Clausius-Clapeyron equation and saturation vapour pressure: Typical hydrometeorological calculations

Demetris Koutsoyiannis
School of Civil Engineering, National Technical University of Athens, dk@itia.ntua.gr
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Abstract. All required equations for quantifying the presence of water vapour in the atmosphere are gathered in one page. They are physically consistent and accurate, and mathematically easy to use for meteorological and hydrological applications. Physical and mathematical details are given in two Appendices.*

1 Nomenclature

Variables	**Constants**
T: temperature (K) T_d: dew point (K) e: saturation water vapour pressure (hPa) e_a: actual water vapour pressure (hPa) p: air pressure (hPa) U: relative humidity (-) q: specific humidity (-) $W_{-1}(z)$: Lambert W function of z (non-principal real branch; see Appendix B)	T_0 = 273.16 K: temperature of the triple point of water e_0 = 6.11657 hPa: vapour pressure of the triple point of water ε = 0.622: ratio of the molecular mass of water to that of the mixture of gases in the dry air a_1 = 24.921 a_2 = 5.06

2 Relationship of temperature and saturation water vapour pressure

$e = e_0 \exp\left(a_1\left(1-\frac{T_0}{T}\right)\right)\left(\frac{T_0}{T}\right)^{a_2}$	$T = T_0 \frac{a_1}{a_2} \frac{1}{-W_{-1}\left(-\frac{a_1}{a_2}\exp\left(-\frac{a_1}{a_2}\right)\left(\frac{e}{e_0}\right)^{\frac{1}{a_2}}\right)}$

Notes: (a) See Koutsoyiannis (2012, 2014) for justification and Appendix A for a summary. (b) The same equations hold true if we substitute $(T_\mathrm{d}, e_\mathrm{a})$ for (T, e).

3 Relationship of relative humidity and dew point

$U \coloneqq \frac{e_\mathrm{a}}{e(T)} = \frac{e(T_\mathrm{d})}{e(T)} = \exp\left(a_1\left(\frac{T_0}{T}-\frac{T_0}{T_\mathrm{d}}\right)\right)\left(\frac{T}{T_\mathrm{d}}\right)^{a_2}$	$T_\mathrm{d} = T_0 \frac{a_1}{a_2} \frac{1}{-W_{-1}\left(-\frac{a_1}{a_2}\frac{T_0}{T}\exp\left(-\frac{a_1}{a_2}\frac{T_0}{T}\right)U^{\frac{1}{a_2}}\right)}$

4 Relationship of specific humidity and relative humidity

$q = \frac{\varepsilon e_\mathrm{a}}{p-(1-\varepsilon)e_\mathrm{a}} = \frac{\varepsilon U e}{p-(1-\varepsilon)Ue}$	$U = \frac{p}{e}\frac{q}{\varepsilon+(1-\varepsilon)q}$

Note: While relative humidity is the ratio of vapour pressures, specific humidity is the ratio of masses or densities, i.e. the water vapour density ρ_v to the total air density $\rho_\mathrm{d}+\rho_\mathrm{v}$ (ρ_d is the dry air density).

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[*] All equations are physically and dimensionally consistent and thus can be used with units other than hPa. Note though that they will not work if we change K to °C. If you find these equations useful and apply them, please cite Koutsoyiannis (2012) or (2014). If you have suggestions please send an email.

Appendix A: Physical background

The Clausius-Clapeyron equation describes the equilibrium law of the liquid and gaseous phase of water. Koutsoyiannis (2014) has highlighted the probabilistic nature of the law deriving it purely by maximizing probabilistic entropy, i.e. uncertainty. In particular, the law was derived by studying a single molecule (Figure A1) and maximizing the combined uncertainty of its state related to:

(a) its phase (whether gaseous, denoted as A, or liquid, denoted as B);
(b) its position in space; and
(c) its kinetic state, i.e., its velocity and other coordinates corresponding to its degrees of freedom and making up its thermal energy.

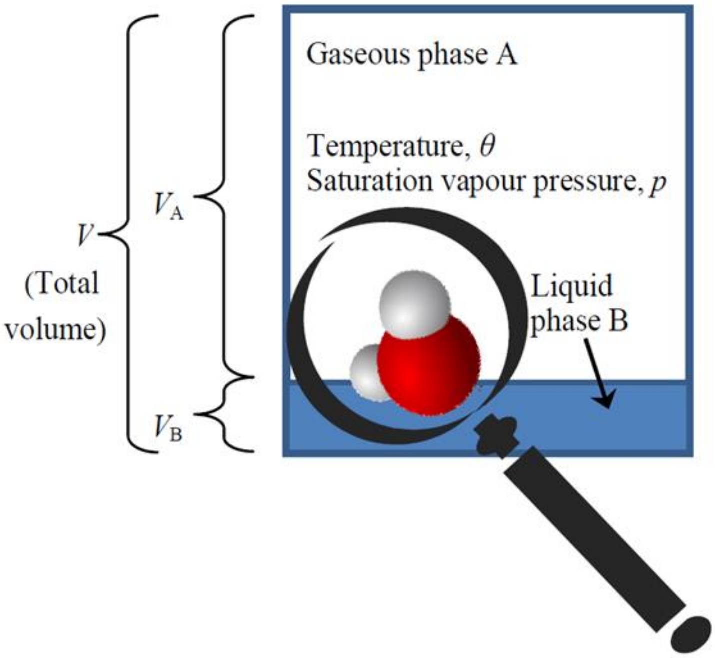

Figure A1 Explanatory sketch indicating basic quantities involved in the equilibrium of the water vapour with liquid water, with zoom on a single molecule which “tries to hide itself” by maximizing the combined uncertainty related to its phase (being either gaseous or liquid with probabilities π_A and π_B, respectively), position and kinetic state.

The partial entropies of the two phases, i.e., the entropies conditional on the particle being in the gaseous (A) or liquid (B) phase, are:

$$\varphi_A = c_A + (\beta_A/2)\ln\varepsilon_A + \ln V_A\,, \qquad \varphi_B = c_B + (\beta_B/2)\ln\varepsilon_B + \ln V_B \tag{A1}$$

with c_i $(i = \mathrm{A}, \mathrm{B})$ denoting a constant (incorporating several physical and mathematical constants), β_i the degrees of freedom of a water molecule, ε_i the (thermal) energy of the water molecule and V_i the volume available for the motion of the water molecule in the specified phase. As the water molecule has a 3-dimensional (not linear) structure, the rotational energy is distributed into three directions, so that the total number of degrees of freedom (translational and rotational) is $\beta_A = 6$. The number of degrees of freedom in the liquid phase is greater than 6 because of the “social behaviour” of water molecules. Specifically, in addition to the translational and rotational degrees of freedom of individual molecules, there are local clusters with low energy vibrational modes that can be thermally excited. The average number of degrees of freedom per molecule (individual and collective involving more than one water molecules) is very high, $\beta_\mathrm{B} = 18$.

The total entropy is:

$$\varphi = \pi_\mathrm{A}\varphi_\mathrm{A} + \pi_\mathrm{B}\varphi_\mathrm{B} + \varphi_\pi \tag{A2}$$

where π_i is the probability that the molecule is at phase i, with corresponding entropy:

$$\varphi_\pi \coloneqq -\pi_\mathrm{A} \ln \pi_\mathrm{A} - \pi_\mathrm{B} \ln \pi_\mathrm{B} \tag{A3}$$

Thus, the total entropy can be written as:

$$\varphi = \pi_\mathrm{A}(\varphi_\mathrm{A} - \ln \pi_\mathrm{A}) + \pi_\mathrm{B}(\varphi_\mathrm{A} - \ln \pi_\mathrm{A}) \tag{A4}$$

The two phases are in open interaction and the constraints are:

$$\pi_\mathrm{A} + \pi_\mathrm{B} = 1, \qquad \pi_\mathrm{A}\varepsilon_\mathrm{A} + \pi_\mathrm{A}(\varepsilon_\mathrm{A} - \xi) = \varepsilon \tag{A5}$$

where ξ is the amount of energy required for a molecule to move from the liquid to gaseous phase (i.e. to break its bonds with other molecules, the phase change energy).

We define the *natural temperature*, θ, which has units of energy (joules, rather than kelvins), in accordance to the probabilistic principle that entropy is a dimensionless quantity φ, as:

$$\frac{1}{\theta} \coloneqq \frac{\partial \varphi}{\partial \varepsilon} \tag{A6}$$

Denoting e the partial pressure of the N_A water molecules being in the gaseous phase and maximizing the entropy in that phase, we obtain the law of ideal gases in the form (Koutsoyiannis, 2014a):

$$e = \frac{N_\mathrm{A}\theta}{V_\mathrm{A}} = \frac{\theta}{v} \Leftrightarrow ev = \theta \tag{A7}$$

where $v \coloneqq V_\mathrm{A}/N_\mathrm{A}$.

Now, by maximizing the combined entropy of the two phases, as given in equation (A4), and converting natural temperature to the conventional absolute temperature (in kelvins) we find the basic equation (left-hand side of the table in section 2) and after some fitting adjustments we find the constants in section 1. Detailed derivations are given in Koutsoyiannis (2014) and a summary in Koutsoyiannis (2021). The good agreement of the derived equation with experimental data is shown in Figure A2.

All other equations of sections 1-4 are readily derived from the basic equation by typical algebraic manipulations. The inversion of the basic equation is made through the Lambert W function which is described in Appendix B.

Appendix B: The Lambert W function

The Lambert W function (or ω-function) is defined to be the inverse of the function $z = f(w) \coloneqq w\mathrm{e}^w$. This function denoted as $W_k(z) \coloneqq f^{-1}(z)$, which thus satisfies $W_k(z)\mathrm{e}^{W_k(z)} = z$, is a multivalued function on the complex plane if the integer k is not specified, or single valued if k is specified. For real z and $-1/\mathrm{e} \le z < 0$, there are two possible real values of $W_k(z)$, denoted as $W_0(z)$, and $W_{-1}(z)$. If $z \ge 0$, there is a single real value $W_0(z)$. The real-valued branch $W_0(z)$ of $W_k(z)$ satisfying $W_0(z) \ge -1$ is called the principal branch of the W function, and the other real-valued branch, $W_{-1}(z)$, which satisfies $W_{-1}(z) \le -1$, is the non-principal real branch.

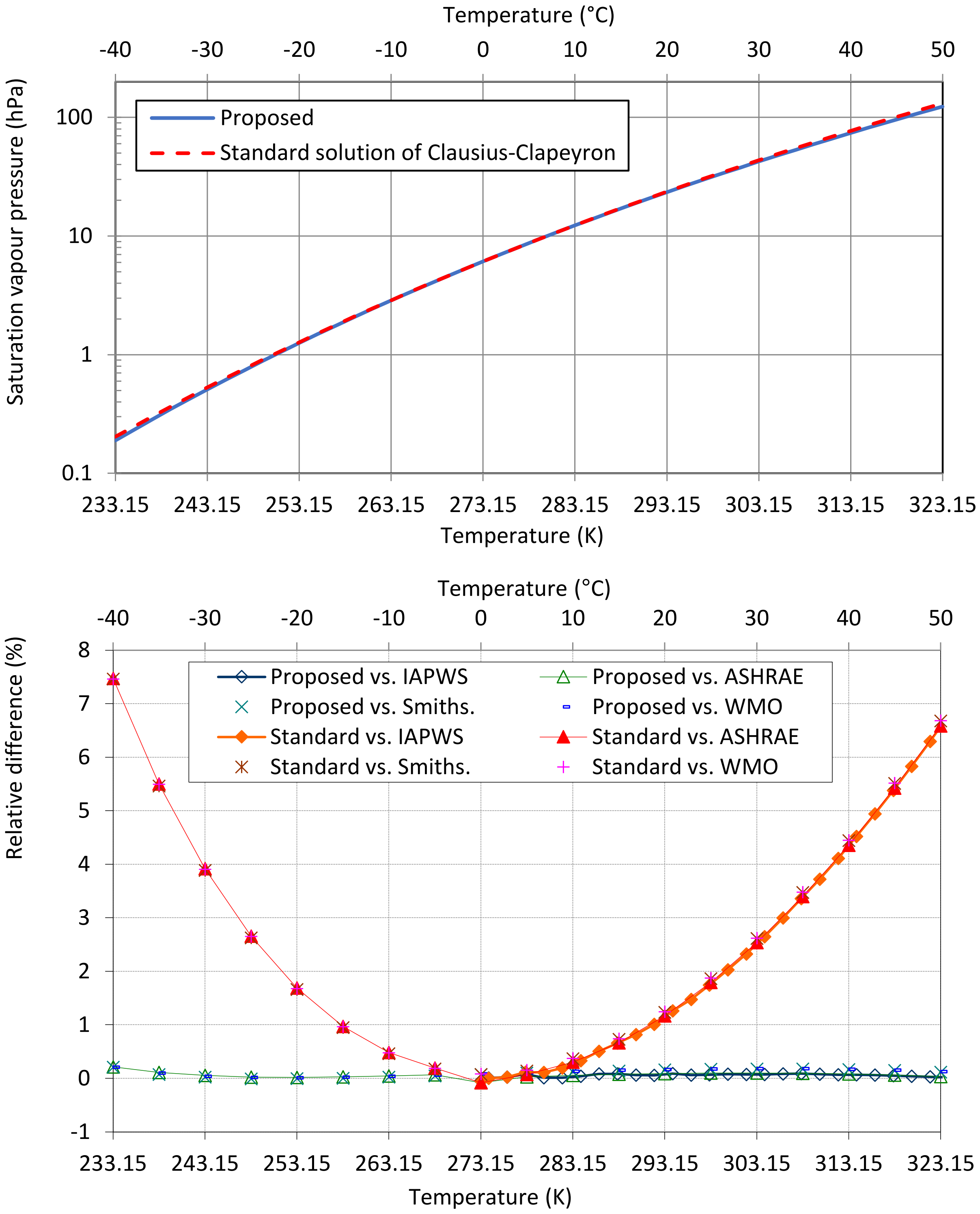

Figure A2 (upper) Comparison of saturation vapour pressure obtained by the proposed equation and by a standard equation of the literature, namely, $e = e_0 \exp(19.84(1 - T_0/T))$. **(lower)** Comparison of relative differences of the saturation vapour pressure obtained by the proposed and the standard equations with accurate measurement data of different origins, as indicated in the legend and detailed in Koutsoyiannis (2012).

The function $W_k(z)$ is available for direct use in most computational environments. In Mathematica and Maple, which perform both symbolic and numerical calculations, the function is named ProductLog and LambertW, respectively. With the latter name, it is also available in

R[*], MATLAB[†], Python[‡], etc., while several functions implementing it are available online for Excel[§] and LibreOffice[**].

Here we deal with the non-principal real branch $W_{-1}(z)$ only. Approximations for this, even for one-shot evaluation, can be found in Chapeau-Blondeau and Monir (2002), Barry et al. (2004) and Chatzigeorgiou (2013).

For values of z that are relevant to our particular problem, in addition to the approximations found in literature, we propose the following, which is very accurate and fast:

$$-W_{-1}(z) = 1.285(-\ln(-z))^{0.933} + 0.872(\ln(-\ln(-z)))^{0.612} \tag{B1}$$

The relative error is negligible, smaller than 3×10^{-5} for the values relevant to our calculations, i.e., those corresponding to the range of temperature shown in Figure A2 (for which $-0.07 \leq z \leq -0.015$). Notice the minus sign in $-W_{-1}(z)$, which makes this quantity positive.

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[*] https://cran.r-project.org/web/packages/LambertW/index.html

[†] https://www.mathworks.com/help/symbolic/lambertw.html

[‡] https://docs.scipy.org/doc/scipy/reference/generated/scipy.special.lambertw.html

[§] https://www.vbforums.com/attachment.php?attachmentid=89337&d=1341009088

[**] https://gist.github.com/m93a/a0199c4f40b43bb8116810daa46dd92d