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NOTES AND CORRESPONDENCE

Accurate, simple equation for saturated vapour pressure over water and ice

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Abstract

We present and assess a simple equation for saturated vapour pressure over water and ice. The equation does not rely on an explicit integration of the Clausius–Clapeyron equation, but instead uses the equality of the Gibbs functions of the vapour and the liquid or ice in equilibrium. The resulting equation is simple, physically consistent with standard thermodynamic assumptions, uses only basic physical parameters, and is at least as accurate as commonly used empirical fits. It is further shown that the finite volume of liquid water has a negligible effect on the vapour pressure. The main variation from accurate tabulated data results from the variation of vapour and liquid isobaric heat capacities. Nevertheless, it is shown that, for the purpose of accurate calculation of saturated vapour pressure, this can usually be ignored.

KEYWORDS
atmosphere, boundary layer, humidity, hydrology, saturated vapour pressure

1 | INTRODUCTION

The common way of calculating the saturated vapour pressure over a liquid is to integrate the Clausius–Clapeyron equation. This equation results from equating the Gibbs functions of the liquid and the vapour—a requirement for thermodynamic equilibrium—and then demanding that any variation of the vapour Gibbs function with temperature and pressure must equal the variation in the liquid Gibbs function, as in, for example, Ambaum (2010).

Such an approach also underlies accurate empirical fits, for example seen in Murphy and Koop (2005) or Bolton (1980).

In the case of water and its saturated vapour under typical atmospheric conditions, this is not necessary: in these circumstances, the vapour and the liquid Gibbs functions can be approximated by simple equations to a high degree of accuracy, resulting in a simple and intuitive expression for saturated vapour pressure.

The resulting expression is tested against the currently accepted tabulated data and found to be at least as accurate as commonly used empirical fits. Because the expression is derived directly from normally assumed thermodynamic properties of air and water, it is consistent with those assumptions, contrary to empirical fits. This approach therefore ties in closely with recent developments describing atmospheric thermodynamics based on Gibbs functions in, for example, Thuburn (2017).

It is also shown that this technique works well for calculating the saturated vapour pressure over ice. This

furthermore leads to an accurate and simple analytical expression for the saturation ratio for supercooled water compared with ice, as relevant for the Bergeron–Findeisen process. It is found that this saturation ratio depends only on the melting properties of water.

In the next section, we will show how to arrive at our expression for saturated vapour pressure over water and compare it with tabulated data. In Section 3, we extend the formalism successfully to determine the saturated vapour pressure over ice. In Section 4, we show the effects of the finite volume of the liquid and nonideality of the vapour and we demonstrate that they can be ignored if we want a highly accurate but simple expression.

2 | SATURATED VAPOUR PRESSURE WITH SIMPLE ASSUMPTIONS

We are going to assume that the vapour is an ideal gas, which requires a constant isobaric heat capacity. This turns out the be the most severe assumption used, and its effects are discussed later. Under the assumption of ideality, the specific enthalpy of the vapour must be

$$h_v = u_{0v} + c_{pv}T, \tag{1}$$

with c_{pv} the isobaric heat capacity of the vapour and u_{0v} the zero-point internal energy.

The entropy of the vapour follows standard equations for ideal gases and equals, using e to denote the vapour pressure,

$$s_v = c_{pv} \log(T/T_0) - R_v \log(e/p_0), \tag{2}$$

with R_v the specific gas constant for water vapour $R_v = 461.52\,\text{J·kg}^{-1}\text{·K}^{-1}$, and T_0 and p_0 integration constants which set the entropy constant. The true values of the integration constants are not important for our application; the more useful function of the integration constants is to compare the vapour specific entropy at (T, e) with that at (T_0, p_0).

The Gibbs function for the vapour is, by definition, equal to

$$g_v = h_v - Ts_v. \tag{3}$$

The specific enthalpy for the liquid is, to a good approximation,

$$h_l = u_{0l} + c_{pl}T, \tag{4}$$

with c_{pl} the isobaric heat capacity of the liquid and u_{0l} the zero-point internal energy. Because, by definition, $h = u + pv$ (with u the specific internal energy and v

the specific volume), one could perhaps argue that $h_l = u_{0l} + c_{vl}T + pv_l$, with c_{vl} the isochoric heat capacity for the liquid, but it turns out that for liquid water c_{pl} varies less with temperature than does c_{vl} (see Figure 1), so the above enthalpy expression in terms of a constant c_{pl} is more accurate.

Note that any residual pressure dependence of the liquid specific enthalpy will not come into play under common atmospheric conditions, because evaporation and condensation typically occur at constant total pressure (dry air plus vapour pressure); the liquid experiences this total pressure and not, for example, the partial pressure of the vapour. This is ultimately the reason why our equation does not include the specific volume of liquid water. It is furthermore shown in Section 4 that this makes negligible difference to the vapour pressure.

The specific entropy for the liquid, when assuming incompressibility, is

$$s_l = c_{pl} \log(T/T_0). \tag{5}$$

Again, the value of the integration constant T_0 plays no physical role in our application. By convention, it is often chosen as the triple-point temperature for water, which turns out to be an appropriate choice here as well. More importantly, we can take it to be equal to the T_0 in the entropy expression for the vapour, so we have two integration constants, T_0 and p_0, to set the two entropy constants for the vapour and the liquid.

The Gibbs function for the liquid is, by definition,

$$g_l = h_l - Ts_l. \tag{6}$$

The saturated vapour pressure is a property of the equilibrium between vapour and liquid. This equilibrium is set by the fundamental phase coexistence relation:

$$g_v = g_l. \tag{7}$$

From the relation between the Gibbs function and the enthalpy, this coexistence relation can be rewritten as

$$h_v - h_l = T(s_v - s_l), \tag{8}$$

which expresses the fact that, at equilibrium, the required enthalpy increase on evaporation is provided by the gain in heat energy through the increase in entropy from liquid to vapour.

We have, by definition,

$$L = h_v - h_l, \tag{9}$$

with L the latent heat of evaporation (enthalpy of vaporization). From the above expressions for enthalpy of

the vapour and liquid, it follows that L is a function of temperature.

Substituting the above entropy expressions, Equation 8 becomes

$$L/T = (c_{pv} - c_{pl}) \, \log(T/T_0) - R_v \, \log(e/p_0). \quad (10)$$

If we take the vapour pressure at $T = T_0$ to be equal to $e = e_{s0}$, then Equation 8 becomes

$$L_0/T_0 = R_v \, \log(p_0/e_{s0}). \quad (11)$$

In effect, this defines the value of the entropy integration constant p_0 in terms of a given vapour pressure e_{s0}. In this expression, L_0 is the latent heat of evaporation at temperature T_0. With this definition of p_0 in terms of e_{s0}, the equilibrium condition Equation 10 can now be rewritten as

$$L/T - L_0/T_0 = (c_{pv} - c_{pl}) \, \log(T/T_0) - R_v \, \log(e/e_{s0}). \quad (12)$$

This equation can, in turn, be rearranged to

$$e = e_{s0} \left(\frac{T_0}{T}\right)^{(c_{pl}-c_{pv})/R_v} \exp\left(\frac{L_0}{R_v T_0} - \frac{L}{R_v T}\right). \quad (13)$$

This is the main result of this note. It gives the equilibrium vapour pressure e at given temperature T if the vapour pressure e_{s0} at temperature T_0 is given. The triple-point pressure and temperature are the most obvious choices here, but other reference points can be chosen. Here we recommend these triple-point values for the physical constants:

$$T_0 = 273.16 \text{ K}, \ e_{s0} = 611.655 \text{ Pa},$$
$$c_{pl} - c_{pv} = 2180 \text{ J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}. \quad (14)$$

The choice for $c_{pl} - c_{pv}$ is explained below. The associated equation for the latent heat is

$$L = L_0 - (c_{pl} - c_{pv})(T - T_0), \quad (15)$$

with $L_0 = 2.501 \times 10^6 \text{ J} \cdot \text{kg}^{-1}$ the latent heat of evaporation at the triple point T_0.

A commonly used approximation to the integral of the Clausius–Clapeyron equation is equivalent to assuming $c_{pl} = c_{pv}$. In that case, L is a constant and the result reduces to the familiar approximate constant-L integral of the Clausius–Clapeyron equation,

$$e \approx e_{s0} \, \exp\left(\frac{L_0}{R_v T_0} - \frac{L_0}{R_v T}\right). \quad (16)$$
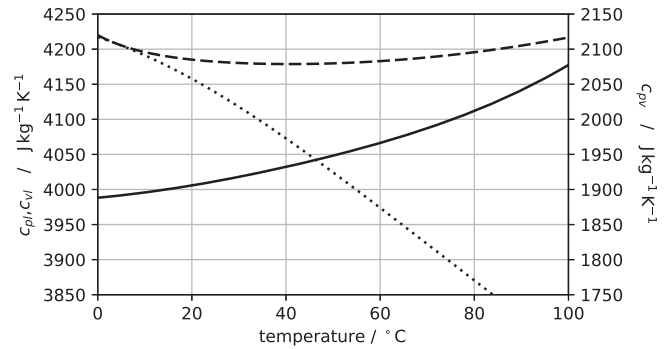

FIGURE 1 Dashed line, left axis: specific isobaric heat capacity c_{pl} for liquid water; dotted line, left axis: specific isochoric heat capacity c_{vl} for liquid water; solid line, right axis: specific isobaric heat capacity c_{pv} for water vapour. Data from Wagner and Pruß (2002)

This approximation is only accurate for small temperature ranges.

Figure 2 shows the fractional error of our new equation, Equation 13, compared with accurate agreed tabulated values from IAPWS-95, described in Wagner and Pruß (2002). The figure also shows the same comparison for Bolton's (Bolton, 1980) empirical version of Teten's equation, which was optimized for low temperatures, as well as for the approximation in Murphy and Koop (2005), their equation 10.

Several other empirical equations exist; Alduchov and Eskridge (1996) present a number of these. Here we just chose to compare our results with two representative empirical equations from simple, as in Bolton (1980), to more complex, as in Murphy and Koop (2005). The purpose in this note is not to give yet another accurate fit to the vapour pressure curve, but to show that our simple, physically based, first principles equation can be as accurate, or more accurate, as published empirical fits.

For the reference values in Equation 14, we used accepted triple-point values for constants for T_0, e_{s0}. The value for c_{pl} remains fairly close to its measured triple-point value, but c_{pv} varies considerably with temperature, from $1888.2 \text{ J} \cdot \text{kg}^{-1}$ at the triple point to $2077.5 \text{ J} \cdot \text{kg}^{-1}$ at 100 °C; see Figure 1. So the ideal gas approximation for vapour (which thermodynamically means that c_{pv} is a constant) is only approximately valid over this temperature range. It turns out that a choice of $c_{pl} - c_{pv} = 2180 \text{ J} \cdot \text{kg}^{-1}$ gives a very good fit across the 0–100 °C temperature range, in particular for temperatures below 70 °C, so this value of $c_{pl} - c_{pv}$ is recommended here. This corresponds to a value of $c_{pv} \approx 2040 \text{ J} \cdot \text{kg}^{-1}$, but other values for c_{pv} would still give good fits, particularly at the lower end of this temperature range.
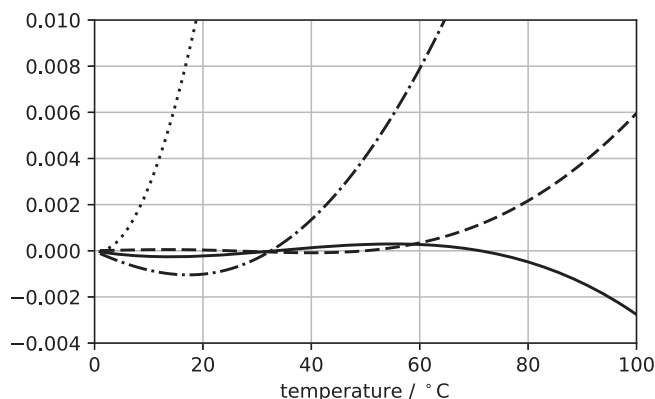
FIGURE 2   Fractional difference of vapour-pressure values compared with Wagner and Pruß (2002) empirical fits. Solid line: this work, Equations 13 and 14; dashed line: Murphy and Koop (2005); dash–dotted line: Bolton (1980); dotted line: constant-L approximation of Equation 16

Below 50 °C, the new approximation deviates from the IAPWS-95 values by a fractional error less than 2.7×10^{-4}, where the Murphy & Koop values deviate by less than 0.9×10^{-4}. Above 60 °C, the new approximation is better than the Murphy & Koop approximation. The fractional errors in the Bolton approximation are typically at least an order of magnitude larger over this temperature range, but remember that this approximation was optimized for low temperatures and supercooled water. The constant-L approximation is not practically useful over such a large range, except for the most crude calculations.

For the vapour pressure at 100 °C, IAPWS-95 gives 1014.18 hPa, Murphy & Koop give 1020.22 hPa, and the new approximation gives 1011.38 hPa. Note that the IAPWS-95 reference value for the vapour pressure is not exactly 1 atm = 1013.25 hPa, because, in the currently accepted practical temperature scale (the International Temperature Scale 1990, ITS–90), the atmospheric boiling point temperature of water, defined as $e(T) = 1$ atm, is 99.974 °C.

The new approximation gives a very accurate value for the vapour pressure over the range 0–100 °C, better than the complicated empirical fit in Murphy and Koop (2005) for higher temperatures, and nearly as good below 60 °C.

Figure 3 shows the comparison between the new equation and the Murphy and Koop (2005) fit, which was optimized specifically for supercooled water, to be within experimental measurement error in that temperature range. The Bolton (1980) fit is included as well. For temperatures down to −25°C, the fits shown are close to the Murphy and Koop (2005) fit to within a fractional difference of 2×10^{-3}. The best fit at low temperatures is from Equation 13 using triple-point values for all constants in the equation, including for c_{pv} and c_{pl}; this particular

version is within 1×10^{-3} of the Murphy and Koop (2005) fit for temperatures down to −25°C.

The new equation, Equation 13, yields accurate vapour pressure values over a very wide temperature range. All fractional differences with more accurate empirical fits and reference data are within or close to experimental error, and certainly within variations implied by the presence of dry air in the atmosphere or impurities in the water. In other words, for application in atmospheric modelling, Equation 13 can serve as a benchmark in terms of accuracy, whilst benefiting from having a clear physical grounding: there are no numerical fitting parameters, just measurable physical constants.

Furthermore, Equation 13 is consistent with other commonly used thermodynamic approximations in models, particularly the ideal gas law for the vapour and incompressibility for the liquid.

Note also that, as expected, the absolute values of the entropy constants and the absolute values of the enthalpy constants do not play a role.

It can be shown that Equation 13 is equivalent to an integral of the Clausius–Clapeyron equation, when taking into account a linear variation with temperature of the latent heat of evaporation and ignoring the finite specific volume of liquid water. Such derivations have been presented before, for example in textbooks such as Iribarne and Godson (1981), Emanuel (1994), Bohren and Albrecht (1998), or Ambaum (2010). Iribarne and Godson (1981) call this type of integral of the Clausius–Clapeyron equation a Magnus equation; Bohren and Albrecht (1998) also present a comparison of their Magnus equation with tabulated values.

The key to the accuracy of our direct calculation, as well as Magnus-type integrals of the Clausius–Clapeyron equation, is the linear variation with temperature of the latent heat of evaporation. A direct calculation for constant latent heat was suggested in Koutsoyiannis (2012), but the inclusion of the essential variation in latent heat presented there also follows the traditional Clausius–Clapeyron approach to arrive at a Magnus equation. The importance of the variation in latent heat was also pointed out in the context of buoyancy calculations in Yano and Ambaum (2017). It appears then that the linear temperature dependence of L is essential for accurate calculations of the effects of condensation and evaporation, whilst the finite volume of water is not.

3 | SATURATED VAPOUR PRESSURE OVER ICE

The arguments presented above can be straightforwardly extended to the calculation of saturated vapour pressure

over ice. Again, because the ice, under common atmospheric conditions, will experience the total pressure, any pressure dependence in the ice specific enthalpy and ice specific entropy can be ignored. The main assumption then is that the heat capacity at constant pressure is constant over the temperature range of interest. This is quite a severe approximation, as the heat capacity of ice at standard pressure reduces, more or less linearly with temperature, from around $2.1 \times 10^3 \mathrm{J \cdot kg^{-1} \cdot K^{-1}}$ at 0 °C to around $1.8 \times 10^3 \mathrm{J \cdot kg^{-1} \cdot K^{-1}}$ at −40 °C. Nevertheless, we can proceed by assuming a constant heat capacity and assess how accurate the resulting vapour pressure is.

Under this assumption of constant heat capacity, the whole derivation above remains valid, and we find a saturated vapour pressure e_i over ice of

$$e_i = e_{i0} \left(\frac{T_0}{T} \right)^{(c_{pi} - c_{pv})/R_v} \exp \left(\frac{L_{s0}}{R_v T_0} - \frac{L_s}{R_v T} \right), \quad (17)$$

where L_s is the latent heat of sublimation, with

$$L_s = L_{s0} - (c_{pi} - c_{pv})(T - T_0). \quad (18)$$

For the reference values, triple-point values can be used:

$$T_0 = 273.16 \text{ K}, \ e_{i0} = 611.655 \text{ Pa},$$
$$c_{pi} - c_{pv} = 212 \text{ J kg}^{-1} \text{ K}^{-1}. \quad (19)$$

Note that the specific heat capacities for ice and vapour are much closer than for liquid and vapour. This means that the naive constant-L approximation works better for saturated vapour over ice. Nevertheless, we do not need to use this approximation.

The difference between the vapour pressure over supercooled water and over ice based on Equations 13 and 17, with triple-point values fixing all reference constants, differs from fits from Murphy and Koop (2005) by a small amount which increases, almost linearly, to a maximum of only 0.001 hPa at $T = -40°C$.

One of the advantages of the explicit formulations of the vapour pressure over ice and supercooled water is that the saturation ratio for supercooled water in the presence of ice can be expressed explicitly as

$$\frac{e}{e_i} = \left(\frac{T_0}{T} \right)^{(c_{pl} - c_{pi})/R_v} \exp \left(\frac{L_{m0}}{R_v T_0} - \frac{L_m}{R_v T} \right), \quad (20)$$

with $L_m = L_s - L = L_{m0} + (c_{pl} - c_{pi})(T - T_0)$ the latent heat of melting. The reference values are, in this case, always evaluated at the triple point. Figure 4 shows this saturation ratio as a function of temperature. The saturation ratio varies from 1 at the triple point to 1.47 at −40°C. This explicit expression for the saturation ratio introduces
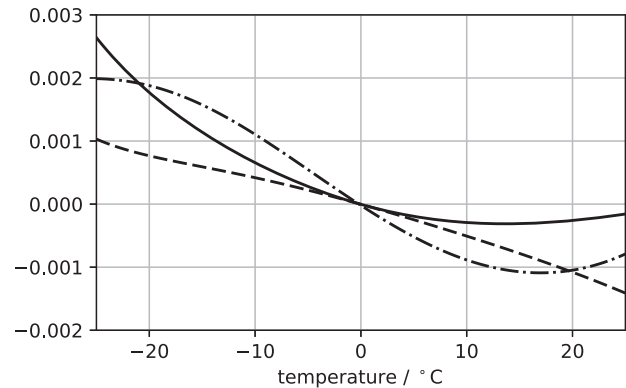

FIGURE 3 Fractional difference of vapour-pressure values compared with Murphy and Koop (2005) empirical fits for supercooled water. Solid line: this work, Equations 13 and 14; dashed line: Equation 13 using triple-point value for all constants, including $c_{pv} = 1888.222 \text{ J} \cdot \text{kg}^{-1}$; dash–dotted line: Bolton (1980)
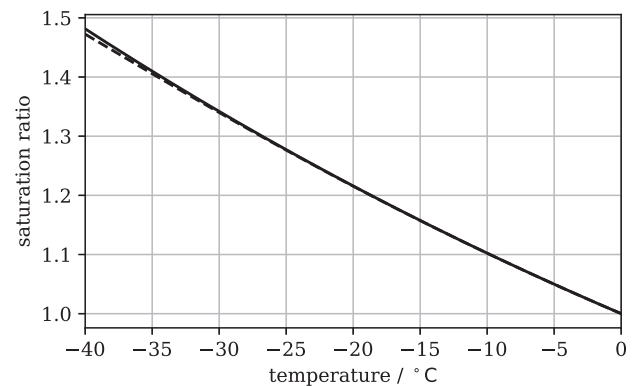

FIGURE 4 Ratio of saturated vapour pressure over supercooled water and and over ice based on Equation 20 (solid line) and based on empirical fits in Murphy and Koop (2005) (dashed line). Triple-point values have been used for all constants: $L_{m0} = 0.3334 \times 10^6 \text{ J} \cdot \text{kg}^{-1}$, $c_{pl} = 4220 \text{ J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$, and $c_{pi} = 2097 \text{ J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$

a relative error compared with the saturation ratio based on empirical fits in Murphy and Koop (2005) of less than 1×10^{-3} for most of the temperature range, increasing to 6×10^{-3} at −40°C.

It can be seen in Equation 20 that this saturation ratio, relevant for the Bergeron–Findeisen process, depends only on the melting properties of water and not on its vapour properties. (R_v depends only on the molar mass of water, not on whether it is solid, liquid, or vapour.)

4 | FINITE-VOLUME EFFECTS AND NONIDEALITY

The finite volume of the liquid water (and ice) is ignored in the derivations above. This is physically justified on the grounds that, under normal atmospheric conditions,

evaporation and condensation occur at constant total pressure, and the liquid component experiences the total pressure rather than the varying vapour pressure. The Gibbs–Duhem relation still requires the vapour specific Gibbs function and the liquid specific Gibbs function to be equal at equilibrium, irrespective of the presence of a dry air component. Because the liquid specific volume is the derivative of the Gibbs function with pressure, this means that we effectively set the liquid specific volume to zero in the Clausius–Clapeyron equation.

To estimate how this may influence the results, we start by writing the Clausius–Clapeyron equation,

$$\frac{de}{dT} = \frac{L}{T(v_v - v_l)}, \qquad (21)$$

with v_v and v_l the specific volumes of the vapour and the liquid. Trivially, we can write

$$v_v - v_l = v_v(1 - v_l/v_v) > v_v(1 - v_l/v_{v0}), \qquad (22)$$

with v_l taken constant and v_{v0} evaluated at the lowest temperature in the range where we want to apply the approximations of the previous section. For the Clausius–Clapeyron equation, this effectively corresponds to a reduction of the specific gas constant for the vapour to $R_v(1 - v_l/v_{v0})$. Substituting this in our main result, we can deduce that the fractional error in the vapour pressure introduced by ignoring the specific volume of the liquid must be less than

$$\left| \frac{\delta e}{e} \right| < \frac{v_l}{v_{v0}} \left(\frac{L_0}{R_v T_0} - \frac{L}{R_v T} \right) \approx 3 \times 10^{-5}, \qquad (23)$$

where for the numeric result we used reference values as in the previous section and the fractional error at 100 °C was calculated. Actual fractional errors will be less than this estimate, certainly at temperatures relevant for the atmosphere.

We conclude that, for applications in atmospheric science, the liquid specific volume of the water can safely be ignored; any corrections are substantially smaller than the expected accuracy of either measurements or approximations used.

Contrary to the liquid water component, the vapour *does* experience its partial pressure rather than the total pressure. This has been taken into account in the derivation above, under the assumption of the vapour being an ideal gas.

It is much harder to address the effect of nonideality of water vapour. Figure 1 shows that the specific isobaric heat capacity of water vapour increases considerably with temperature across the temperature range of interest. Incorporating this variation would add
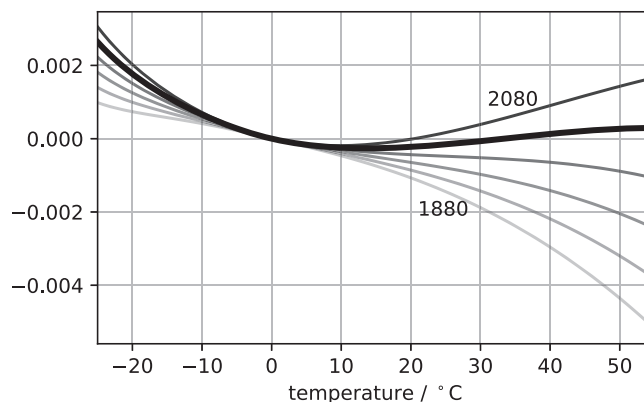

FIGURE 5 Fractional difference in saturated vapour pressure compared with reference values for different choices of c_{pv} with an interval of $40 \, \mathrm{J \cdot kg^{-1} \cdot K^{-1}}$. Here $c_{pl} = 4220 \, \mathrm{J \cdot kg^{-1} \cdot K^{-1}}$. The thick line corresponds to the recommended value of Equation 14

substantial complexity to the temperature dependence of both the vapour enthalpy and entropy, and would lead to an implicit equation for vapour pressure, Equation 7, which cannot be inverted in terms of a closed form expression, such as Equation 13.

Instead, c_{pv} can be chosen to optimize the range of validity of Equation 13, which for the 0–100 °C range leads to the recommended value of $c_{pl} - c_{pv} = 2180 \, \mathrm{J \cdot kg^{-1} \cdot K^{-1}}$, as in Equation 14.

For a large range of temperatures, we plot the saturated vapour pressure for different choices of c_{pv} in Figure 5, taking for c_{pl} its triple-point value $c_{pl} = 4220 \, \mathrm{J \cdot kg^{-1} \cdot K^{-1}}$. Strictly speaking, this is not an assessment of the effect of nonideality, but it provides an envelope of possible ranges that the choice of c_{pv} would introduce in our equation. It can be seen that the variations introduced remain rather small, even across the whole range up to 100 °C (not shown). For temperatures below 30 °C, the fractional variations remain below 2×10^{-3}. So c_{pv}, or $c_{pl} - c_{pv}$, can be optimized for any required temperature range, but its effect is limited for temperature ranges relevant to the atmosphere.

5 | CONCLUSION

Equation 13 results from solving the implicit equation $g_v = g_l$ for the vapour pressure, when ideality of the vapour is assumed and the heat capacity of the liquid is taken as constant across the temperature range of interest.

We have shown that this equation is at least as accurate as some more complex empirical fits, and is accurate enough for atmospheric applications where other effects, such as the presence of dry air and the presence of solutes in the water, will also play a role.

The equation does not have fitting parameters, but only measurable physical constants. Contrary to empirical fits,

it is fully consistent with the usual basic thermodynamic assumptions used in atmospheric modelling.

It is further shown that the finite volume effect of liquid water can be safely ignored, as it introduces variations that are substantially smaller than the uncertainties with which reference values for vapour pressure are determined or the variations introduced by varying atmospheric conditions.

The nonideality of the water vapour is the most severe approximation used to arrive at the main result, but its maximum influence remains limited to less than about 1% for temperatures up to 100 °C and less than 2‰ for atmospheric temperatures. In practice, any physically plausible choice for fixing the isobaric heat capacity of the vapour gives highly accurate results for a large useful temperature range.

It is suggested that Equation 13 (and Equation 17, in the case of vapour pressure over ice) can replace empirical equations for saturated vapour pressure in models: it is as accurate as many complex empirical fits, it can be optimized further for a temperature range of interest, it can be modified for other chemical components, it has clear physical content, and it is consistent with the usual thermodynamic approximations (ideality of vapour, incompressibility of liquid) normally applied in models of the atmosphere.

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