, inorganic acids, organic salts, and alkali metals.

Of the specific models, the Chen correlation, Eq. (2), which has a very different analytical form from that used by the DIPPR project, and which is older and simpler than other specific proposals, is the appropriate choice for most of the families. Our results confirm those obtained by Chen [12] and Reid et al. [7], but indicate that the AAD reported by Vetere [16] when the Chen correlation is used for alcohols and esters (1.31%) is clearly very low. Also the AAD given by Liu [23] for 160 fluids (4.04%) is higher than those we obtained for most of the families. We showed that the Chen correlation gives AADs less than or equal to 3% for 61 families (73.5% of the 83 selected families), being greater than 6% only for 7 families. In particular, for cycloaliphatic alcohols, other aliphatic acids, and unsaturated aliphatic esters it gives AADs clearly lower than those given by all the other specific models. Moreover, only for 6 families – in particular n-alcohols, anhydrides, C−H−NO$_2$ compounds, sodium chloride, alkali metals, and other simple elements – does

it give AADs clearly greater than the lowest value obtained with the other models. The alternative models for these families are the following. The V-95 correlation developed to be applied only for alcohols, Eq. (6), is the best specific model for *n*-alcohols, and those developed specifically for non-polar or polar fluids, Eqs. (5) or (7), are the appropriate choice for C–H–NO$_2$ compounds. The V-79 and Liu correlations are adequate alternatives for anhydrides, and the V-73 one is adequate for sodium chloride, alkali metals, and other simple elements.

The simplest model we considered here is that given by Riedel, Eq. (1). We showed that this model works well, in a general sense, for many of families of fluids. This confirms the conclusions of other authors [7,9,23], with the extension to other families that had not been considered until now. Indeed, we showed that it is in very good agreement with the DIPPR values for some complex substances including cycloalkenes, terpenes, other hydrocarbon rings, epoxides, and C–H-multihalogen compounds. We showed, however, that it is generally clearly inadequate (although it may be adequate for some individual fluids) for 30 of the 83 families considered here, including *n*-alkanes, 1-alkenes, *n*-alkylbenzenes, alcohols, and four families of organic acids. It is important to bear in mind that the poor results obtained for *n*-alkanes are due to the large deviations found for some of the higher *n*-alkanes. It can be reliably used for the lower alkanes.

The V-73 and V-79 models behave similarly to each other, although one or the other gives clearly lower AADs for several families. Thus, for dicarboxylic acids, aromatic carboxylic acids, nitroamines, polyfunctional acids, and sodium chloride, the V-73 model is better than V-79. The contrary is the case for other alkanes, cycloalkanes and multiring cycloalkanes, alkylcyclopentanes, 1-alkenes, and cycloalkenes. As mentioned above, the V-73 model gives clearly lower AADs than the other specific models only for a few families (sodium chloride, alkali metals, and other simple elements), and only for these families can it be especially recommended. The V-79 model, however, cannot be especially recommended for any of the families studied, i.e., there is no family for which this model works clearly better than the others. Hence, we cannot recommend the general use of this model. This does not mean that it cannot give low AADs for some families or substances.

The V-95 model has the greatest degree of specificity, and is the only one that includes the molecular weight as an input parameter in addition to the boiling temperature. The results depend greatly on the families considered, so that it is not an adequate model for general use. Thus, for example, while it is very appropriate for ethyl and higher alkanes, other condensed rings, *n*-alcohols, other aliphatic alcohols, and inorganic halides, it clearly disagrees with the DIPPR values and also with the other model values for cycloaliphatic and aromatic alcohols, and for polyols. Moreover, it is clearly inadequate also for 4 families of organic acids, peroxides, nitroamines, 10 families of polyfunctional substances, inorganic gases and acids, organic/inorganic compounds, organic and especially (AADs greater than 100%) sodium salts, alkali metals, and other simple elements.

The Liu model gives AADs below 3% for 46 families. It is a clear alternative to the Chen model for all the families of hydrocarbons included in Table 2. We cannot confirm, however, the conclusion given by Liu [23] that this correlation works better than the classical ones in a general sense. While on the one hand it clearly reduces the AADs obtained with the Chen model for polyfunctional C–H–O–S compounds and other inorganic fluids, on the other it gives higher AADs for most of the other families. In particular, as is observed in Tables 2–7, the Liu model is clearly generally inadequate for other aliphatic alcohols, dicarboxylic acids, aromatic carboxylic acids, peroxides, polyfunctional acids, inorganic acids, sodium salts, alkali elements, and other simple elements.

Of the general models, we must recommend the use of the MK model if critical parameters are used, and of the FMC model if molecular parameters are preferred. The two models have similar accuracies for most of the families. In particular, the MK model gives a significantly lower AAD than FMC for *n*-alkylbenzenes, polyols, dicarboxylic acids, aromatic carboxylic acids, nitroamines, polyfunctional nitriles, and especially for polyfunctional acids and esters, and other polyfunctional C–H–O compounds. This does not mean, however, that the FMC model always gives a large deviation for these families or for some of the substances included in them. As indicated in the previous section, with some exceptions, the FMC model does not work well when the boiling enthalpy is very high.

For some families, there are general models that clearly reduce the AADs obtained with the MK or FMC models (the contrary is the case for most of the other families). Thus, the SMK model is an adequate alternative to these two models for alkylcyclohexanes and dialkenes, *n*-alcohols, *n*-aliphatic primary amines, and polyfunctional C–H–O–S compounds. The CK model can slightly reduce the AADs obtained with the other models for C–H–I and C–H–NO$_2$ compounds and organic salts, and more clearly for other inorganics. In any case, it is clear that with only few exceptions the good results obtained by Morgan and Kobayashi [21] for long *n*-alkanes can be extended to a very large number of fluids.

Our results show that when one chooses appropriately a general model, the use of specific models is clearly needed only for inorganic gases, alkali metals, sodium chloride, and other simple elements. Also one can slightly reduce the AADs by using an appropriate specific model for alkynes, C1/C2 aliphatic chlorides, C–H–Br and C–H–I compounds, and inorganic halides and acids. For all the other families considered here, the general models give results generally as good as those given by the specific models. In particular, for peroxides the general models clearly work better than the specific ones.

As far as we know, this has been the most extensive study of the calculation of the boiling enthalpy from correlations. Although other workers have previously checked the validity of some of the correlations used here, far fewer fluids and correlations were considered. Our results permit one to choose an appropriate specific or general model for each of the 83 families of fluids we have studied. In any case, we have shown that the specific correlation proposed by Chen [12], and the general correlations proposed by Sivaraman et al. [17] and by Faúndez et al. [32], the latter being the only one that includes molecular parameters, are the best overall choices.

Acknowledgements

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