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Vapour pressure and vaporization heat of molecules that associate in the gas phase

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Abstract

A model of the temperature dependence of the vapour pressure and the heat of vaporization of associated liquids whose vapours contain associates is presented for two cases: dimers and linear associates in the gas phase. The results are analytic generalizations of the Clausius-Clapeyron equation, valid with accuracy of 0.1-1%, as demonstrated with 11 liquids: formic and acetic acids, methanol, ethanol, *n*-propanol, *n*-butanol, water, benzene, toluene, heptane, and isooctane. The model involves only readily available handbook parameters: the room-temperature vaporization heat, vapour pressure, heat capacities, 2nd virial coefficient, and heat of dissociation of the dimers in the gas phase.

Keywords: vapour pressure, Clausius-Clapeyron equation, dimerization, hydrogen bond, carboxylic acid, virial coefficient

Introduction

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 $\Delta_v H$ and the normal boiling temperature, already allows the prediction of p with decent accuracy through the Clausius-Clapeyron equation, at least far from the critical point. Better accuracy can be achieved[1–6] by accounting for the fugacity coefficient of the gas and the detailed temperature dependence of $\Delta_v H$, but 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[7,8] and many others[1] that involve parameters with 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 for extrapolation outside this range.

In this work, we evaluate two models of the vapour pressure of a class of single-component systems – liquids with a significant level of associate formation in the gas phase. Common substances such as carboxylic acids and NO_2 have a significant degree of dimerization in the vapour phase; short-chained fatty alcohols form linear associates, and within a wide vapour pressure interval, the same approximation can be used for the vapours of water, amines, a variety of hydrocarbons, mercury, and many more. The models presented here combine accuracy with simplicity, and involve only standard thermodynamic quantities that can be found in many handbooks. They allow also the accurate prediction of the vaporization heat.

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:

$$A_2 \xrightleftharpoons{K_d} 2A\,; \qquad K_d = p_1^2 / p_2\,, \tag{1}$$

where p_1 and p_2 are partial pressures of the monomer and the dimer, and K_d is the dissociation constant (cf. S8 for a list of symbols). ***The equation of state*** of such a gas is obtained[9] by solving the mass balance $1/V_m^g = p_1/RT + 2p_2/RT$, Dalton's law $p = p_1 + p_2$, and the equilibrium condition (1) for p_1, p_2, and V_m^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_m^g reads

$$V_m^g = \frac{RT}{2p}\left[1 + \left(1 + 4p/K_d\right)^{-1/2}\right]. \tag{2}$$

This constitutive relation has been derived many times in various forms[9–11], but is due to Gibbs[12]. In the limit of weakly dimerized gas ($p << K_d$), it simplifies to the virial expansion:

$$V_m^g \xrightarrow{p \to 0} \frac{RT}{p} - \frac{RT}{K_d} \ldots \tag{3}$$

In general, a description of imperfect gases based on molecular associates or clusters (such as ours) is fully equivalent to the virial expansion[13], and a rigorous definition of *associate* can be given based on this equivalency (some useful theoretical results are summarized in S1). In the other limit of completely dimerized gas ($p >> K_\mathrm{d}$), Eq (2) yields $V_\mathrm{m}^\mathrm{g} = RT/2p$, reflecting that in such a gas the molar volume V_m2^g per dimer is twice that per molecule ($V_\mathrm{m2}^\mathrm{g} = 2V_\mathrm{m}^\mathrm{g}$). The fugacity f of the vapour follows[14,15] from the integration of the fundamental equation $RT(\partial \ln f / \partial p)_T = V_\mathrm{m}^\mathrm{g}$,

$$f = p \exp \int_0^p \left(\frac{V_\mathrm{m}^\mathrm{g}}{RT} - \frac{1}{p} \right) \mathrm{d}p = K_\mathrm{d} y \,, \quad \text{where} \quad y = \frac{1}{2}\left(\sqrt{1 + 4p/K_\mathrm{d}} - 1 \right). \tag{4}$$

The physical meaning of y is molar/pressure ratio between dimers and monomers, $y \equiv p_2/p_1$. The relation $f = p_1$ holds, as required by the general theory of associated solutions[14,15]. The weight fractions w_1 of molecules in monomers and w_2 in dimers are given by

$$w_1 = 1/(1+2y) = (1 + 4p/K_\mathrm{d})^{-1/2}\,; \quad w_2 = 1 - w_1 \,. \tag{5}$$

Using these, one can write Eq (2) in the more transparent form $V_\mathrm{m}^\mathrm{g} = w_1 RT/p + w_2 RT/2p$.

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

$$K_\mathrm{d} = -RT/B \,. \tag{6}$$

This relation can be derived alternatively by introducing an appropriate definition of "dimer", cf. S1. The van 't Hoff equation can be utilized to relate $K_\mathrm{d}(T)$ to the dissociation heat $\Delta_\mathrm{d}H$:

$$\frac{\mathrm{d} \ln K_\mathrm{d}(T)}{\mathrm{d}T} = \frac{\Delta_\mathrm{d}H(T)}{RT^2}\,, \quad K_\mathrm{d}(T) = K_\mathrm{d}^\ominus \exp \int_{T^\ominus}^{T} \frac{\Delta_\mathrm{d}H(T)}{RT^2} \mathrm{d}T \,; \tag{7}$$

here, $T^\ominus$ is 25 °C, and $K_\mathrm{d}^\ominus$ is the dissociation constant at $T^\ominus$.

The vaporization heat $\Delta_\mathrm{v}H$ ***for dimerizing vapours*** depends on the degree of dissociation of the vapour, as it follows from the Gibbs-Helmholtz equation:

$$\Delta_\mathrm{v}H = -T^2 \frac{\partial}{\partial T} \frac{\mu^\mathrm{g} - \mu^\mathrm{l}}{T} = \Delta_\mathrm{v}H_1 - \frac{RT^2}{f}\frac{\partial f}{\partial T} = \Delta_\mathrm{v}H_1 - w_2 \frac{\Delta_\mathrm{d}H}{2}\,; \tag{8}$$

here, μ^g and μ^l are the chemical potentials of the gas and the liquid, and $\mu^\mathrm{g} = \mu^\ominus + RT\ln f$; w_2 is the weight fraction from Eq (5) (which leads to a dependence of $\Delta_\mathrm{v}H$ on the pressure); $\Delta_\mathrm{v}H_1$ is the heat of evaporation of the monomer, and $\Delta_\mathrm{v}H_1$ and $\mu^\ominus - \mu^\mathrm{l}$ 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_d. The result (8) reflects Hess's law: the evaporation heat $\Delta_\mathrm{v}H$ is the sum of the heats $\Delta_\mathrm{v}H_1$ for evaporating monomers and $-w_2\Delta_\mathrm{d}H/2$ released from the dimerization of a fraction w_2 of them[11].

The vapour pressure p for dimerizing vapours is the solution to Clapeyron's equation,

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta_\mathrm{v}H}{TV_\mathrm{m}^\mathrm{g}\left(1 - V_\mathrm{m}^\mathrm{l}/V_\mathrm{m}^\mathrm{g}\right)}\,, \tag{9}$$

where V_m^l is the molar volume of the liquid. For the liquids considered below, $V_\mathrm{m}^\mathrm{l}/V_\mathrm{m}^\mathrm{g}$ can be neglected. For example, for acetic acid at 140 °C, $V_\mathrm{m}^\mathrm{l}/V_\mathrm{m}^\mathrm{g} = 0.5\%$ so setting $1 - V_\mathrm{m}^\mathrm{l}/V_\mathrm{m}^\mathrm{g}$ 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) and (5) in (9), V_m^l being neglected, and using the relations (7) and $p = K_\mathrm{d}y(1+y)$ following from (4), one obtains the following form of the Clausius-Clapeyron equation valid for dimerizing vapours:

$$\frac{\mathrm{d}\ln y}{\mathrm{d}T} = \frac{\Delta_\mathrm{v}H_1 - \Delta_\mathrm{d}H}{RT^2}\,, \tag{10}$$

which integrates to

$$\ln\frac{y}{y^{\ominus}} = \int_{T^{\ominus}}^{T} \frac{\Delta_{\mathrm{v}} H_1 - \Delta_{\mathrm{d}} H}{RT^2}\,\mathrm{d}T\,. \tag{11}$$

Here, $y^{\ominus}$ stands for

$$y^{\ominus} = \frac{1}{2}\left(\sqrt{1+4p^{\ominus}/K_{\mathrm{d}}^{\ominus}} - 1\right), \tag{12}$$

where $p^{\ominus}$ is the vapour pressure at 25 °C. We assume that the linear dependence $\Delta_{\mathrm{v}}H_1 = \Delta_{\mathrm{v}}H^{\ominus} + \Delta_{\mathrm{v}}C_1(T - T^{\ominus})$ holds for the heat of evaporation of monomers, with $\Delta_{\mathrm{v}}H^{\ominus} \equiv \Delta_{\mathrm{v}}H_1(T^{\ominus})$ being the enthalpy change for the vaporization process under standard conditions; $\Delta_{\mathrm{v}}C_1 = C_1^{\mathrm{g}} - C_{\mathrm{m}}^{\mathrm{l}}$, where C_1^{g} is the partial molar heat capacity of the monomer at constant pressure and $C_{\mathrm{m}}^{\mathrm{l}}$ is the molar capacity of the liquid (the dependence of the enthalpy of the liquid on pressure is neglected, an approximation that holds within an error of $\mathrm{O}(V_{\mathrm{m}}^{\mathrm{l}}/V_{\mathrm{m}}^{\mathrm{g}})$ in the result for p). Similarly, we use $\Delta_{\mathrm{d}}H = \Delta_{\mathrm{d}}H^{\ominus} + \Delta_{\mathrm{d}}C(T - T^{\ominus})$ for the enthalpy of dimer dissociation, Eq (1), where $\Delta_{\mathrm{d}}H^{\ominus} \equiv \Delta_{\mathrm{d}}H(T^{\ominus})$; $\Delta_{\mathrm{d}}C = 2C_1^{\mathrm{g}} - C_2^{\mathrm{g}}$ is the change of constant-pressure heat capacity upon dimerization, with C_2^{g} denoting the partial molar heat capacity of the dimer. Using these assumptions, one obtains from (11) the explicit formula

$$y = y^{\ominus}\left(\frac{T}{T^{\ominus}}\right)^{\frac{\Delta_{\mathrm{v}}C_1 - \Delta_{\mathrm{d}}C}{R}} \exp\left[-\frac{\Delta_{\mathrm{v}}H_1^{\ominus} - \Delta_{\mathrm{d}}H^{\ominus} - T^{\ominus}\left(\Delta_{\mathrm{v}}C_1 - \Delta_{\mathrm{d}}C\right)}{R}\left(\frac{1}{T} - \frac{1}{T^{\ominus}}\right)\right]. \tag{13}$$

The temperature dependence of the dissociation constant K_{d} that corresponds to the linear $\Delta_{\mathrm{d}}H(T)$ follows from Eq (7):

$$K_{\mathrm{d}}(T) = K_{\mathrm{d}}^{\ominus}\left(\frac{T}{T^{\ominus}}\right)^{\Delta_{\mathrm{d}}C/R} \exp\left[-\frac{\Delta_{\mathrm{d}}H^{\ominus} - T^{\ominus}\Delta_{\mathrm{d}}C}{R}\left(\frac{1}{T} - \frac{1}{T^{\ominus}}\right)\right]; \tag{14}$$

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

$$\frac{p}{[p]} = \left(\frac{T}{T^{\ominus}}\right)^{\Delta_{\mathrm{v}}C_1/R} \mathrm{e}^{A_1 - E_1/RT} + \left(\frac{T}{T^{\ominus}}\right)^{\Delta_{\mathrm{v}}C_2/R} \mathrm{e}^{A_2 - E_2/RT}\,, \tag{15}$$

where $\Delta_{\mathrm{v}}C_2 \equiv 2\Delta_{\mathrm{v}}C_1 - \Delta_{\mathrm{d}}C = C_2^{\mathrm{g}} - 2C_{\mathrm{m}}^{\mathrm{l}}$, $[p]$ are the units of pressure, and the 4 parameters A and E are related to the thermodynamic parameters of the liquid and the gas:

$$E_1 = \Delta_{\mathrm{v}}H_1^{\ominus} - T^{\ominus}\Delta_{\mathrm{v}}C_1, \quad E_2 = 2E_1 - \Delta_{\mathrm{d}}H^{\ominus} + T^{\ominus}\Delta_{\mathrm{d}}C\,;$$

$$A_1 = \ln\frac{y^{\ominus}K_{\mathrm{d}}^{\ominus}}{[p]} + \frac{E_1}{RT^{\ominus}}, \quad A_2 = \ln\frac{K_{\mathrm{d}}^{\ominus}y^{\ominus 2}}{[p]} + \frac{E_2}{RT^{\ominus}}\,. \tag{16}$$

The result (15) can be called *Kirchhoff's equation for the pressure of dimerizing vapours*, generalizing Kirchhoff's equation for the vapour pressure when the gas phase is ideal, see Reid et al.[1], *p. 174*, as well as Dake[4]. The two addends in Eq (15) are in fact the partial pressures of the monomers and the dimers. For most practical purposes, where the degree of association is less than 10%, the capacity $\Delta_{\mathrm{d}}C$ can be set to 0 as it does not affect p significantly. For a liquid for which $\Delta_{\mathrm{v}}H^{\ominus}$, $p^{\ominus}$, $\Delta_{\mathrm{v}}C_1$, $K_{\mathrm{d}}^{\ominus}$, $\Delta_{\mathrm{d}}H^{\ominus}$ and $\Delta_{\mathrm{d}}C$ are known with high precision, the vapour pressure can be predicted via Eq (15) with accuracy that outmatches the one of, e.g., the 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).

Let us now examine the case with "linear" associates A_n of arbitrary size $n = [1, \infty)$. We will consider the dissociation process

$$\mathrm{A}_n \xrightleftharpoons{K_{\mathrm{d}}} \mathrm{A} + \mathrm{A}_{n-1}, \quad \text{where} \qquad K_{\mathrm{d}} = p_1 p_{n-1}/p_n\,; \tag{17}$$

we will assume that the dissociation constant K_{d} is independent of n (a model often used for solutions of alcohols in non-polar liquids[14,16,17]). This assumption usually underestimates the stability of the trimers, as discussed in S1. Following the same line of reasoning as above, we obtain the following equation for the ***heat of evaporation for vapours forming linear associates***:

$$\Delta_\mathrm{v} H = \Delta_\mathrm{v} H_1 - \frac{RT^2}{f}\frac{\partial f}{\partial T} = \Delta_\mathrm{v} H_1 - y\Delta_\mathrm{d} H\,,\ \text{ with }\quad y = \frac{p}{p+K_\mathrm{d}}\,. \tag{18}$$

We have used that, since K_d for all dissociation steps are equivalent, the respective dissociation enthalpies $\Delta_\mathrm{d}H$ are also equal. The factor y is equal to $\Sigma(i-1)w_i/i$ and stands for the average number of bonds per molecule in the associated vapours. The quantity y is analogous to the one for dimers in Eq (4): the relations $f = K_\mathrm{d}y$ and $y = p_2/p_1$ still hold true for the case of linear associates, see S1. In addition, the form (10) of the Clausius-Clapeyron equation is still valid, and so is its solution (13), but with a different $y^\ominus$:

$$y^\ominus = \frac{p^\ominus}{p^\ominus + K_\mathrm{d}^\ominus}\,. \tag{19}$$

The end result for the ***vapour pressure for vapours forming linear associates*** is obtained as $p = K_\mathrm{d}y/(1-y)$ following from Eq (18), and Eqs (13) and (14):

$$p = \left[\frac{1}{\left(T/T^\ominus\right)^{\Delta_\mathrm{v}C_1/R}\,\mathrm{e}^{A_1 - E_1/RT}} - \frac{1}{K_\mathrm{d}}\right]^{-1}. \tag{20}$$

This result can be called *Kirchhoff's equation for the pressure of vapours forming linear associates*. Here, K_d is given by Kirchhoff's Eq (14), and A_1 and E_1 are given by Eqs (16), but this time $y^\ominus$ stands for the expression (19).

Since the trimers (and the higher associates) are usually more stable than what follows from the assumption $K_\mathrm{d3} = K_\mathrm{d2}$, Eq (18) and (20) can be expected to be only moderately improved compared to their analogues for pure dimerization, Eqs (8) and (15); both models will fail at pressures and temperatures at which aggregates of size $n \geq 3$ are significant. A better approach to associating gases would use, in principle, K_d3 determined from data for the 3rd virial coefficient. Unfortunately, we find the published collections of 3rd virial coefficients extremely unreliable, especially for polar gases (an example is given in S2), which makes the effort futile.

Comparison with experiment

The vapours of **formic and acetic acid** are classical examples for strong dimerization, and generations of scientists have studied the effect of the dimers on their physicochemical properties[12,18]. Several complications lead to discordant results for all relevant experimental quantities (p-V_m^g-T data, vapour pressure, $\Delta_\mathrm{v}H$) – these are: **(i)** tendency for adsorption of the acid at the walls of the container[19]; **(ii)** tendency to decompose to CO and H_2O[20]; **(iii)** water impurities[21,22]; **(iv)** slow kinetics of equilibration between the monomers and the dimers[23]. In confirmation of the last point, Faubel and Kisters[24] 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 average kinetic energy of the dimers is higher than that of the monomers, corresponding to an effective difference in temperature of 100-200 K [24]. The existence of trimers and tetramers has been postulated[25], and later rejected[18]; the analysis in S2 confirms that only dimers exist in appreciable amounts in the acid vapours. In result of these complications, the handbook values 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 obtain the temperature dependence $K_d(T)$ of the dissociation constant of the dimer directly from the published p-V_m^g-T data[25–28], Gibbs' *Table IV*[29], limiting ourselves to the temperature range of 10 to 180 °C since the available vapour pressure data are within a similar interval. We use Eqs (2) and (14) to fit the p-V_m^g-T data. The three parameters of Eq (14) are sought: $K_d^\ominus$, $\Delta_d H^\ominus$, and $\Delta_d C$. The heat capacity change $\Delta_d C$ is not required with high precision, so we used for it the theoretical value at 25 °C, $\Delta_d C = -10.37$ J/molK, as it follows from the calculations of Chao and Zwolinski[30]. The other two parameters are determined from the regression as $K_d^\ominus = 60.33$ Pa and $\Delta_d H^\ominus = 64.16$ kJ/mol; the average difference between the experimental and computed V_m^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 ones, $K_d^\ominus = 79.2$ Pa and $\Delta_d H^\ominus = 63.2$ kJ/mol, that follow from Ref. [30]; the latter correspond to a deviation of 2.3% from the experimental p-V_m^g-T (much higher than the one with our values). Comparison with data for the 2nd virial coefficient B is made in S2; the 3rd virial coefficient is also discussed there.

We further compare Eq (15) to vapour pressure data from various authors[31–35] in the range $T = [25, 142]$ °C and $p = [2, 200]$ kPa, to determine the values of $p^\ominus$, $\Delta_v H^\ominus$, and $\Delta_v C_1$ 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 region where the data from the different authors deviate from one another (Figure S3). The best-fit $p^\ominus = 2.0706$ kPa from our regression analysis compares well to 2.08 kPa cited by Marcus[36], within the precision of his value, and $\Delta_v H^\ominus = 52.380$ kJ/mol agrees with 52.1 kJ/mol from the CRC Handbook[37] – 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 $\Delta_v C_1 = -47.26$ J/molK and the heat capacity of the liquid, $C_m^l = 123.3$ J/molK[36,37], the capacity of the monomer follows, $C_1^g = C_m^l + \Delta_v C_1 = 76.0$ J/molK. Chao and Zwolinski[30] calculated that C_1^g varies from 63.4 to 94 J/molK in the interval [300, 500] K; thus, the fitted $\Delta_v C_1$ value evidently corresponds to an average. The temperature dependence of $\Delta_v C_1$ can be accounted for easily, but it does not significantly affect the precision of the final result, so we neglect it.

We further test the parameters we obtained by calculating the heat of evaporation $\Delta_v H$ via Eq (8). The result at 25 °C is 23.03 kJ/mol, within 0.1% from the value 23.00 kJ/mol in Marcus's book[36]; at 117.4 °C, we calculate 24.28, comparing well with Brown's[38] experimental 24.38 kJ/mol. The second test consists in calculating 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[36,37].

Formic acid. The p-V_m^g-T data[20,26] in the temperature range [10, 156] °C are used together with Eqs (2) and (14) to determine $K_d^\ominus = 325.1$ Pa and $\Delta_d H^\ominus = 58.53$ kJ/mol ($\Delta_d C$ is fixed to its theoretical[30] value at 25 °C, -4.782 J/molK). The average deviation between the experimental and computed V_m^g is 0.7%, approaching the experimental precision, whereas for comparison, the values of Chao and Zwolinski[30], $K_d^\ominus = 282$ Pa and $\Delta_d H^\ominus = 63.8$ kJ/mol, correspond to a large deviation of 2.6%. Comparison with handbook data for B is given in Figure S1.

We further simultaneously fit Eq (15) to vapour pressure data[21,22,39] falling in the range $T = [-5, 120]$ °C and $p = [1, 170]$ kPa, and Eq (8) to vaporization heat data[21,23,40]. The parameters $p^\ominus = 5.692$ kPa, $\Delta_v H^\ominus = 45.902$ kJ/mol, and $\Delta_v C_1 = -39.3$ J/molK are thus obtained (cf. S2 for details). The average deviation from the measurements is 0.5%, comparable to the experimental dispersion, both for vapour pressure and $\Delta_v H$. A 3-parametric fit over the vapour pressure data with the Antoine equation has been performed for comparison, which gives $\ln(p/[\mathrm{Pa}]) = 21.755 - 3530.6/(T/[\mathrm{K}] - 28.85)$, and the average deviation is inferior, 0.6%. Our value of $p^\ominus$ agrees with 5.75 kPa cited by Marcus[36], but $\Delta_\mathrm{v}H^\ominus = 46.3$ kJ/mol from the CRC Handbook[37] is too high. The normal boiling temperature following from Eq (15) is 100.86 °C, compared to the literature values[36,37] 100.55-101 °C.

For both formic and acetic acid, the dispersion between the model and the vaporization data is very sensitive to $\Delta_\mathrm{v}H^\ominus$: inaccuracy in the 4th digit (0.01%) causes a significant increase of the deviation (cf. S7 for details). The fit is also sensitive to $p^\ominus$ (0.05% change in it affects the deviation), and is only affected by inaccuracies of 1% or more in $\Delta_\mathrm{v}C_1$. For both acids, the dissociation degree *increases* with T, due to the endothermicity of the process (1) − the weight fraction drops from more than 90% dimers at 0 °C to $w_2 < 80\%$ above 100 °C, see Figure S4-right. The monomers require more energy to evaporate, so as the fraction of dimers decreases, the vaporization heat anomalously increases (Figure S4-left). At higher T, the vaporization heat must pass through a maximum and drop to 0 at the critical point.

The vapours of the **fatty alcohols** also associate to a significant degree, and unlike acids, they have a tendency to form linear associates. Polymerization in alcohol vapours has been probed experimentally and theoretically, for instance by Kell and McLaurin[41] who analysed p-V_m^g-T data of methanol vapours; and by Tucker et al.[42] who used a monomer-trimer-octamer model to interpret p-V_m^g-T, IR and NMR data in vapours and in alkane solutions. Other authors[43] have asserted that only monomers, dimers and tetramers are present in the gas phase. The form of the associates has been a subject of debate – both linear and cyclical structures have been proposed[42]. The associates affect the vapour pressure significantly: for the cases we study below, associates form up to 20% of the total mass of the vapours.

We use experimental data for B in the range [20,200] °C to calculate the parameters $K_\mathrm{d}^\ominus$ and $\Delta_\mathrm{d}H^\ominus$; unfortunately, the available data are highly discordant. To minimize the problem, we use Eqs (14) and (6) to fit data for four homologues simultaneously: from methanol to butanol. This is helpful for distinguishing realistic data from artefacts: for methanol, we use all data from Refs. [37,44]; for ethanol, we employ data from Refs. [37,44,45–47]; for propanol – from Refs. [44,48] and for butanol – from Refs. [37,44,48]. The data for methanol and ethanol from Dymond et al.[48] and for propanol from CRC were tested separately and were found to lead to p and $\Delta_\mathrm{v}H$ that disagree with the experimental data, so we ignored them. For the fit of B, we assume (i) that $\Delta_\mathrm{d}H^\ominus$ is the same for all alcohols, (ii) that a linear dependence of $\ln K_\mathrm{d}^\ominus$ on the number of carbon atoms holds, and (iii) that $\Delta_\mathrm{d}C$ can be neglected, see SI 3 for details. The values we obtained are given in **Table 2**.

Methanol. We use handbook values for all other parameters of the model, Table 2. As observed with the acids, the fit for p is very sensitive to $\Delta_\mathrm{v}H^\ominus$; the CRC Handbook[37] cites $\Delta_\mathrm{v}H^\ominus = 38.2$ kJ/mol for it, while Marcus[36] gives $\Delta_\mathrm{v}H(T^\ominus) = 37.43$ kJ/mol, from which $\Delta_\mathrm{v}H^\ominus = 37.71$ follows via Eq (18). Using one of these values in Eq (20) yields large positive deviations, and the other yields large negative deviations from the vapour pressure data assembled by Goodwin[49], of the order of 2-4%; we found a similar tendency of Marcus[36] to underestimate and the CRC Handbook[37] to overestimate $\Delta_\mathrm{v}H^\ominus$ for nearly all liquids considered below. Using the average of the two values ($\Delta_\mathrm{v}H^\ominus = 37.95$ kJ/mol) leads to 0.6% average error with respect to data from Refs.[49–52] in the range 15-130 °C (corresponding to 10-850 kPa), an impressive precision for a model of no adjustable parameters. Formula (20) gives reasonably accurate results even with extrapolation well outside the interval 50-160 °C which the B data for methanol cover – the predictions of Eq (20) deviate by 3.6% from Goodwin's[49] experimental vapour pressures for the temperature range [-98, -93] °C (comparable with the experimental dispersion in this range). The deviation can be further decreased by tuning the parameters as done with the acids, but as 0.6% accuracy is enough for most applications, we have not done so. For comparison, we fitted the data in the range [15, 130] °C with the Antoine equation, obtaining $\ln(p/\mathrm{Pa}) = 23.343 - 3555.6/(T/[\mathrm{K}]-36.80)$; this leads to 0.3% error, and nearly any similar 3-parameter formula would lead to the same error. However, as is typical of empirical formulae, extrapolation is very inaccurate – the Antoine equation has 42% error in the temperature range [-98, -93] °C. Furthermore, $\Delta_\mathrm{v}H$ predicted by Eq (18) compares well to experimental data from Counsell et al.[51] and Svoboda et al.[53], with an average deviation of 1.5%, similar to the experimental uncertainty.

Ethanol. All required parameters are taken from the same sources and dealt with in the same manner as those of methanol – cf. Table 2 and SI 3. We compare the predictions of Eq (20) with the parameters in Table 2 to vapour pressure data[50,54–58]; the average deviation is 0.6%. We also compare Eq (18) to vaporization heat measurements from Counsell et al.[54] and Dong and Lin[56]; the deviation is again small, 0.6% – it is commensurate with the 0.2-0.4% deviation between the two $\Delta_\mathrm{v}H$ datasets.

n-Propanol and n-butanol. With the parameters taken from the sources used for methanol and ethanol ($p^\ominus$ = 2.73 kPa and $\Delta_\mathrm{v}H^\ominus$ = 47.5 kJ/mol for propanol; $p^\ominus$ = 0.82 kPa and $\Delta_\mathrm{v}H^\ominus$ = 52.4 kJ/mol for butanol[36,37]), the discrepancy between the theory and the experimental data for $p(T)$[55,57,59] and $\Delta_\mathrm{v}H(T)$[53,59,60] is relatively high. For the evaporation of propanol at 19-105 °C, Eq (20) deviates from the vapour pressure data[55,57,59] by an average of 1.6%; Eq (18) deviates by 2.3% with respect to the vaporization heat data[53,59,60]. This is due to the low accuracy of the handbook values. Therefore, we fit the experimental data to determine $p^\ominus$ = 2.83 kPa and $\Delta_\mathrm{v}H^\ominus$ = 47.14 kJ/mol (leading to *dev p* = 0.7% and $dev\Delta_\mathrm{v}H^\ominus$ = 1.7%). The discordance between the handbook values for $p^\ominus$ and $\Delta_\mathrm{v}H^\ominus$ and the experimental data for $p(T)$ [35,55,61] and $\Delta_\mathrm{v}H(T)$ [53,62] of butanol at 0-126 °C is even larger. If $p^\ominus$ and $\Delta_\mathrm{v}H^\ominus$ are obtained from a regression instead, substantially lower standard deviations are obtained, *dev p* = 0.59% and $dev\Delta_\mathrm{v}H^\ominus$ = 2.13%, with parameter values of $p^\ominus$ = 0.956 kPa and $\Delta_\mathrm{v}H^\ominus$ = 51.35 J/mol.

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 S7-right. This trend is the result of the increased vapour pressure at high temperature, causing the equilibrium (17) to favour dimers increasingly at higher T in spite of the rising K_d – compare with acids, where the second effect dominates. The vaporization heat has the normal decreasing trend with the increase of temperature (see Figure S7-left). All other conditions being equal, the weight fraction of multimers decreases as a function of the number of carbons in the chain. At the boiling temperature under p = 101325 Pa, dimers constitute several per cent of the total mass of the vapours, and the weight fraction drops by approximately an order of magnitude for each of the next two multimers. The fraction of dimers ranges from 7.7% for methanol to 6.0% for butanol, that of trimers – from 0.5% to 0.3%, and that of tetramers – from 0.03% to 0.01%.

Our third example is the **water-steam** equilibrium. We investigate the range $p < 500$ kPa only, since at higher pressures the fraction of trimers (for which our model accounts only approximately, cf. S1) becomes significant. We take the values of $p^\ominus$, $\Delta_\mathrm{v}H^\ominus$ and $\Delta_\mathrm{v}C_1$ from handbook data[36,37], cf. Table 2. For the K_d parameters, we minimize the difference between the regression formula for the second virial coefficient of water of Harvey and Lemmon[63] in the range 0-200 °C and B from Eqs (6) and (14) to obtain $K_\mathrm{d}^\ominus$, $\Delta_\mathrm{d}H^\ominus$ and $\Delta_\mathrm{d}C$ given in Table 2 (cf. S4 for details). The average difference between Eq (20) with these parameters and the experimental vapour pressure[64–69] in the range T = [-2.5, 150] °C is 0.4%; above 100 °C, however, it is comparatively high, 1-2%, – cf. S4. The difference between Eq (8) and the vaporization heat data of Osborne et al.[70,71] is 0.2%.

For our final example, we turn to four **hydrocarbons** that are of practical 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), and as an example for a very different nature of the associates: association of alkanes is driven by dispersion forces, and of arenes – of dispersion and quadrupole interactions; these are not localized to a specific chemical group and do not orient the interacting monomers as strongly as the hydrogen-bonded associates above. The linear associate model has relatively limited applicability to hydrocarbons due to their significant trimerization (see e.g. Chirico and Steele[72]), so we consider only the range of vapour pressures below $p < 100\text{-}200$ kPa where the monomers and dimers dominate; this is no great limitation for practical purposes, as this range is the most relevant one with regard to applications. Details are given in S5.

Toluene. We use B data[37,44] in the range [75, 165] °C to calculate $K_\mathrm{d}^\ominus$ and $\Delta_\mathrm{d}H^\ominus$. The monomer vaporization heat is an average between those in Refs [36] and [37], and $\Delta_\mathrm{v}C_1$ is calculated from the values of C_m^l from Ref. [36] and C_1^g from Ref. [73] at 25 °C. The values we find for the vapour pressure of toluene at 25 °C in the handbooks are all of accuracy too low for our aims; therefore, we determine $p^\ominus$ as an adjustable parameter, using vapour pressure data from Chirico and Steele[72] and Goodwin[74] (only the sources 14,16,18,19,22-26,30 and 33 in the latter reference are considered). The fit leads to $p^\ominus = 3.804$ kPa and an average deviation between the data and Eq (20) of 0.34%, compared to 1.5% with Marcus' value $p^\ominus = 3.75$ kPa [36]. We also compare Eq (18) with vaporization heat data from Natarajan and Viswanath[75]; the average deviation is again satisfactory, 0.27%.

Benzene. We fit $K_\mathrm{d}^\ominus$ and $\Delta_\mathrm{d}H^\ominus$ to B data from the CRC Handbook[37] and Kogan et al.[44] in the range [17, 177] °C, setting $\Delta_\mathrm{d}C$ to 0. We use handbook data[36] for $p^\ominus$ and $\Delta_\mathrm{v}H^\ominus$ and compare the predictions of the model to experimental data for $p(T)$ form various sources[75–78] in the temperature range [11, 112] °C and $\Delta_\mathrm{v}H(T)$ from Refs. [53,79]. Thus, we obtain $dev\ p = 0.9\%$ and $dev\Delta_\mathrm{v}H = 0.7\%$.

Heptane. We use the average between the value of $\Delta_\mathrm{d}H^\ominus$ determined from Ref. [36] and that given by Ref. [37] and data for B data from Ref. [37] in the range [25, 425] °C, as described in Table 2. Substituting these in Eq (20) leads to an accuracy of 0.14% compared to vapour pressure measurements from various authors[77,78,80,81]. Eq (18) predicts vaporization heats by 0.4% different from the experimental ones from Waddington et al.[80].

Isooctane (2,2,4-Trimethylpentane). As no data for B of isooctane is available to us, we use data for normal octane from the CRC Handbook[37] to calculate $K_\mathrm{d}^\ominus$ and $\Delta_\mathrm{d}H^\ominus$. The other parameters are taken from handbooks as described in Table 2. Substituting these in Eq (20) leads to accuracy of 0.7% compared to vapour pressure data from Willingham et al.[77]. This is acceptable accuracy, in view of the gross approximation for B.

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.

Discussion

Our work revisits two old models of a non-ideal gas: the largely forgotten model of Gibbs for dimerizing gases[12] and the model for linear associates popular for alcohols in non-polar solution[14,16,17,82] but not tested for the gas phase. We demonstrate the capabilities of two direct consequences of these models: the formulae for 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 most accurate experimental data we have 140 years later, and the simplicity of the final results is remarkable. The models allow readily available handbook data to be used to predict p and $\Delta_v H$ in a vast range of temperatures and pressures.

The usefulness of the model and the formulas (15) and (8) for dimers and (18) and (20) for linear associates 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[24,83]); **(ii)** the problem for the vapour pressure of mixtures with association in the gas phase (which has been considered in some detail already[11]) – unlike the empirical models and the established detailed theories for the vapour pressure of single-component liquids, the model considered in this work is straightforward to generalize to these more complicated cases.

The limitations of the models are: **(i)** the neglected dependence of the heat capacity $\Delta_v C$ on the temperature; **(ii)** the neglected molar volume V_m^l in Eq (9), in the pressure dependence of the enthalpy of the liquid, and the related contribution of the van der Waals repulsion to the 2nd virial coefficient; **(iii)** the crude approximation for K_d independent of n for the linear association model, and the neglected trimerization in the dimer model. The approximations **(i)** and **(ii)** are relatively easy to overcome, but they start to play a role at conditions where **(iii)** fails as well, and **(iii)** requires much more effort (cf. S1 for additional discussion).

Table 1: Parameters of Kirchhoff's equation(15) for the pressure of dimerizing vapours of formic and acetic acids.

compound range	$p^\ominus$ kPa	$\Delta_v H^\ominus$ kJ/mol	$\Delta_v C_1$ J/molK	$\ln K_d^\ominus$ /[Pa]	$\Delta_d H^\ominus$ kJ/mol	$\Delta_d C$ J/molK	A_1 [c]	E_1 kJ/mol [c]	A_2 [c]	E_2 kJ/mol [c]	*dev p* [d]	*dev* $\Delta_v H$ [d]	$\Delta_v H(T^\ominus)$ kJ/mol[e]	T_b °C[f]
HCOOH [-5, 120] °C, [1, 170] kPa	5.69_{23} [a]	45.90_2 [a]	-39.3_4 [a]	5.78_{42} [b]	58.5_{33} [b]	-4.782 30	30.34_4	57.63_1	30.71_7	55.30_3	0.5%	0.6%	20.10_8	$100._{86}$
CH_3COOH [25, 140] °C, [2, 200] kPa	2.070_6 [a]	52.38_0 [a]	-47.2_6 [a]	4.1_{00} [b]	$64._{16}$ [b]	-10.37 30	32.59_6	66.47_0	33.96_3	65.68_7	0.3%	0.9%	23.02_8	$117._{89}$

[a] Determined by comparing Eqs (8) and (15) to experimental data for vapour pressure and vaporization heat (formic acid[21–23,39,40], acetic acid[31–35]; cf. S2 for details). [b] Determined from the comparison between the equation of state (2) and p-V_m^g-T data for formic[20,26] and acetic[25–29] acids. [c] From Eqs (16) and (12). [d] Average deviation of Eqs (8) and (15) from the experimental data in the considered T range (cf. S2 for definition and the text for the data sources). [e] Vaporization heat at 25 °C calculated via Eq (8) (note that $\Delta_v H^\ominus$ and $\Delta_v H(T^\ominus)$ differ, as $\Delta_v H^\ominus = \Delta_v H_1(T^\ominus)$). [f] Normal boiling temperature, obtained as solution to $p(T) = 101325$ Pa, with p given by Eq (15).

Table 2: Parameters of Kirchhoff's equation (20) for the pressure of vapours forming linear associates.

compound range	$p^{\ominus}$ kPa	$\Delta_v H^{\ominus}$ kJ/mol	$\Delta_v C_1$ J/molK	$\ln K_d^{\ominus}$ /[Pa]	$\Delta_d H^{\ominus}$ kJ/mol	$\Delta_d C$ J/molK	A_1 [f]	E_1 kJ/mol [f]	*dev p* [g]	*dev* $\Delta_v H$ [g]	$\Delta_v H(T^{\ominus})$ kJ/mol[h]	T_b °C[i]
CH_3OH [15, 130] °C, [10, 850] kPa	16.9 36	37.96 36,37-**b**	-37 37	13.84 **d**	17.29 **d**	0 (neglected)	29.48_0	48.98_6	0.6%	1.5%	37.67_4	$64._{67}$
C_2H_5OH [0, 125] °C, [1, 500] kPa	7.89 36	42.34 36,37-**b**	-46.7 37	13.65 **d**	17.29 **d**	0 (neglected)	31.66_0	56.26_2	0.6%	0.6%	42.18_1	$78._{39}$
C_3H_7OH [20, 105] °C, [2, 130] kPa	2.833_4 a	47.1_{35} a	-58.3 37	13.47 **d**	17.29 **d**	0 (neglected)	33.97_1	64.51_7	0.7%	1.7%	47.06_6	$96._{97}$
C_4H_9OH [0, 125] °C, [0.1, 130] kPa	0.955_9 a	51.3_{50} a	-68.63 c	13.29 **d**	17.29 **d**	0 (neglected)	35.83_0	71.81_1	0.6%	2.1%	51.32_2	$117._{61}$
H_2O [0, 150] °C, [0.5, 450] kPa	3.169 37	43.990 37	-41.7 37	14.54 **e**	14.91 **e**	-0.88 **e**	30.82_0	56.42_3	0.4%	0.2%	43.96_0	$100._{20}$
$C_6H_5CH_3$ [0, 135] °C, [1, 200] kPa	3.80_4 a	38.07 36,37-**b**	-50.7 37,73	13.6_2 **e**	$12._6$ **e**	0 (neglected)	29.69_4	53.18_5	0.3%	0.3%	38.01_6	$110._{64}$
C_6H_6 [11, 166]°C, [6,841] kPa	12.7 36	33.93 36	-53.6 37	14.2_9 **e**	10.4_7 **e**	0 (neglected)	29.62_3	50.03_2	0.9%	0.7%	33.96_9	$80._{06}$
n-C_7H_{16} [25, 100] °C, [6, 100] kPa	6.10 36,37	36.64 36,37-**b**	-55.4 37,73	13.5_1 **e**	$13._2$ **e**	0 (neglected)	30.15_4	53.16_5	0.14%	0.4%	36.53_6	$98._{45}$
i-C_8H_{18} [25, 100] °C, [6, 100] kPa	6.50 36	35.26 36,37-**b**	-48.2 36,73	13.1_3 **e**	$13._{95}$ **e**	0 (neglected)	28.78_7	49.62_9	0.7%	-	35.08_6	$98._{98}$

[a] Determined by comparing Eqs (20) and (18) to experimental data for vapour pressure and vaporization heat of propanol[53,55,57,59,60], butanol[35,53,55,59,61] and toluene[72,74]; cf. S3 and S5 for details. [b] An average value of two sources[36,37]; Marcus[36] cites only the value of $\Delta_v H(T^{\ominus})$ – Eq (18) is used to calculate the respective $\Delta_v H^{\ominus} \equiv \Delta_v H_1(T^{\ominus})$. [c] To calculate $\Delta_v C_1$, we use a linear extrapolation to $n = 4$ from the data of the shorter alcohols. [d] Obtained by comparison of Eq (14) with data for *B* for the four alcohols together, with the assumption for *n*-independent $\Delta_d H^{\ominus}$, $\ln K_d^{\ominus}$ linearly dependent on *n*, and negligible $\Delta_d C$, see S3 for details. [e] Obtained by comparison of Eq (14) with handbook[37,44,48] data for *B*, see the main text for details ($\Delta_d C$ is neglected), except for water where Ref. [63] is used. No data for isooctane was found, and *B* data for n-octane is used instead. [f] From Eqs (16) and (19). [g] Average deviation of Eqs (20) and (18) from the experimental data in the considered *T* range (cf. S2-S3 for definition and the text for the data sources). [h] Vaporization heat at 25 °C calculated via Eq (18). [i] Normal boiling temperature, obtained as solution to $p(T) = 101325$ Pa, with *p* given by Eq (20).

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The publication contains supplementary materials: S1. Theory. **S2.** Carboxylic acids. **S3.** Alcohols. **S4.** Water. **S5.** Hydrocarbons. **S6**. Sensitivity analysis. **S7.** Sample Maple code for the calculation of p, w_2 and $\Delta_v H$. **S8.** List of symbols. **S9.** Additional references.

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