

The Rankine–Kirchhoff approximations for moist thermodynamics

Recently in this journal, Ambaum (2020) derived an expression for the saturation vapor pressure using three approximations: ideal gas, constant heat capacities, and zero specific volume of condensates. In so doing, Ambaum joined a great number of researchers, myself included, who have derived this expression independently with incomplete awareness of previous such work. To save others the trouble of reinventing the wheel, a brief history and overview of the Rankine–Kirchhoff equation is given below.

The first breakthrough in quantifying the saturation vapor pressure occurred at the beginning of the 19th century. Around that time, Dalton had discovered that the saturation vapor pressure for water is roughly exponential in temperature. When the temperature is raised successively by equal increments, Dalton (1802) noted that “there appears something like a geometrical progression in the forces of vapour; the ratio however, instead of being constant, is a gradually diminishing one.” Thus, to first approximation, we can capture the “geometrical progression” by writing the saturation vapor pressure p_v^* as

$$\log p_v^* = A + BT, \quad (1)$$

where T is the temperature and A and B are constants. While this is suitable for small temperature intervals, it does not capture the “gradually diminishing ratio”. Throughout the 19th century, well over a dozen empirical expressions were proposed for the saturation vapor pressure, all striving to account for that diminishing ratio. Among them was the popular empirical expression

$$\log p_v^* = A + \frac{BT}{1 + CT}, \quad (2)$$

which replaced B with $B/(1 + CT)$ to emulate a quasi-exponential dependence on T in which the fractional change of p_v^* per temperature increment (i.e., the ratio minus one) decreases with warming. This form for p_v^* was proposed simultaneously and independently by August (1828) and M. Roche (the 1828 memoir has been lost to time, but it is discussed by Avogadro, 1833; Russell, 1841; Barlow, 1845; Alexander, 1849; Callendar, 1911). Although first proposed by August and Roche,

atmospheric scientists most often refer to this as the “Magnus formula” (in reference to Magnus, 1844) or the “Tetens equation” (in reference to the particular constants advocated by Tetens, 1930). While the $1 + CT$ term does generate a “diminishing ratio”, it is important to note that it had no theoretical justification: it was simply a convenient way to fit the data.

It turns out, however, that we can capture the “diminishing ratio” with an analytic expression derived from first principles using some simplifying approximations. If water vapor can be approximated as an ideal gas, and if the temperature dependence of heat capacities can be ignored, and if the specific volumes of condensates can be treated as zero, then equating the Gibbs free energy of water vapor to that of the relevant condensed phase (either liquid or solid) yields a saturation vapor pressure of the form

$$\log p_v^* = A + B/T + C \log T. \quad (3)$$

Alternatively, defining p_{v0}^* to be the value of p_v^* when $T = T_0$, this can then be written as

$$\log (p_v^*/p_{v0}^*) = B(1/T - 1/T_0) + C \log(T/T_0). \quad (4)$$

A convenient choice for T_0 is the triple-point temperature, since that makes p_{v0}^* the same whether we are talking about saturation with respect to liquid or saturation with respect to solid. Instead of B and C being empirical values, their values are given by the derivation in terms of the fundamental physical properties of the phases of water, such as the heat capacities and internal energies.

The expressions for B and C depend on whether we have calculated the thermodynamic equilibrium between vapor and liquid or between vapor and solid. Substituting the relevant values and exponentiating, we find that the saturation vapor pressures with respect to liquid $p_v^{*,l}$ and with respect to solid $p_v^{*,s}$ are

$$p_v^{*,l} = p_{v0}^{*,l} \left(\frac{T}{T_0} \right)^{(c_{pv} - c_{vl})/R_v} \times \exp \left[\frac{E_{0v} - (c_{vv} - c_{vl})T_0}{R_v} \left(\frac{1}{T_0} - \frac{1}{T} \right) \right],$$

$$p_v^{*,s} = p_{v0}^{*,s} \left(\frac{T}{T_0} \right)^{(c_{pv}-c_{vs})/R_v} \times \exp \left[\frac{E_{0v} + E_{0s} - (c_{vv} - c_{vs})T_0}{R_v} \left(\frac{1}{T_0} - \frac{1}{T} \right) \right], \quad (5)$$

where c_{vv} , c_{vl} , and c_{vs} are the specific heat capacities at constant volume for vapor, liquid, and solid; c_{pv} equals $c_{vv} + R_v$; R_v is the specific gas constant for vapor; E_{0v} is the difference in specific internal energy between water vapor and liquid water at T_0 ; and E_{0s} is the difference in specific internal energy between liquid water and solid water at T_0 . Noting that the specific latent enthalpies of evaporation L_e and sublimation L_s are

$$L_e(T) = E_{0v} + R_v T + (c_{vv} - c_{vl})(T - T_0), \quad (6)$$

$$L_s(T) = E_{0v} + E_{0s} + R_v T + (c_{vv} - c_{vs})(T - T_0), \quad (7)$$

the vapor pressures can be written in terms of L_e and L_s (Rao, 1957; Novikov, 1976; Bogillo and Staszczuk, 1999; Smith, 2002; Ambaum, 2020) as

$$p_v^{*,l} = p_{v0}^{*,l} \left(\frac{T}{T_0} \right)^{(c_{pv}-c_{vl})/R_v} \exp \left(\frac{L_e(T_0)}{R_v T_0} - \frac{L_e(T)}{R_v T} \right),$$

$$p_v^{*,s} = p_{v0}^{*,s} \left(\frac{T}{T_0} \right)^{(c_{pv}-c_{vs})/R_v} \exp \left(\frac{L_s(T_0)}{R_v T_0} - \frac{L_s(T)}{R_v T} \right). \quad (8)$$

Returning to the history, it turns out that Equation 3 was originally derived, from first principles, by Kirchhoff (1858). Eight years later, Rankine (1866) derived the same expression independently, making the dependence on the heat capacities explicit as in Equation 5. Three years after that, Dupré (1869) derived Equation 3 independently on the basis that the latent enthalpy is linear in temperature, but did not relate the constants to heat capacities. These works were published in German, English, and French, respectively, which may explain why Rankine was unaware of Kirchhoff's work, and Dupré unaware of both Kirchhoff's and Rankine's.

The fact that these works were published in different languages and different countries likely also explains why the equation has been referred to by a bewildering array of names:

- Rankine–Kirchhoff (Cornelissen and Waterman, 1956; Biddiscombe and Martin, 1958; Waldenstrøm and Stølevik, 1980; Mishra and Yalkowsky, 1991; Yalkowsky and Mishra, 1991; Griesser *et al.*, 1999; Lobo and Ferreira, 2001; Wisniak, 2001; Smith, 2002; Tetko, 2007),
- Kirchhoff–Rankine (Laby, 1908b; Bradley and Swanwick, 1958; 1959; Davies and Taylor, 1964; Miller, 1964; 1966; Mazdiyasi *et al.*, 1967; Roder, 1977),

- Kirchhoff–Rankine–Dupré (Laby, 1908a; Smith and Menzies, 1910; Menzies, 1919; Kaye and Laby, 1921; Hine, 1924; Emmet, 1925; Holm, 1933; Gottschal and Korvezee, 1953; Jobson, 1973; Novikov, 1976; Wilcox and Bauer, 1991; Bogillo and Staszczuk, 1999; Mianowski and Urbańczyk, 2017),
- Rankine–Dupré (Cragoe *et al.*, 1920; Peirce, 1929),
- Dupré–Rankine (Juliusburger, 1900; Bittrich *et al.*, 1962; Siedler *et al.*, 1969; Schmeling and Strey, 1983), and
- Kirchhoff–Dupré–Rankine (Le Fèvre and Tideman, 1931).

Rankine's name is included in nearly all references because he derived Equation 5 with an explicit dependence on heat capacities (see equation B of Rankine, 1866), and, understandably, Kirchhoff is included in the vast majority of references since he was the first to derive the equation. On the other hand, Dupré is often omitted because he published third and, while he derived Equation 3, he did not express the coefficients in terms of heat capacities. It is arguable, therefore, that Equation 5—and all equivalent presentations such as Equation 8—should be referred to as either the Rankine–Kirchhoff or the Kirchhoff–Rankine equation. Of those two, modern usage favors Rankine–Kirchhoff, so that is the term I use here.

The three independent derivations in the mid-1800s were the first to be published, but they were not the last. Even as early as 1900, it was remarked that the same derivation had likely been repeated independently “von einer grosseren Zahl von Forschern” (“by a large number of researchers”: Juliusburger, 1900). One example is Hertz (1882), who derived the expression without making any reference to Rankine, Kirchhoff, or Dupré and was, therefore, likely unaware of those results. Adding to the confusion, some later authors have referred to the Rankine–Kirchhoff equation as Kirchhoff–Rankine–Dupré–Hertz (Menzies, 1927), Rankine–Kirchhoff–Dupré–Hertz (Miles and Menzies, 2002), and even Dupré–Hertz (Pospielow, 1907). In the 20th century, several textbooks derived the Rankine–Kirchhoff equation without giving it a name or referencing the literature (e.g., Emanuel, 1994; Bohren and Albrecht, 1998), so it is unclear if those were independent derivations or if, in the common style of textbooks, the references to the original literature were simply omitted. Another example is the textbook of Holmboe *et al.* (1945), which derived the expression, but referenced neither Rankine nor Kirchhoff. Instead, it incorrectly referred to the equation as the Magnus formula. Unfortunately, the misattribution to Magnus (1844) spread from Holmboe

et al. (1945) to several other publications (Parish and Putnam, 1977; Baldus *et al.*, 2015; Sarkar, 2015; Sanger and Kirkpatrick, 2017; Frasca *et al.*, 2018).

In 2008, I was unaware of this literature and the textbook derivations, but I used the same approximations as Rankine and Kirchhoff in developing the governing equations for my cloud-resolving model (Das Atmosphärische Modell: DAM) and for studying its entropy budget (Romps, 2008). By equating the Gibbs free energies of vapor and condensates, I derived the same p_v^{*1} and p_v^{*s} that had been derived, unbeknownst to me, exactly 150 years earlier by Kirchhoff (1858). I did not claim any novelty in having derived them, but I also did not search the literature to see if they had a name. It was just this year that I encountered Parish and Putnam (1977), who derived the same equations and erroneously attributed them to Magnus, which led me to pull on the thread of history. In the process of doing so, I came across Ambaum (2020), which convinced me that this history was worth sharing.

Unlike many other works, Ambaum (2020) made clear that the equation he derived had been derived before. Indeed, Ambaum (2020) cited several recent textbooks that gave derivations of it, including Ambaum (2010), although neither Ambaum (2020) nor any of those textbooks referred to the Rankine–Kirchhoff equation by its name. It is also worth noting that the derivation used by Ambaum (2020), which was to equate the Gibbs free energies of vapor and condensate, is the same method that was used to derive the Rankine–Kirchhoff equation by Gibbs himself (see the extended footnote beginning on page 152 of Gibbs, 1906).

Finally, there is an argument to be made that Rankine (1866) and Kirchhoff (1858) should be remembered not just for their saturation vapor-pressure equation, but also for how they derived it. They employed three powerful approximations: that the vapor behaves as an ideal gas; that the heat capacities are independent of temperature; and that the specific volumes of condensed water can be treated as zero for the purposes of thermodynamic calculations. These approximations may not be good choices for the wide range of conditions encountered in engineering applications, but they are perfectly suitable for the study and modeling of moist thermodynamics in Earth's atmosphere (Parish and Putnam, 1977; Romps, 2017; Ambaum, 2020). These approximations lead not only to an accurate and analytic expression for the saturation vapor pressure: they also lead more broadly to a whole system of accurate and analytic expressions relevant to the atmosphere, including the equivalent potential temperature (Hauf and Höller, 1987; Emanuel, 1994; Romps and Kuang, 2010), the quantity conserved by an adiabatically lifted parcel (Romps, 2015), the lifting condensation level (Romps,

2017), the dew point (Romps, 2021), and more. Since these three approximations are so powerful, and so worthy of being more widely known, I propose they be given a name. In recognition of those who first put them to notable use, a fitting candidate would be the “Rankine–Kirchhoff approximations”.

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