

Vapour pressure and vaporization heat of molecules able to dimerize

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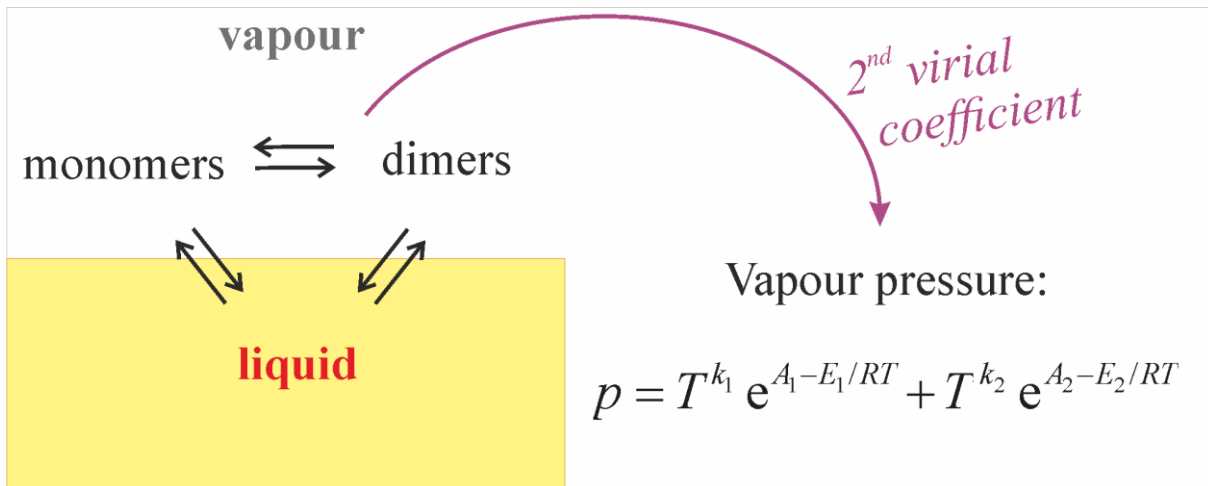
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Abstract

A model of the temperature dependence of the vapour pressure and the heat of vaporization of associated liquids with dimerizing vapours is presented. The result is a simple analytic generalization of the Clapeyron equation, valid with accuracy of 0.1-0.5%, as demonstrated with 8 liquids: formic and acetic acids, methanol, ethanol, water, toluene, heptane and isooctane. It involves only standard handbook parameters: the room temperature vaporization heat and vapour pressure, heat capacities, 2nd virial coefficient, heat of dissociation of the dimers in the gas phase.



Highlights

- A model of vapour-liquid 1-component equilibrium with vapour dimerization.
- Predicts analytically vapour pressure, vaporization heat and dimer fraction vs. T .
- No fitting – input is 6 standard handbook thermodynamic parameters only.
- Reversely, accurate thermodynamic parameters obtained from vapour pressure data.
- High precision for fuel components under cylinder conditions.

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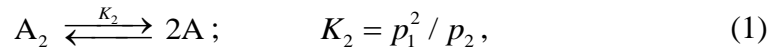
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The vapour pressure p of a single component liquid is a well-understood quantity [1]. The knowledge of two standard thermodynamic parameters, the heat of evaporation h_e and the normal boiling temperature, already allows the prediction of p with decent accuracy through the Clapeyron equation. Higher accuracy of a vapour pressure model can be achieved by accounting for the fugacity coefficient of the gas and the detailed temperature dependence of h_e [1-6], however, at the expense of simplicity. For this reason, the most widely used equations for the vapour pressure in everyday engineering are empirical, such as the Antoine equation [7] and many others [1], and involve parameters of unclear physical meaning. The validity of the empirical equations is limited by the accuracy of the experimental data behind them, and they hold only within the experimental temperature range; they cannot be used to extrapolate outside this range.

In this work, we evaluate a model of the vapour pressure of a class of single component systems – associated liquids with significant level of dimerization in the gas phase. This class contains such common liquids as carboxylic acids, NO_2 , and also – within a limited but wide vapour pressure interval – water, alcohols, amines, a variety of hydrocarbons, mercury and many more. The model combines accuracy with simplicity, and involves only standard thermodynamic quantities that can be found in many handbooks. It allows also the accurate prediction of the heat of evaporation and the weight fraction w_2 of dimers.

Theory

Let the vapour be an ideal gas mixture of monomers A and dimers A_2 . A dimerization equilibrium is established in the gas phase:



where p_1 and p_2 are partial pressures of the monomer and the dimer, and K_2 is the dissociation constant (cf. S1 for a list of symbols). **The equation of state** of such a gas is obtained [8] by solving the mass balance $1/v^G = p_1/RT + 2p_2/RT$, Dalton's law $p = p_1 + p_2$, and the equilibrium condition (1) for p_1 , p_2 , and v^G (the molar volume defined with respect to the total number of molecules in the gas phase, contained in both monomers and dimers); the result for v^G reads

$$v^G = \frac{RT}{2p} \left[1 + (1 + 4p/K_2)^{-1/2} \right]. \quad (2)$$

This constitutive relation has been re-derived many times in various forms [8-10], but is due to Gibbs [11]. In the limit of weakly dimerized gas ($p \ll K_2$), it simplifies to the standard virial expansion:

$$v^G \xrightarrow{p \rightarrow 0} \frac{RT}{p} - \frac{RT}{K_2} \dots \quad (3)$$

In the other limit of completely dimerized gas ($p \gg K_2$), it yields $v^G = RT/2p$, reflecting the fact that in such gas the molar volume v_2^G per dimer is twice that per molecule ($v_2^G = 2v^G$). The fugacity f of the vapour follows [12] from the integration of the fundamental equation $RT(\partial \ln f / \partial p)_T = v^G$:

$$f = p \exp \int_0^p \left(\frac{v^G}{RT} - \frac{1}{p} \right) dp = K_2 y, \quad \text{where} \quad y = \frac{1}{2} \left(\sqrt{1 + 4p/K_2} - 1 \right). \quad (4)$$

The physical meaning of y is ratio between dimers and monomers, i.e. $y \equiv p_2/p_1$. The relation $f = p_1$ holds. The weight fractions w_1 of molecules in monomers and w_2 in dimers are given by

$$w_1 = 1/(1 + 2y) = (1 + 4p/K_2)^{-1/2}; \quad w_2 = 1 - w_1. \quad (5)$$

Using these, one can write Eq (2) in the more transparent form $v^G = w_1 RT/p + w_2 RT/2p$.

The dissociation constant K_2 is a function of the temperature. It can be determined directly from p - v^G - T data by solving Eq (2) for K_2 (cf. S2). A second option is to use virial coefficient data – the expansion in series (3) shows that K_2 is related to B_2 as

$$K_2 = -RT / B_2. \quad (6)$$

The van ‘t Hoff’s equation can be utilized to relate $K_2(T)$ to the dissociation heat h_2 :

$$\frac{d \ln K_2(T)}{dT} = \frac{h_2(T)}{RT^2}, \quad K_2(T) = K_2^\circ \exp \int_{T^\circ}^T \frac{h_2(T)}{RT^2} dT; \quad (7)$$

here, T° is a standard temperature (25°C), and K_2° is the dissociation constant at T° .

The vaporization heat h_e depends on the degree of dissociation of the vapour, as it follows from the Gibbs-Helmholtz equation:

$$h_e = -T^2 \frac{\partial}{\partial T} \frac{\mu^G - \mu^L}{T} = h_{e1} - \frac{RT^2}{f} \frac{\partial f}{\partial T} = h_{e1} - w_2 \frac{h_2}{2}; \quad (8)$$

here, μ^G and μ^L are the chemical potentials of the gas and the liquid, and $\mu^G = \mu_0^G + RT \ln f$; w_2 is the weight fraction from Eq (5) (which leads to a dependence of h_e on the pressure); h_{e1} is the heat of evaporation of the monomer, and h_{e1} and $\mu_0^G - \mu^L$ are related through another Gibbs-Helmholtz equation. In the derivation of Eq (8), formula (4) has been used for f together with van ‘t Hoff’s relation (7) for K_2 . The result (8) reflects Hess’s law: the evaporation heat h_e is the sum of the heats h_{e1} for evaporating monomers and $-w_2 h_2/2$ released from the dimerization of a fraction w_2 of them [10].

The vapour pressure p is the solution to the Clausius-Clapeyron equation,

$$dp / dT = \frac{h_e}{T v^G (1 - v^L / v^G)}, \quad (9)$$

where v^L is the molar volume of the liquid. For the liquids considered below, v^L/v^G can be neglected. For example, for acetic acid at 140°C, $v^L/v^G = 0.5\%$ so setting $1 - v^L/v^G$ equal to one results in error in p of the order of 0.5%. As the available vapour pressure experiments for CH_3COOH are of similar or lower accuracy, this is a reasonable approximation. Substituting Eqs (2),(8)&(5) in (9), v^L being neglected, and using the relations (7) and $p = K_2 y(1+y)$ following from (4), one obtains the following form of the Clausius-Clapeyron equation valid for dimerizing vapours:

$$\frac{d \ln y}{dT} = \frac{h_{e1} - h_2}{RT^2}, \quad (10)$$

which is integrated to

$$\ln \frac{y}{y^\circ} = \int_{T^\circ}^T \frac{h_{e1} - h_2}{RT^2} dT. \quad (11)$$

If the linear dependence $h_{e1} = h_{e1}^\circ + c_{e1}(T - T^\circ)$ holds for the heat of evaporation of monomers (with $c_{e1} \equiv c_{p1}^G - c_p^L$, where c_{p1}^G is the heat capacity of the monomer), and $h_2 = h_2^\circ + c_2(T - T^\circ)$ holds for the heat of dimer dissociation, one obtains from (11) the explicit formula

$$y = y^\circ \left(\frac{T}{T^\circ} \right)^{(c_{e1} - c_2)/R} \exp \left[- \frac{h_{e1}^\circ - h_2^\circ - (c_{e1} - c_2)T^\circ}{R} \left(\frac{1}{T} - \frac{1}{T^\circ} \right) \right]. \quad (12)$$

Here, y° stands for

$$y^\circ = \frac{1}{2} \left(\sqrt{1 + 4p^\circ / K_2^\circ} - 1 \right), \quad (13)$$

where p° is the standard vapour pressure (at 25°C). The constant K_2 corresponding to the linear dependence $h_2(T)$ follows from Eq (7):

$$K_2(T) = K_2^\circ \left(\frac{T}{T^\circ} \right)^{c_2/R} \exp \left[-\frac{h_2^\circ - c_2 T^\circ}{R} \left(\frac{1}{T} - \frac{1}{T^\circ} \right) \right]; \quad (14)$$

this is the Kirchhoff's equation for K_2 . The vapour pressure is related to the pressure fraction y as $p = K_2 y(1+y)$, which leads to the final result:

$$\frac{p}{[\text{Pa}]} = \left(\frac{T}{T^\circ} \right)^{c_{e1}/R} e^{A_1 - E_1/RT} + \left(\frac{T}{T^\circ} \right)^{c_{e2}/R} e^{A_2 - E_2/RT}, \quad (15)$$

where $c_{e2} \equiv 2c_{e1} - c_2 = c_{p2}^G - c_p^L$, with c_{p2}^G being the heat capacity of the dimer, and the 4 parameters A & E are related to the thermodynamic parameters of the liquid and the gas:

$$E_1 = h_{e1}^\circ - c_{e1} T^\circ, \quad E_2 = 2E_1 - h_2^\circ + c_2 T^\circ; \\ A_1 = \ln \frac{y^\circ K_2^\circ}{[\text{Pa}]} + \frac{E_1}{RT^\circ}, \quad A_2 = \ln \frac{K_2^\circ y^{\circ 2}}{[\text{Pa}]} + \frac{E_2}{RT^\circ}. \quad (16)$$

The result (15) can be called *the Kirchhoff's equation for the pressure of dimerizing vapours* (generalizing the well-known Kirchhoff's equation for the vapour pressure when the gas phase is ideal, *p. 174* of Ref. [1] & Ref. [4]). For most practical purposes, where the degree of association is less than 10%, the capacity c_2 can be set to 0 as it does not affect p significantly. For a liquid for which h_e° , p° , c_{e1} , K_2° , h_2° and c_2 are known with high precision, the vapour pressure can be predicted via Eq (15) with accuracy that outmatches the one of, e.g., Antoine equation; in addition, the model allows the fraction of dimers in the gas phase to be calculated via Eq (5), and the vaporization heat – via Eq (8).

Comparison with experiment

The vapours of **formic and acetic acid** are classical examples for strong dimerization, and generations of scientists studied the effect of the dimers on their physicochemical properties [11,13]. Several complications lead to discordant results for all relevant experimental quantities (p - v^G - T data, vapour pressure, h_e) – these are: **(i)** tendency for adsorption of the acid at the walls of the container [14]; **(ii)** tendency to decompose to CO and H₂O [15]; **(iii)** water impurities [16,17]; **(iv)** experimental evidence for slow kinetics of equilibration between the monomers and the dimers exists [18]. In confirmation of the last point, Faubel and Kisters [19] found the evaporative flux carries strongly non-equilibrated mixture of monomers and dimers: what vaporizes from the surface at 252 K is a mixture of 70% monomers and 30% dimers, while the equilibrium fraction of dimers is approximately $w_2 = 96\%$ at this temperature; in addition, the dimers are by 100-200 K hotter than the monomers [19]. Existence of trimers and tetramers has been postulated [20], and later rejected [13]; the analysis that follows seems to confirm that only dimers exist in appreciable amounts in the acid vapours. In result of these complications, the handbook data for the quantities involved in Eq (15) are not accurate enough to predict the vapour pressure with the accuracy of the available experimental data. We therefore re-determined the relevant parameters.

Acetic acid. We obtained the temperature dependence $K_2(T)$ of the dissociation constant of the dimer directly from the published p - v^G - T data [20-24], limiting ourselves to the temperature range 10...180°C since the available vapour pressure data are within a similar interval. We used Eqs (2)&(14) to fit the p - v^G - T data. The three parameters of Eq (14) were sought: K_2° , h_2° , and c_2 . The heat capacity change c_2 is not required with high precision, so we used for it the theoretical value at 25°C, $c_2 = -10.37$ J/molK, as it follows from the calculations of Chao and Zwolinski [25]. The other two parameters were determined from the regression as $K_2^\circ = 60.33$ Pa and $h_2^\circ = 64.16$ kJ/mol; the average difference between the experimental and

computed v^G values is 1.4%, similar to the discrepancy between the data sets of the different authors (cf. Figure S1 in S2). Our values can be compared to the theoretical values $K_2^\circ = 79.2$ Pa and $h_2^\circ = 63.2$ kJ/mol following from [25] (these correspond to deviation 2.3% from the experimental p - v^G - T , much higher than the one with the parameter values above), and with data for the second virial coefficient (which are not accurate enough as well, as discussed in S2).

We further compared Eq (15) to vapour pressure data from Refs. [26-30] in the range $T = 25 \dots 142^\circ\text{C}$ and $p = 2 \dots 200$ kPa, to determine the values of p° , h_{e1}° , and c_{e1} given in **Table 1** (cf. S2 for details about the procedure). The average deviation from the experiment is 0.3%; the dispersion is most significant in the low temperature range where the data from the different authors deviate from one another (Figure S2). The value of $p^\circ = 2.0706$ kPa following from our regression analysis compares well to 2.08 kPa cited by Marcus, within the precision of his number [31], and $h_{e1}^\circ = 52.380$ kJ/mol agrees with 52.1 kJ/mol from the CRC Handbook [32] – however, the 3 valid digits of the handbook values are insufficient to calculate the vapour pressure with the experimental precision. From our fitted value of $c_{e1} = -47.26$ J/molK and the heat capacity of the liquid, $c_p^L = 123.3$ J/molK [31,32], the capacity of the monomer follows, $c_{p1}^G = c_p^L + c_{e1} = 76.0$ J/molK. Chao and Zwolinski calculated c_{p1}^G varying from 63.4 to 94 J/molK in the interval 300...500 K [25]; thus, the fitted c_{e1} value evidently corresponds to an average. The temperature dependence of c_{e1} can be accounted for easily, but it is not affecting significantly the precision of the final result so we neglected it.

We further tested the parameters so-obtained by calculating the heat of evaporation h_e via Eq (8). The result at 25°C is 23.03 kJ/mol, within 0.1% from the value 23.00 kJ/mol in [31]; at 117.4°C , we calculate 24.28, comparing well with the experimental 24.38 kJ/mol of Brown [33]. The second test was to calculate the normal boiling temperature by solving the equation $p(T) = 101325$ Pa, where p is given by (15). The result is 117.89°C , compared to 117.85 - 117.9°C [31,32].

Formic acid. The p - v^G - T data from [15,21] in the temperature range $10 \dots 156^\circ\text{C}$ were used together with Eqs (2)&(14) to determine $K_2^\circ = 325.1$ Pa and $h_2^\circ = 58.53$ kJ/mol (c_2 was fixed to its theoretical value at 25°C , -4.782 J/molK [25]). The average deviation between the experimental and computed v^G is 0.7%, approaching the experimental precision (for comparison, the values of Chao and Zwolinski, $K_2^\circ = 282$ Pa and $h_2^\circ = 63.8$ kJ/mol [25], correspond to a large deviation of 2.6%). Comparison with handbook data for B_2 is given in Figure S1.

We further fitted Eq (15) to vapour pressure data from Refs. [16,17,34] falling in the range $T = -5 \dots 120^\circ\text{C}$ and $p = 1 \dots 170$ kPa, and simultaneously Eq (8) to vaporization heat data from Refs. [16,18,35]. The parameters $p^\circ = 5.692$ kPa, $h_{e1}^\circ = 45.902$ kJ/mol, and $c_{e1} = -39.3$ J/molK were thus obtained (cf. S2). The average deviation from the measurements is 0.5%, comparable to the experimental dispersion, both for p_e and h_e . A 3-parametric fit with Antoine equation has been performed for comparison, which gave $\ln(p/[\text{Pa}]) = 21.755 - 3530.6/(T/[\text{K}] - 28.85)$, and the average deviation was inferior, 0.6%. Our value of p° agrees with 5.75 kPa cited by Marcus [31], but $h_{e1}^\circ = 46.3$ kJ/mol from the CRC Handbook [32] is too high. The normal boiling temperature following from Eq (15) is 100.86°C , compared to the literature values 100.55 - 101°C [31,32].

For both formic and acetic acid, the dispersion between the model and the vaporization data is very sensitive to h_{e1}° : inaccuracy in the 4th digit (0.01%) causes significant increase of the deviation. The standard pressure is also a sensitive parameter (0.05%), and c_{e1} is the least sensitive one (1%). For both acids, the dissociation degree *increases* with T , due to the endothermicity of the process (1) (weight fraction drops from more than 90% dimers at 0°C to

$w_2 < 80\%$ above 100°C , see Figure S3-right). As the fraction of dimers decreases, the vaporization heat increases (the monomers require more energy to evaporate, Figure S3-left).

The vapours of the **fatty alcohols** also associate to a significant degree. We will use the data for methanol and ethanol as an example where $p(T)$ and $h_e(T)$ can be predicted accurately based on a few standard handbook parameters only.

Methanol. To determine K_2° and h_2° , we compared Eqs (14)&(6) to the second virial coefficient data assembled in [32,36] falling in the range $50\dots160^\circ\text{C}$; as the B_2 data are not very accurate, c_2 has been neglected (Table 1). The deviation between the B_2 data and Eqs (14)&(6) is 5%. Handbook values are used for all other parameters of the model. As observed with the acids, h_{e1}° is a very sensitive parameter; the CRC Handbook cites $h_{e1}^\circ = 38.2$ kJ/mol for it [32], while Marcus gives $h_e^\circ = 37.43$ kJ/mol [31], from which $h_{e1}^\circ = 37.67$ follows (obtained by solving Eq (8)). Using one of these values in Eq (15) yields large positive deviations, and the other yields large negative deviations from the vapour pressure data assembled in [37], of the order of 2-4%; we found similar tendency Ref. [31] to underestimate and [32] to overestimate h_{e1}° in nearly all cases considered below. Using the average of the two values ($h_{e1}^\circ = 37.94$ kJ/mol) leads to 0.5% average error in the range $15\text{-}180^\circ\text{C}$ (corresponding to $10\text{-}2700$ kPa), an impressive precision for a model of no adjustable parameters. Formula (15) works reasonably well even with serious extrapolation outside the interval $50\text{-}160^\circ\text{C}$ in which the B_2 data stand – the experimental vapour pressures for the temperature range $-98\dots-93^\circ\text{C}$ in [37] deviate by 1.5% from Eq (15), and those in the range $180\dots234^\circ\text{C}$ – by 2%. The deviation can be further decreased by tuning the parameters as done with the acids, but as 0.5% accuracy is enough for most applications, we have not done that. For comparison, we fitted the data in the range $15\dots180^\circ\text{C}$ with Antoine equation, which results in $\ln(p/\text{Pa}) = 23.437 - 3609.6/(T/[\text{K}] - 34.63)$; this leads to 0.1% error (and nearly any similar 3-parameter formula would lead to the same error). However, as with all empirical formulae, extrapolation is very inaccurate – the Antoine equation has 40% error in the temperature range $-98\dots-93^\circ\text{C}$.

Ethanol. All required parameters are taken from the same sources and dealt with in the same manner as those of methanol (cf. Table 1; B_2 data in the range $25\dots160^\circ\text{C}$ [32,36] have been utilized to determine K_2° and h_2°). Above vapour pressure of 5 atm, tetramerization can be expected, so data above 125°C were disregarded. We compared the outcome of Eq (15) with the parameters in Table 1 to vapour pressure data from Refs [38-42]; the average deviation is 0.5%. We also compared Eqs (8)&(5) to vaporization heat measurements from [38,41]; the deviation is again small, 0.6% (for comparison, there is 0.2-0.4% deviation between the two h_e -datasets of Dong and Counsell).

For the alcohols, in contrast to the acids, the dissociation degree of the saturated vapour *decreases* with the temperature ($w_2 < 5\%$ at 0°C and $w_2 > 15\%$ above 100°C , Figure S5-right). This trend is the result of the increased vapour pressure at high temperature, causing the equilibrium (1) to proceed forward in spite of the falling K_2 (compared to acids, where the second effect dominates). The increased dimer fraction results in decreased vaporization heat at high temperature (see Figure S5-left).

Our third example is the **water-steam** equilibrium. We investigate the range $p < 500$ kPa only, since trimerization becomes non-negligible above this threshold. The values of p° , h_{e1}° and c_{e1} were taken from handbook data [31,32], cf. Table 1. For the K_2 parameters, we minimized the difference between the regression formula for the second virial coefficient of water of Harvey and Lemmon [43] in the range $0\text{-}200^\circ\text{C}$ and what follows for B_2 from Eqs (6)&(14) to obtain K_2° , h_2° and c_2 given in Table 1 (cf. S4 for details). The average difference between Eq (15) with these parameters and the experimental p from Refs. [44-49] in the range $T = -2.5\dots150^\circ\text{C}$ is 0.5% (but it is comparatively high, 1-2%, above 100°C , cf. S4). The difference between Eq (8) and the vaporization heat data of Osborne et al. [50,51] is 0.2%.

The final example are three **hydrocarbons** which are of interest as components of gasoline – the results for them will be used in a subsequent paper to investigate the evaporation of a mixture of hydrocarbons and ethanol (*gasohol*). The model has relatively limited applicability to hydrocarbons due to non-negligible trimerization (e.g., [52]), and we considered only the range of vapour pressures below $p < 100\text{--}200$ kPa; the limitation is not large for practical purposes, as this range is the most relevant one with regard to applications. Details are given in S5.

Toluene. We used B_2 data in the range $75\text{--}165^\circ\text{C}$ from Refs. [32,36] to calculate K_2° and h_2° . The monomer vaporization heat is an average from [31,32], and c_{e1} is calculated from the values of c_p^L from [32] and c_p^G from [53] at 25°C . The values we found for the normal vapour pressure of toluene in the handbooks were all of accuracy too low for our aims; therefore, p° was determined as an adjustable parameter, using vapour pressure data from [52,54] (only the sources 14,16,18,19,22-26,30&33 by Goodwin were considered). The fit leads to $p^\circ = 3.805$ kPa and average deviation between the data and Eq (15) of 0.35% (compared to 1.5% with Marcus' value $p^\circ = 3.75$ kPa [31]). We also compared Eq (8) with vaporization heat data from [55]; the average deviation is again satisfactory, 0.35%.

Heptane. We use handbook data from the same sources as for the alcohols, toluene and water (B_2 data in the range $25\text{--}425^\circ\text{C}$), as described in Table 1. Substituting these in Eq (15) leads to accuracy of 0.2% compared to vapour pressure measurements from [56-59]. Eq (8) predicts vaporization heats by 0.5% different from the experimental ones from Ref. [56].

Isooctane. We found no data for B_2 of isooctane; we used data from [32] for normal octane instead to calculate K_2° and h_2° . The other parameters were taken from handbooks as described in Table 1. Substituting these in Eq (15) leads to accuracy of 0.66% compared to vapour pressure data from [57]. This is acceptable accuracy, in view of the gross approximation for B_2 .

Conclusion

Our work revisits an old, and largely forgotten, model of a non-ideal gas [11], and demonstrates the capabilities of two direct consequences of it: a model of the vapour pressure and the vaporization heat of associating compounds. With most of the liquids for which we tested it, the precision of the model is equal to the precision of the best experimental data we have 140 years later, and the simplicity of the final results is remarkable. It allows readily available handbook data to be used to predict p and h_e in a vast range of temperatures and pressures. A sample Maple code for the calculation of the vapour pressure, the vaporization heat and the dimerization degree using the full set of handbook parameters is given in S6.

The usefulness of the model and the formulas (15)&(8) will become evident as the concept is extended to **(i)** the problem for the kinetics of evaporation (with contribution from the dimer evaporation, the role of which has been under investigation in the last decades [19,60]); **(ii)** the problem for the vapour pressure of mixtures with association in the gas phase (which has been considered in some detail already [10]) – unlike the empirical models and the established detailed theories for the vapour pressure of 1-component liquids, the model considered in this work is straightforward to generalize to these more complicated cases.

Table 1: Parameters of the generalized Clausius-Clapeyron equation (15).

compound range	p° kPa	h_{e1}° kJ/mol	c_{e1} J/molK	$\ln K_2^\circ$ /[Pa]	h_2 kJ/mol	c_2 J/molK	A_1 f	E_1 kJ/mol ^f	A_2 f	E_2 kJ/mol ^f	$dev(p)$ g	$dev(h_e)$ g	h_e° kJ/mol ^h	T° °C ⁱ
HCOOH -5...120°C, 1...170 kPa	5.69 ₂₃ b	45.90 ₂ b	-39.3 ₃₉ b	5.78 ₄₂ d	58.5 ₃₃ a	-4.782 [25]	30.34 ₄	57.63 ₁	30.71 ₇	55.30 ₃	0.5%	0.6%	20.10 ₈	100. ₈₆
CH₃COOH 25...140°C, 2...200 kPa	2.070 ₆ b	52.38 ₀ b	-47.2 ₅₆ b	4.1 ₀₀ d	64. ₁₆ a	10.37 [25]	32.59 ₆	66.47 ₀	33.96 ₃	65.68 ₇	0.3%	0.3%	23.02 ₈	117. ₈₉
CH₃OH 15-170°C, 10-2000 kPa	16.9 [31]	37.9 ₄ [31,32] ^c	-37 [32]	13.8 ₉ e	16.4 ₄ e	0 (neglected)	29.47 ₄	48.97 ₀	38.43 ₁	81.50 ₃	0.5%	-	37.69 ₁	64.7 ₂
C₂H₅OH 0...125°C, 1...500 kPa ^a	7.8 ₉ [31]	42.3 ₆ [31,32] ^c	-46.7 [32]	13.5 ₀ e	19. ₂ e	0 (neglected)	31.66 ₇	56.28 ₄	42.08 ₇	93.36 ₄	0.5%	0.6%	42.15 ₉	78.3 ₉
H₂O 0...150°C, 0.5...450 kPa ^a	3.16 ₉ [32]	43.96 ₅ [31,32] ^c	-41.7 [32]	14.5 ₄ e	14.9 ₁ e	-0.88 e	30.81 ₀	56.39 ₈	39.14 ₃	93.11 ₇	0.5%	0.2%	43.93 ₅	99.9 ₄
C₆H₅CH₃ 0-135°C, 1-200 kPa ^a	3.80 ₆ b	38.0 ₇ [31,32] ^c	-50.7 [32,53]	13.6 ₂ e	12. ₆ e	0 (neglected)	29.69 ₄	53.18 ₄	40.68 ₅	93.77 ₉	0.35%	0.35%	38.01 ₆	110. ₆₇
n-C₇H₁₆ 25-100°C, 6-100 kPa ^a	6.1 ₀ [31]	36.6 ₄ [31,32] ^c	-55.4 [32,53]	13.5 ₁ e	13. ₂ e	0 (neglected)	30.15 ₄	53.16 ₄	41.47 ₄	93.13 ₀	0.2%	0.5%	36.53 ₇	100. ₂₆
i-C₈H₁₈ 25-100°C, 6-100 kPa ^a	6.5 ₀ [31]	35.2 ₆ [31,32] ^c	-48.2 [31,53]	13.1 ₃ e	13. ₉₅ e	0 (neglected)	28.78 ₆	49.62 ₇	38.81 ₈	85.30 ₃	0.66%	-	35.08 ₈	99.1 ₁

^a Tri- and tetramerization is significant at higher pressures. ^b Determined by comparing Eqs (8)&(15) to experimental data for vapour pressure and vaporization heat (formic acid [16,17,18,34,35], acetic acid [26-30], toluene [52,54]; cf. S2&S5 for details). ^c An average value of those from Ref [31,32]; Ref. [31] cites only the value of h_e° – Eq (8) is used to calculate the respective h_{e1}° . ^d Determined from the comparison between the equation of state (2) and p - v^G - T data from Refs. [15,21] (formic acid) and [20-24] (acetic acid). ^e Obtained by comparison of Eq (14) with handbook [32,36] data for B_2 (c_2 is neglected), except for water where Ref. [43] was used. No data for isooctane was found, and B_2 data for normal octane was used instead. ^f From Eqs (16)&(13). ^g Average deviation of Eqs (8)&(15) from the experimental data in the considered T range (cf. the text for the data sources). ^h Vaporization heat at 25°C calculated via Eq (8). ⁱ Normal boiling temperature, obtained as solution to $p(T) = 101325$ Pa, with p given by Eq (15).

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References

The publication contains supplementary materials: S1. List of symbols. **S2.** Carboxylic acids. **S3.** Alcohols. **S4.** Water. **S5.** Hydrocarbons. **S6.** Sample Maple code for the calculation of p , w_2 and h_e .

1. R.C. Reid, J.M. Prausnitz, T.K. Sherwood. The properties of gases and liquids, 3rd ed. McGraw-Hill (1977), chap. 6.
2. J.E. Haggemacher, *J. Am. Chem. Soc.* **68** (1946) 1633.
3. A.A. Frost, D.R. Kalkwarf, *J. Chem. Phys.* **21** (1953) 264.
4. J.M.K. Dake, *Water Resour. Res.* **8** (1972) 1087.
5. A. Wexler, *J. Res. Natl. Bur. Stand.* **80A** (1976) 775.
6. B. Henderson-Sellers, *Q. J. R. Meteorol. Soc.* **110** (1984) 1186.
7. C. Antoine, *Compte Rend.* **107** (1888) 681 & 836.
8. V.K. Filippov, I.M. Balashova, *Theor. Exp. Chem.* **5** (1969) 546.
9. J. Marek, *Collect. Czech. Chem. Commun.* **20** (1955) 1490.
10. A. Tamir, C. Dragoescu, A. Apelblat, J. Wisniak, *Fluid Phase Equilib.* **10** (1983) 9.
11. J.W. Gibbs, *Trans. Conn. Acad.* **III** (1875-1876) 108-248 & (1877-1878) 343-524. Reprinted in: The scientific papers of J. Willard Gibbs, vol. 1. Longmans Green (1906), p. 176 & 389.
12. I. Prigogine, R. Defay. Chemical thermodynamics. Longmans Green (1954), sec. 11, eq. 11.59.
13. J.B. Togeas, *J. Phys. Chem. A* **109** (2005) 5438.
14. D.M. Mathews, R.W. Sheets, *J. Chem. Soc. A* (1969) 2203.
15. A.S. Coolidge, *J. Am. Chem. Soc.* **50** (1928) 2166.
16. A.S. Coolidge, *J. Am. Chem. Soc.* **52** (1930) 1874.
17. D. Ambrose, N.B. Ghiassee, *J. Chem. Thermodyn.* **19** (1987) 505.
18. J.W. Stout, L.H. Fisher, *J. Chem. Phys.* **9** (1941) 163.
19. M. Faubel, T. Kisters, *Nature* **339** (1989) 527.
20. E.W. Johnson, L.K. Nash, *J. Am. Chem. Soc.* **72** (1950) 547.
21. J.R. Barton, C.C. Hsu, *J. Chem. Eng. Data* **14** (1969) 184.
22. H.L. Ritter, J.H. Simons, *J. Am. Chem. Soc.* **67** (1945) 757.
23. M.D. Taylor, *J. Am. Chem. Soc.* **73** (1951) 315.
24. J.W. Gibbs, *Amer. J. Science* **18** (1879). Reprinted in: The Scientific Papers of J. Willard Gibbs, vol. 1. Longmans Green (1906), p. 389, table IV.
25. J. Chao, B.J. Zwolinski, *J. Phys. Chem. Ref. Data* **7** (1978) 363.
26. F.H. MacDougall, *J. Am. Chem. Soc.* **58** (1936) 2585.
27. A.E. Potter, H.L. Ritter, *J. Phys. Chem.* **58** (1954) 1040.
28. R.A. McDonald, S.A. Shrader, D.R. Stull, *J. Chem. Eng. Data* **4** (1959) 311.
29. D. Ambrose, J.H. Ellender, C.H.S. Sprake, R. Townsend, *J. Chem. Thermodyn.* **9** (1977) 735.
30. L.A.L. Muñoz, M.A. Krähenbühl, *J. Chem. Eng. Data* **46** (2001) 120.

31. Y. Marcus. The properties of solvents. John Wiley & Sons (1998), p. 79-81.
32. CRC Handbook of chemistry and physics, 98th ed. Editor-in-chief: J.R. Rumble.
33. J.C. Brown, *J. Chem. Soc., Trans.* **83** (1903) 987.
34. M.D. Taylor, J. Bruton, *J. Am. Chem. Soc.* **74** (1952) 4151.
35. J Konicek, I Wadsö, *Acta Chem. Scand.* **24** (1970) 2612.
36. V.B. Kogan, V.M. Fridman, V.V. Kafarov. Equilibrium between liquids and vapours, vol. 1. Nauka (1966), p. 70. See also V.P. Belousov, A.G. Morachevskiy, in: Chemistry and thermodynamics of solutions, LGU (1964), p. 119.
37. R.D. Goodwin, *J. Phys. Chem. Ref. Data* **16** (1987) 799.
38. J.F. Counsell, J.O. Fenwick, E.B. Lees, *J. Chem. Thermodyn.* **2** (1970) 367.
39. D. Ambrose, C.H.S. Sprake, *J. Chem. Thermodyn.* **2** (1970) 631.
40. D. Ambrose, C.H.S. Sprake, R. Townsend, *J. Chem. Thermodyn.* **7** (1975) 185.
41. J.-Q. Dong, R.-S. Lin, W.-H. Yen, *Can. J. Chem.* **66** (1988) 783.
42. J. Ortega, P. Susial, C. de Alfonso, *J. Chem. Eng. Data* **35** (1990) 216.
43. A.H. Harvey, E.W. Lemmon, *J. Phys. Chem. Ref. Data* **33** (2004) 369.
44. N.S. Osborne, H.F. Stimson, E.F. Fiock, D.C. Ginnings, *J. Res. Natl. Bur. Stand.* **10** (1933) 155.
45. D.R. Douslin, A. Osborn, *J. Sci. Instrum.* **42** (1965) 369.
46. H.F. Stimson, *J. Res. Natl. Bur. Stand.* **73** (1969) 493.
47. L.M. Besley, G.A. Bottomley, *J. Chem. Thermodyn.* **5** (1973) 397.
48. L.A. Guildner, D.P. Johnson, F.E. Jones, *Science* **191** (1976) 1261.
49. G.S. Kell, G.E. McLaurin, E. Whalley, *Phil. Trans. R. Soc. Lond. A* **315** (1985) 235.
50. N.S. Osborne, H.F. Stimson, D.C. Ginnings, *J. Res. Natl. Bur. Stand.* **18** (1937) 389.
51. N.S. Osborne, H.F. Stimson, D.C. Ginnings, *J. Res. Natl. Bur. Stand.* **23** (1939) 197.
52. R.D. Chirico, W.V. Steele, *Ind. Eng. Chem. Res.* **33** (1994) 157.
53. C.L. Yaws. Handbook of thermodynamic diagrams. Gulf (1996).
54. R.D. Goodwin, *J. Phys. Chem. Ref. Data* **18** (1989) 1565.
55. G. Natarajan, D.S. Viswanath, *J. Chem. Eng. Data* **30** (1985) 137.
56. G. Waddington, S.S. Todd, H.M. Huffman, *J. Am. Chem. Soc.* **69** (1947) 22.
57. C.B. Willingham, W.J. Taylor, J.M. Pignocco, F.D. Rossini, *J. Res. Natl. Bur. Stand.* **35** (1945) 219.
58. A.F. Forziati, W.R. Norris, F.D. Rossini, *J. Res. Natl. Bur. Stand.* **43** (1949) 555.
59. M.-A. Michou-Saucet, J. Jose, C. Michou-Saucet, J.C. Merlin, *Thermochim. Acta* **75** (1984) 85.
60. I. Napari, H. Vehkamäki, *J. Chem. Phys.* **121** (2004) 819.

Vapour pressure and vaporization heat of molecules able to dimerize

Supplementary information

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S1. List of symbols

B_2	second virial coefficient
$c_2 = 2c_{p1}^G - c_{p2}^G$	change of the heat capacity per mole yield of the reaction (1)
$c_{e1} = c_{p1}^G - c_p^L$	change of the heat capacity upon evaporation of a mole of the monomer
$c_{e2} = c_{p2}^G - c_p^L$	change of c_p upon evaporation of a mole of the dimer
c_{p1}^G and c_{p2}^G	partial molar heat capacities of the monomer and the dimer in the gas phase
c_p^L	molar heat capacity of the liquid
f	fugacity, Eq (4)
h_2	heat of dimer dissociation
h_2°	h_2 at T°
h_e	heat of evaporation (for non-ideal gas)
h_e°	h_e at T°
h_{e1}	heat of evaporation of monomers (h_e at $p \rightarrow 0$)
h_{e1}°	h_{e1} at T°
K_2	dissociation constant of A_2 in the gas phase, Eq (1)
K_2°	value of K_2 at T°
p	pressure, or saturated vapour pressure
p°	standard vapour pressure at T°
p_1 and p_2	partial pressures of the monomers and the dimers
R	universal gas constant
T	temperature
T°	standard temperature (25°C in this work)
v^G	molar volume of the gas, Eq (2)
v^L	molar volume of the liquid
y	pressure ratio p_2/p_1 , Eq (4)
y°	value of y at standard pressure and temperature, Eq (13)
w_1 and w_2	mass fraction of the monomers and the dimers in the gas

S2. Carboxylic acids

The values of K_2° and h_2° for the acetic acid were obtained by optimization of the merit function

$$dev^2(K_2^\circ, h_2^\circ) = \frac{1}{N-2} \sum_i \left(1 - \frac{v_i^G}{v_{th}^G(p_i, T_i; K_2^\circ, h_2^\circ)} \right)^2; \quad (17)$$

here, v_{th}^G is the theoretical molar volume of the gas as given by Eq (2); p_i , v_i^G and T_i are the experimental values from the i -th measurement; N is the number of data points (taken from Refs. [20-24] in the range 10...180°C). The theoretical value $c_2 = -10.37$ J/molK [25] has been used for Eq (2).

The values of K_2° and h_2° obtained from the optimization of (17) (cf, Table 1) determine the function $K_2(T)$ through Eq (14). It is illustrated in Figure S1-right (line), and compared to K_2 values calculated directly from each experimental point $\{p_i, v_i^G, T_i\}$ as

$$K_2 = \frac{4p}{\left(\frac{2pv^G}{RT} - 1 \right)^{-2} - 1}, \quad (18)$$

which follows from Eq (2) (blue dots in Figure S1). The dispersion of the dots around the line is a measure of the accuracy of the equation of state (2) and the formula (14) for $K_2(T)$: in the range 30-150°C, its precision is excellent; the systematic deviation below 30°C shows that the assumption for constant c_2 is failing at low temperature; on the other hand, the high dispersion above 150°C is due to a combination of inaccuracy of Eq (2) and little sensitivity of the experimental data to K_2 at high temperature and low pressures (where the behaviour of the gas is close to ideal).

Figure S1 shows also K_2 values calculated from the B_2 data assembled in Ref. [36] through Eq (6) (red asterisks). As seen, the B_2 data lead to relatively large error, the reason being that, for acetic acid vapours, the equation of state (2) is more accurate than the virial expansion used to determine the B_2 values in Ref. [36].

The results for formic acid in Figure S1 are obtained in the same manner.

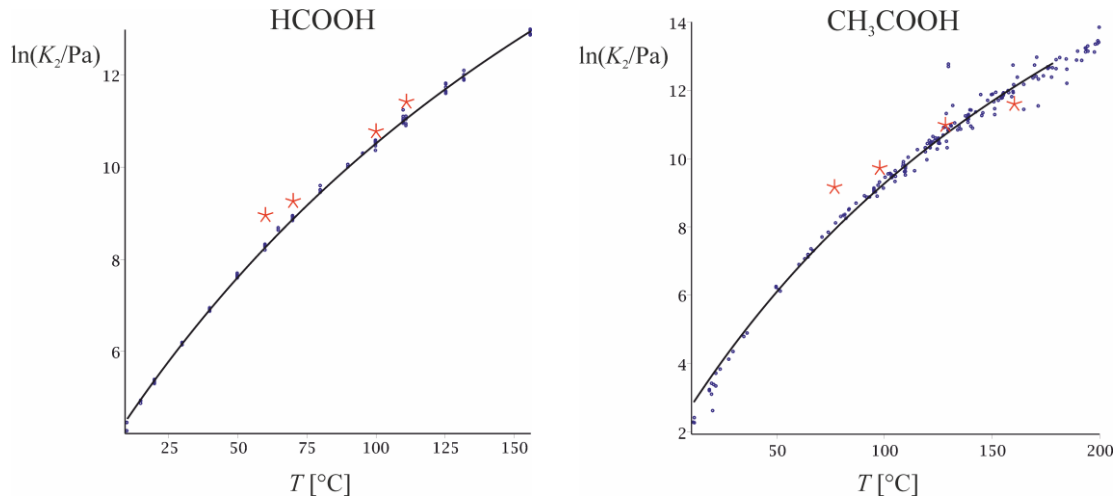


Figure S1. Dissociation constants of formic (left) and acetic (right) acid as functions of the temperature. Lines: Eq (14) with the parameters from Table 1. Blue dots: K_2 calculated directly from the p - v^G - T data from Refs. [15,20-24] through Eq (18). Red asterisks: K_2 computed from B_2 data from Ref. [36] through Eq (6).

The other three parameters of the model (p° , h_{e1}° and c_{e1}) have been obtained by comparing the theoretical expressions Eqs (15)&(8) (indicated with subscript “th”) to experimental data for the vapour pressure (p_i) and for the vaporization heat ($h_{e,j}$), via the optimization of the merit function

$$dev^2(p^\circ, h_{e1}^\circ, c_{e1}) = \frac{1}{N-3} \left[\sum_i \left(1 - \frac{p_{th}(T_i; p^\circ, h_{e1}^\circ, c_{e1})}{p_i} \right)^2 + \sum_j \left(1 - \frac{h_e(T_j; p^\circ, h_{e1}^\circ, c_{e1})}{h_{e,j}} \right)^2 \right]. \quad (19)$$

In the case of formic acid, the data for the vapour pressure and the vaporization heat were optimized together, by minimizing dev^2 from Eq (19). For the acetic acid, only the vapour pressure data have been optimized (dev^2 without the second sum in the square brackets). The results are illustrated and compared to the data in Figure S2 (vapour pressure) and Figure S3 (vaporization heat and weight fraction of the dimer).

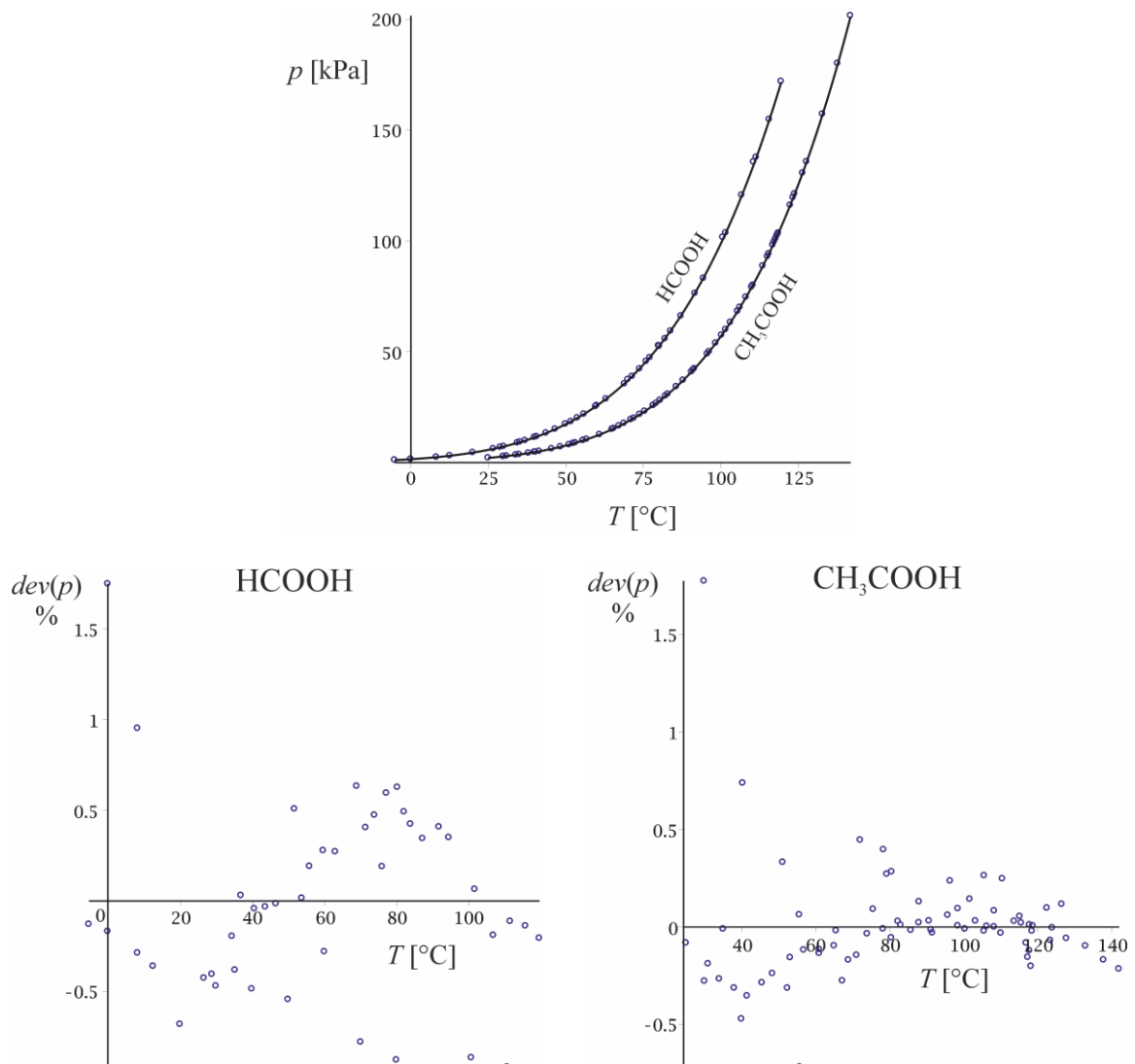


Figure S2. Up: vapour pressure of HCOOH and CH₃COOH vs. temperature. Lines: Eq (15) with the parameters from Table 1. Dots: experimental data from Refs. [16,17,26-30,34].
Down: % deviation between theory and experimental points.

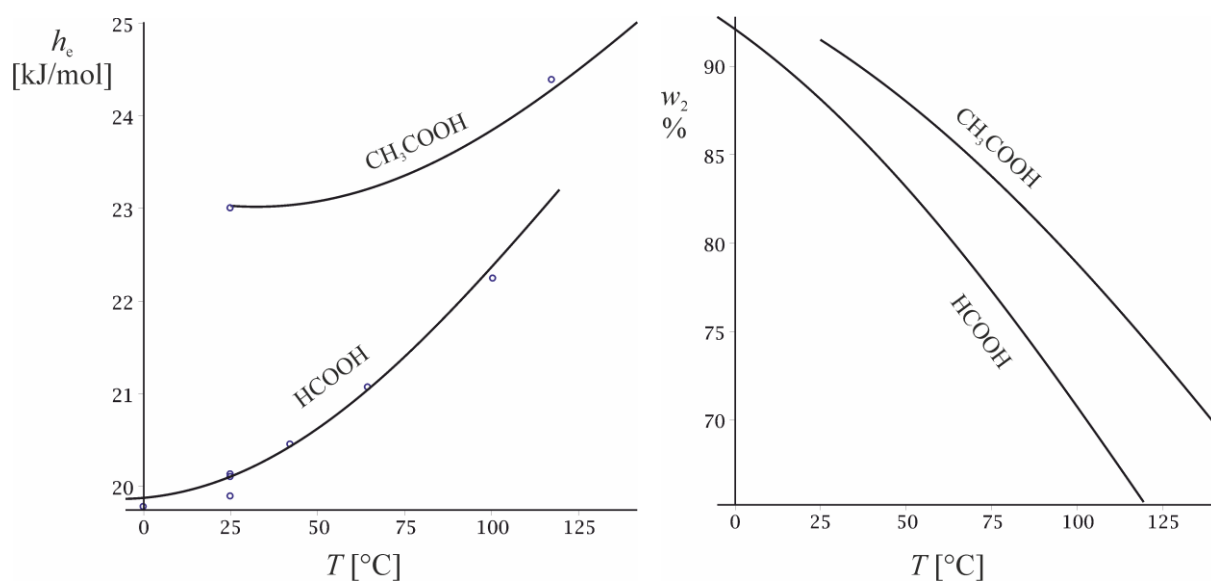


Figure S3. Heat of evaporation (left, Eq (8)) and weight fraction of carboxylic acid dimers in the saturated vapours (right, Eq (5)) as a function of the temperature. Data are from Refs. [16,18,31,33,35].

S3. Alcohols

In this case, all parameters were taken from handbook data as described in Table 1. The results are illustrated in Figure S4 & Figure S5.

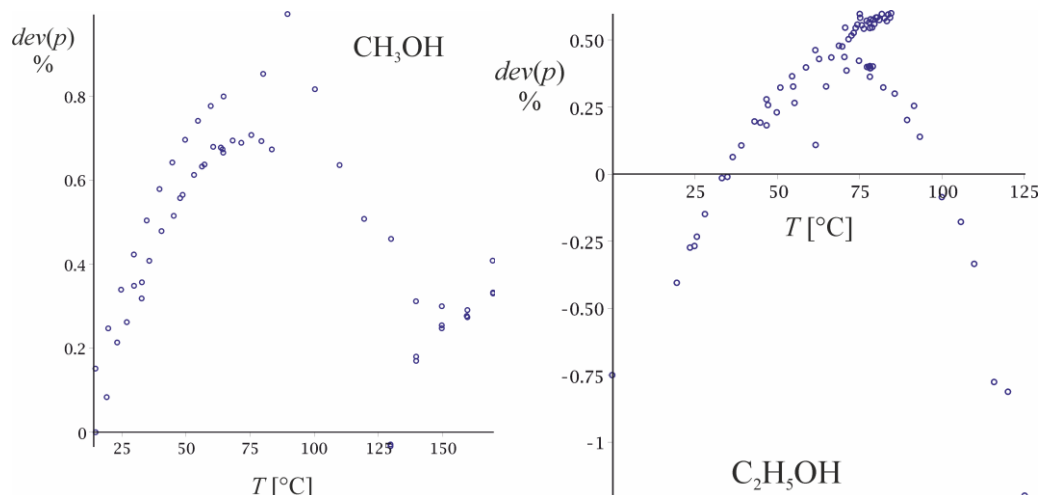


Figure S4. Vapour pressure of CH_3OH and $\text{C}_2\text{H}_5\text{OH}$ vs. temperature: deviation of Eq (15) with the parameters in Table 1 from the experimental data from Refs. [32,36,38-42].

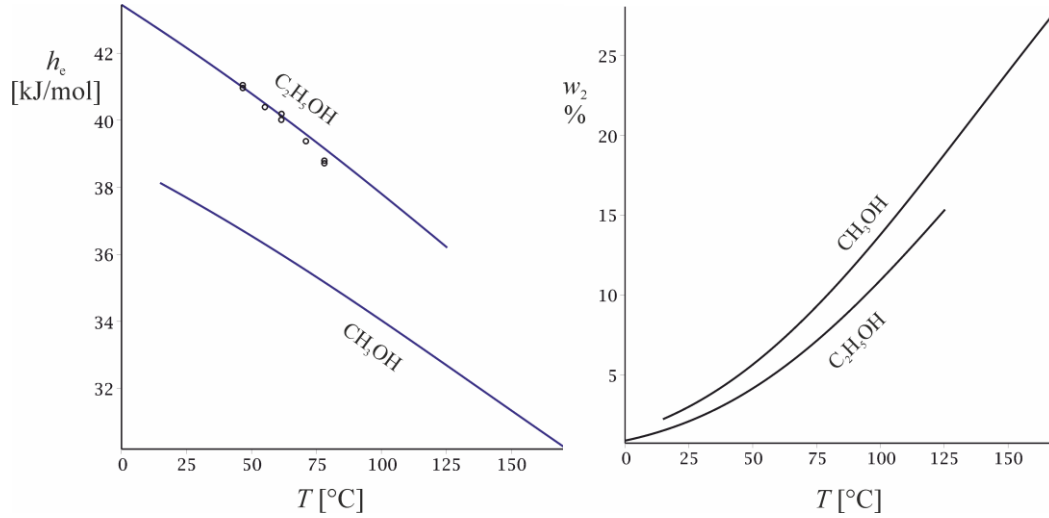


Figure S5. Heat of evaporation (left, Eq (8)) and weight fraction of alcohol dimers in the saturated vapours (right, Eq (5)) as function of the temperature. Data are from Refs. [38,41].

S4. Water

For water, we calculated the dimerization parameters from the second virial coefficient data assembled by Harvey and Lemmon [43]. To obtain the values of K_2° , h_2° , and c_2 in Table 1, we minimized the merit function

$$dev(K_2^\circ, h_2^\circ, c_2) = \frac{1}{200 \text{ K}} \int_{273 \text{ K}}^{473 \text{ K}} \left| B_2(T) + \frac{RT}{K_{2,\text{th}}(T; K_2^\circ, h_2^\circ, c_2)} \right| dT, \quad (20)$$

where $B_2(T)$ is the regression equation of Harvey and Lemmon [43] and $K_{2,\text{th}}$ is Kirchoff's model (14) for the dissociation constant; $-RT/K_{2,\text{th}}$ is the theoretical B_2 , cf. Eq (6). The difference between the two formulae with the parameters in Table 1 is 1-2% above 150°C and less than 0.5% between 0 and 150°C. The other parameters were handbook data, as explained in Table 1. The comparison of the model with vapour pressure and vaporization heat data is given in Figure S6 & Figure S7.

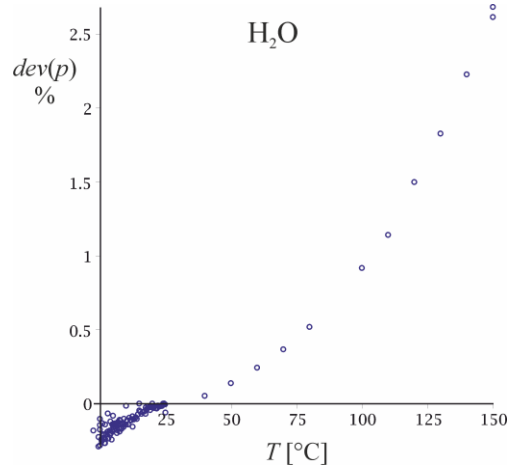


Figure S6. Vapour pressure of water vs. temperature: deviation of Eq (15) with the parameters from Table 1 from the experimental data from Refs. [44-49]. At high temperatures, the formula is inaccurate because of trimerization.

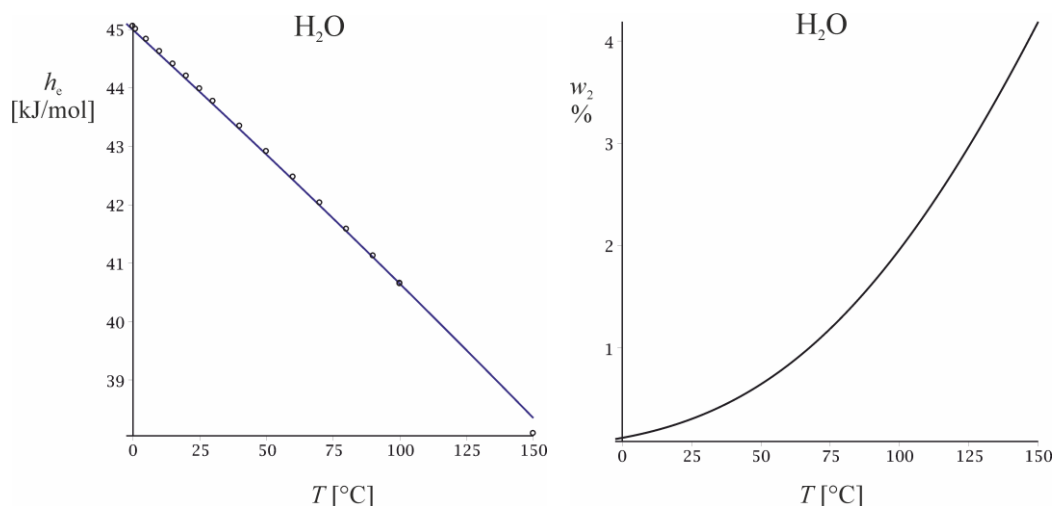


Figure S7. Heat of evaporation (left, Eq (8)) and weight fraction of dimers in the saturated steam (right, Eq (5)) as functions of the temperature. Data are from Refs. [50,51].

S5. Hydrocarbons

The data for hydrocarbons were dealt similarly to those for alcohols. The only exception was toluene: the handbook value of the room temperature vapour pressure p° was found rather inaccurate, and we used the experimental vapour pressure from Refs. [52,54] and a merit function of the type (19) (but with fixed h_{e1}° and c_{e1}) to determine it. All results are illustrated in Figure S8 & Figure S9.

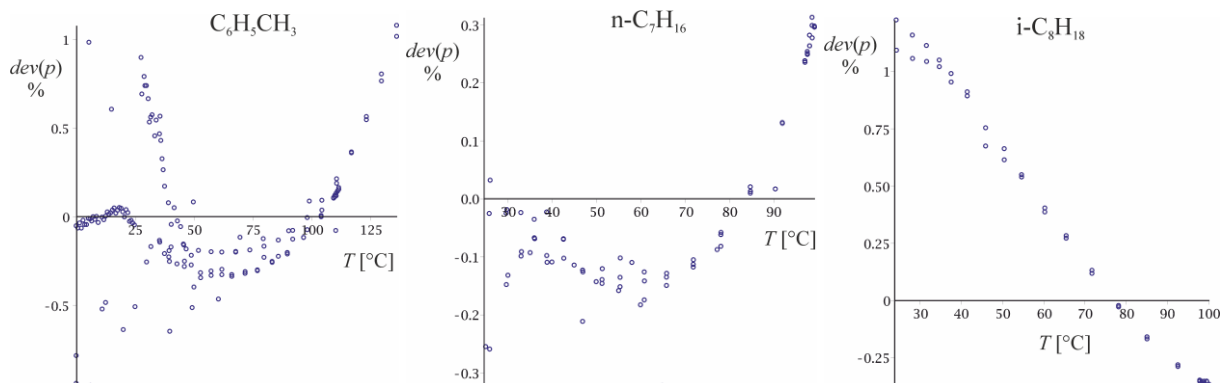


Figure S8. Vapour pressure of toluene, heptane and isoctane vs. temperature: deviation of Eq (15) with the parameters from Table 1 from the experimental data from Refs. [32,36,38-42].

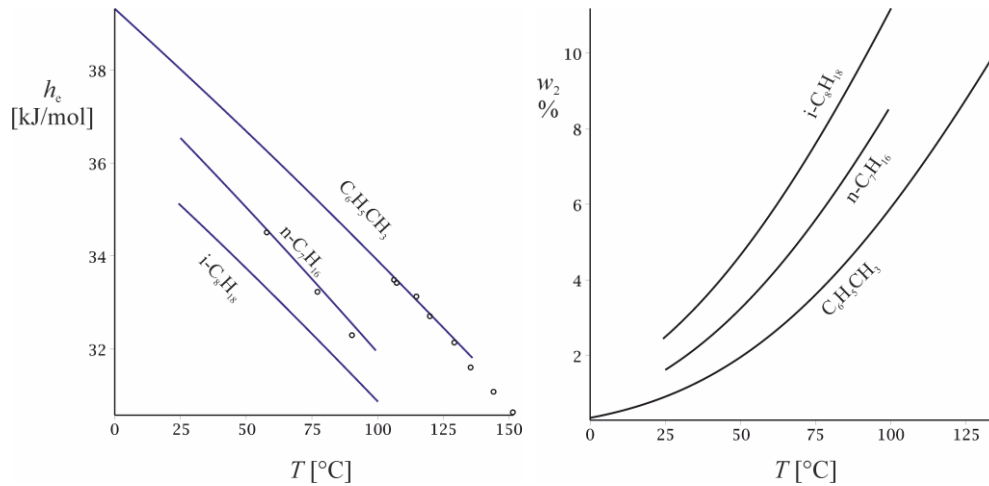


Figure S9. Heat of evaporation (left, Eq (8)) and weight fraction of dimers in the saturated vapours (right, Eq (5)) of toluene, heptane and isooctane as function of the temperature. Data are from Refs. [55,56].

S6. Sample Maple code for calculation of p , w_2 and h_e

The following code for the computations of the vaporization characteristics can be pasted in a Maple worksheet:

```

restart;
#1. Formulae. Hess's equation (8) for the vaporization heat he
he:= he1-w2*h2/2;
#Weight fraction of the dimers, Eq (5)
w2:= 1-1/sqrt(1+4*p/K2);
#The linear approximations for h2(T) and he1(T)
h2:= h20+c2*(T-T0); he1:= he10+ce1*(T-T0);
#The vapour pressure (15)
p:=(T/T0)^(ce1/R)*exp(A1-E1/R/T)+(T/T0)^(ce2/R)*exp(A2-E2/R/T);
#with parameters from Eqs (16)
A1:=ln(K20*y0)+E1/R/T0;
A2:=ln(K20*y0^2)+E2/R/T0;
E1:=he10-ce1*T0;
E2:= 2*E1-h20+c2*T0;
ce2:= 2*ce1-c2;
y0:=1/2*(sqrt(1+4*p0/K20)-1);
#Kirchhoff's equation (14) for K2
K2:= K20*(T/T0)^(c2/R)*exp(-(h20-T0*c2)*(1/T-1/T0)/R);
#2. Values of the parameters
R:= 8.314472; #J/molK
T0:= 298.15; #standard temperature, K
#standard thermodynamic parameters for water (Table 1)
p0:= 3.169e3; #room temperature vapour pressure, Pa
he10:= 43.965e3; #room temperature heat of evaporation of the monomers, J/mol
ce1:= -41.7; #change of cp upon evaporation of monomers, J/molK
K20:= exp(14.54); #dissociation constants of the dimers, Pa
h20:= 14.91e3; #dissociation heat, J/mol
c2:= -0.88; #heat capacity change upon dissociation, J/molK
#3. Computations. Calculation of the boiling temperature:
eqT_boil:= p=101325;
T_boil:= fsolve(eqT_boil,T);
#graphs of p, he & w2 as functions of T
plot(p/1e3,T=273..423,'p'); #in kPa
plot(he/1e3,T=273..423,'he'); #in kJ/mol
plot(w2*100,T=273..423,'w2'); #in %

```