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On moist air and dew points

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Dynamics of moist air and condensation of water vapor in terrestrial atmosphere is responsible for many essential weather phenomena, some of them also quite hazardous. To understand many atmospheric phenomena and weather dynamics, we need to tour the field of thermodynamics and more specifically atmospheric thermodynamics and psychrometry. Thermodynamics is well-established fundamental scientific discipline essential to many engineering and atmospheric sciences, but is rather absent from the aviation/aeronautics curriculums. Hence, to understand the basics of moist air, atmospheric temperature lapse rates (ALR), dew points (and frost points), lifting condensation levels (LCL), etc., we need to comprehend fundamental thermodynamic processes first.

In aviation sciences and operations, moist air also affects aircraft performance, pressurization and air-conditioning systems (HVAC, HLS, and ECS systems), etc. Density altitude (DA) is a weak, nevertheless not negligible function of air moisture content. This is especially important for jet- and non-turbocharged piston-engines operations in warm climates and weather conditions with expected reduced performance in high air humidity. Air conditioning for use in aircraft's pressurized vessels necessarily has to remove large quantities of moisture to prevent ice formation and fuselage structural damages. Even such relatively dry cabin air will lead to swift cooling and condensation in the case of explosive/rapid decompressions filling the cabin with mist.

The main purpose of this review article is the desire to summarize and present fundamental thermodynamic considerations of moist air, atmospheric-water phase transitions, and dew points in a clear way. Of course, like in everything else it is not possible to cover every aspect of the topic presented. The goal is also to provide consistent derivations with necessary mathematical rigor. In addition, we provide some practical working equations for computation of specific- and relative-humidity (RH) from measured (dry) air and dew point (DP) temperatures and vice versa. Intent is also to provide deeper understanding of atmospheric thermodynamics and stress its importance and consequences, directly or indirectly, to flight operations. Thermodynamics is of essential important to meteorologists, but it is also important to aviation and aeronautics professionals, practitioners, pilots, operators, aviation/aeronautics education and air transportation in general.

To spare an average reader from simultaneously reading and consulting many expert books in theoretical, applied, and statistical thermodynamics, kinetic theory of gases, quantum statistics, and hundreds of articles dealing with the fundamental problems of thermodynamics, air motion and instability, we have summarized basic concepts. We tried to present this complex topic in a coherent uniform way using standard terminology. Nomenclature is provided at the end and just before references. Hence, parts of this lengthy article can be seen as short tutorials in important elements of atmospheric and engineering thermodynamics intended for professionals and students of aeronautics, aerospace, and aviation. In addition to this basic tailored review, we are also providing some new alternative working relationships for useful computations.

We consulted several expert books in equilibrium and non-equilibrium theoretical and applied (engineering) thermodynamics, statistical physics/mechanics, molecular physics, and kinetic theory of gases to verify our derivations. Among these are de Groot and Mazur (1984), Hansen (1976), Hill (1987), Holman (1980), Kennard (1938), Lay (1963), Reif (1965), Saad (1966), Sears (1953), Tribus (1961), and Wannier (1987). From books with specific emphasis on atmospheric thermodynamics we used texts by Iribarne and Godson (1981), Bohren and Albrecht (1998), and Tsonis (2007). We also used ASHRAE (2001) fundamentals manual with the focus on HVAC engineering and applications where physics of moist air is of paramount importance. Of the atmospheric science/physics, cloud physics, and dynamic meteorology books we consulted Fleagle and Businger (1980), Dutton (2002), Houghton (2002), Iribarne and Cho (1980), Rogers (1979), Saucier (1989), Stull (2016), and Wallace and Hobbs (2006). Popular meteorology and weather books by Forrester (1981) and Tufty (1987) were also consulted. Aviation and pilot-oriented meteorology and weather texts, such as, FAA (2016) do not provide much information on this matter. Many articles dealing with the specific topic discussed here were used and will be cited where and when appropriate.

This article is structured so that the basic thermodynamic theory, principles and properties of dry and moist air mixtures are summarized first. Next, derivation of phase transition equations and analytical integration of various phase transitions is presented. Finally, we introduce the concept of dew point and present some practical equations for computations of DPs and RH. This article primarily serves as a review of essential important atmospheric thermodynamic processes and provides a list of most relevant references that readers may use in further learning and research. We are also clarifying some common and widespread misconceptions about the moist air.

Theoretical Considerations

In this section, we present basic thermodynamic theory of dry and moist air and treat it as an ideal gas. While dry air in lower atmosphere behaves closely as an ideal gas, the fact is that moist air having a condensable phase shows larger departure from an ideal gas approximation.

Dry Air as an Ideal Gas

Homosphere's atmospheric air is a dilute mixture of gases (overwhelmingly diatomic molecular Nitrogen and Oxygen). Dry air is a mixture of non-condensable gases, i.e., gases that will not change phase (e.g., liquefy) in terrestrial atmospheric conditions. Gas per se is defined as a state-of-the-matter at temperatures above respective critical point (CP) temperature. Atmospheric dry air exists at temperatures well above its critical temperatures. No amount of pressure increase will liquefy gas, while vapors will liquefy (condense) under increasing pressures (or reduced temperatures). Humid or moist air contains variable amount of water vapor that could change into liquid (condensate) and/or solid (ice). For most practical applications, air is considered an ideal- or perfect-gas as the pressures are relatively low and temperatures not too high:

$$pV = \tilde{n}\Re T = mR_d T \qquad p\cdot\tilde{v} = \Re T \qquad p\cdot v = \frac{p}{\rho} = R_d T \tag{1}$$

Mass specific volume v, molar specific volume $\tilde{v}$, dry air gas-constant R_d, mass m, amount of mass (number of moles) $\tilde{n}$, molar mass M, and the molecular mass $\tilde{M}$ are:

$$v = \frac{V}{m}\left[\mathrm{m^3/kg}\right] \quad \tilde{v} = \frac{V}{\tilde{n}}\left[\mathrm{m^3/kg\cdot mol}\right] \quad R_d = \frac{\Re}{M}\left[\mathrm{J/kgK}\right] \quad m = \tilde{n}M = \tilde{n}N_0\tilde{M}\left[\mathrm{kg}\right] \quad N_0 = \frac{M}{\tilde{M}}$$

In ideal-gases, the internal energy u and the enthalpy h are both functions of temperature alone. An ideal-gas is also sometimes called *thermally perfect*, while if additionally, the specific heat capacities are constant (temperature independent) then it is also *calorically perfect* (Holman, 1980). Important physical constants are *Avogadro* number N_0, which defines the number of molecules per g-mol (or kilogram-mol) of substance, the universal gas-constant $\mathscr{R}$, which is related to specific gas-constant through molecular mass per mole, and the Boltzmann's constant k_B, given as:

$$N_0 = \left(6.022045 \pm 0.000031\right)\times 10^{26}\ \frac{\mathrm{molecules}}{\mathrm{kg\cdot mol}} \qquad \Re = 8314.41\,\frac{\mathrm{J}}{\mathrm{kg\cdot mol\cdot K}}$$

$$k_B = \frac{\Re}{N_0} = 1.3807\times 10^{-23}\ \frac{\mathrm{J}}{\mathrm{molecule\cdot K}}$$

The molar mass of dry air is 28.9644 (kg/kg-mol). Vapors are defined as gaseous phases below critical point's (CP) temperature (T_{CP}) close enough to the gas-liquid equilibrium curves where increasing pressure alone will liquefy the vapor. Vapors do not necessarily follow ideal-gas laws. Since the partial pressure of water vapor at room temperatures is very low in moist-air mixture, it is behaving closely to an ideal gas. Small deviations are taken care by using an *enhancement factor*, which is a weak function of pressure and temperature. Often, such corrections are omitted in practice other than for very accurate computations. Hence a kinetic model of air is represented as a system of many discrete particles (mono-atomic, di-atomic, tri-atomic, etc., molecules), which are widely separated and each particle is essentially unaffected by the presence of others. No molecular forces exist due to large distances, other than during brief perfectly elastic collisions in which linear-momentum between particles is exchanged. An air-parcel is an imaginary small volume of air containing huge number of molecules. The mean free-path (MFP) or the average distance a molecule travels before colliding with another molecule can be calculated using the classical kinetic theory of gases (Hansen, 1976; Kennard, 1938; Sears, 1953; Saad, 1966; Tribus, 1961):

$$\lambda = \frac{1}{\sqrt{2}\sigma n} = \frac{1}{\sqrt{2}\pi d^2 n} = \frac{k_B T}{\sqrt{2}\pi d^2 p} \qquad n = \frac{N}{V} = \frac{p}{k_B T}\left[\frac{\text{molecules}}{\text{m}^3}\right] \tag{2}$$

A typical Oxygen (O_2) or Nitrogen (N_2) molecule scattering cross-section areas are on the order of 10^{-10} m (0.1 nm). At SL ISA atmospheric pressure and temperature, the number of molecules per cm^3 (0.06 inch^3) is about 2.54×10^{19}. At one standard absolute atmosphere (1 ata or 760 torr or 1013.25 hPa/mbar or 29.92 inches Hg) and 15°C, MFP is approximately 10^{-8} m (10 nm) or two-orders of magnitude larger than the representative molecular linear size. It is also about one order-of-magnitude larger than the average linear spacing between molecules. In fact, molecular near-misses are more frequent then than collisions. The collision frequency of air molecules in a cm^3 at standard SL ISA conditions is about 10^9 collisions per second. Although, a large number, the fact is that molecules miss each other much more often than collide. An air-parcel volume can be defined using linear scale dimension of about 1 to 10 micrometers (at least two-orders of magnitude larger than MFP) for that matter. The "individuality" of molecules is completely lost in an air parcel and thermodynamic pressure, temperature, density, specific volume, etc., are defined within the realm of the continuum mechanics. More advanced MFP models involve, for example, *Lennard-Jones* potential implying distant molecules are slightly attracted, while closer particles are first attracted more as the distance between particles is reduced and then powerfully repelled when "too" close. Dry air behaves practically as a perfect-gas up to high pressures of about 200 bar (2,900 psi). Beyond that pressure, the molecules are “squeezed” so tightly that real-gas effects and inter-molecular forces should be taken into account. For the non-interacting non-condensable ideal-gas mixture, we can write (Holman, 1980):

$$\begin{gathered}
p=\sum_{i=1}^{n} p_i=\sum_{i=1}^{n} f_i p \qquad V=\sum_{i=1}^{n} V_i=\sum_{i=1}^{n} f_i V \\
M=\sum_{i=1}^{n} f_i M_i \qquad m=\sum_{i=1}^{n} m_i=\sum_{i=1}^{n} \tilde{n}_i M_i \qquad \sum_{i=1}^{n} f_i=\frac{1}{\tilde{n}}\sum_{i=1}^{n} \tilde{n}_i=\frac{1}{p}\sum_{i=1}^{n} p_i=\frac{1}{V}\sum_{i=1}^{n} V_i=1
\end{gathered} \tag{3}$$

These are the famous *Dalton* (partial pressures) and *Amagat-Leduc* (partial volumes) laws and apply to dilute gas mixture (Holman, 1980; Lay, 1963; Saad, 1966). Here, f_i’s are molal or volume fractions and differ from mass fractions. *Dalton* law implies that various gases coexist independently. The molar masses M and volume (concentration) fractions of the most abundant gases in the atmosphere are given in (National Oceanic and Atmospheric Administration, 1976). The average molar mass and the gas constant of dry air mixture up to about 86 km is (Daidzic, 2015):

$$\sum_{i=1}^{n} f_i M_i = M_d = 28.9644\,[\text{kg/kmol}] \qquad R=\frac{\Re}{M_d}=287.056\,[\text{J kg}^{-1}\ \text{K}^{-1}]$$

It is common to include all nonreactive trace gases (Argon, CO_2, etc.) with the molecular nitrogen and call it *atmospheric Nitrogen* (Saad, 1966). While most of the atmospheric Oxygen is in diatomic form, some O_3 and atomic Oxygen also exist. Practically, atmospheric dry air consists of inert atmospheric Nitrogen, Oxygen, and variable amount of atmospheric water. At standard SL atmospheric pressure and 273 K (about 0^{o}C) conditions one kg-mol of air occupies volume of 22.4 m^3. For an ideal gas, the specific heats at constant-pressure and constant-volume are:

$$c_p=\left(\frac{\partial h}{\partial T}\right)_p \qquad c_v=\left(\frac{\partial u}{\partial T}\right)_v \qquad c_p-c_v=R \qquad \tilde{c}_p-\tilde{c}_v=\Re \qquad \gamma=\frac{c_p}{c_v} \qquad \frac{c_p}{R}=\frac{\gamma}{\gamma-1} \tag{4}$$

Classical and statistical thermodynamics shows that for diatomic gases (N_2, O_2) at moderate temperatures (Sears, 1953):

$$c_p=\frac{7}{2}R \qquad c_v=\frac{5}{2}R \quad \Rightarrow \quad c_p-c_v=R \qquad \gamma=\frac{7}{5}=1.4 \tag{5}$$

We could model specific heat capacity (at constant pressure or constant volume) bit more generally and accurately with a polynomial fit:

$$c_x(T) = \alpha_x + \beta_x T + \gamma_x T^2 + \delta_x T^3 + \ldots$$

For example, in Tribus (1961) we find a correlation (originally due to Kobe, K. A.) for dry air valid for temperature range 273-1,800 K with maximum error of 0.72% and with coefficients converted in SI units here:

$$c_p(T) = a_0 + a_1 T + a_2 T^2 + a_3 T^3 \ [\text{J/kgK}] \tag{6}$$

where: $a_0 = 970.177 \quad a_1 = 67.8821 \quad a_2 = 165.767 \quad a_3 = -67.86764$

Enthalpy of dry air using Eq. (6) is:

$$h_d = \int c_p(T)\, dT = a_0 T + a_1 \frac{T^2}{2} + a_2 \frac{T^3}{3} + a_3 \frac{T^4}{4} \tag{7}$$

The isentropic process (ds=0) for an ideal gas is described as:

$$pv^{\gamma} = \text{const.} \qquad \gamma \equiv \frac{c_p}{c_v} = \frac{vdp}{-pdv} = -\frac{(dp/p)}{(dv/v)} = -\frac{d(\ln p)}{d(\ln v)} \tag{8}$$

Using the ideal-gas law (Eq. 1) in logarithmic form and keeping in mind that dry-air gas-constant is a constant, we obtain:

$$d(\ln v) = d(\ln T) - d(\ln p) \tag{9}$$

The ideal-gas dry-air isentropic relations follow from Eqs. (8) and (9):

$$\frac{p_1}{p_2} = \left(\frac{v_2}{v_1}\right)^{\gamma} = \left(\frac{T_1}{T_2}\right)^{\frac{\gamma}{\gamma-1}} \tag{10}$$

Isentropic relationships (Eq. 10) are used to define *potential temperatures* or *Poisson's equation* (Dutton, 2002):

$$\vartheta = T\left(\frac{1000}{p}\right)^{\frac{\gamma_d - 1}{\gamma_d}} \qquad \frac{R_d}{c_{pd}} = \frac{\gamma_d - 1}{\gamma_d} = \frac{2}{7} \approx 0.2857 \tag{11}$$

It is a temperature that air parcel will have at reference pressure of 1,000 mbar (or hPa) if isentropically expanding or compressing. As Iribarne and Cho (1980) state - air ascending isentropically (hence also adiabatically) in the atmosphere will have T and p varying according to *Poisson's* equation (Eq. 11). If air is moved adiabatically to reference 1,000 mbar pressure level, it will acquire potential temperature according to Eq. (11). This fact is used in construction of dry adiabats in meteorological thermodynamic diagrams. Selected physical and thermodynamic properties of most abundant gases found in terrestrial atmosphere are given in Table 1 (Holman, 1980; Saad, 1966; Sears, 1953).

Often vapors and gases do not follow ideal-gas model faithfully. For example, water vapor deviates from the ideal-gas behavior. In general, real gases can be described using the virial equation of state (Holman, 1980; Lay, 1963; Saad, 1966; Sears, 1953):

$$\frac{p\tilde{v}}{\Re T} = Z\left(p,T\right) = 1 + A\frac{p}{\Re T} + B\frac{p^2}{\Re T} + C\frac{p^3}{\Re T} + \ldots = 1 + A^{'}p + B^{'}p^2 + C^{'}p^3 + \ldots \tag{12}$$

Table 1

Selected Gas Properties at 15 to 20^{o}C and Atmospheric Pressure of 1 ata

Gas	M [kg/kg-mol]	c_p [J/kg K]	c_v [J/kg K]	R [J/kg K]	γ [-]	Λ [-]	T_{cr} [K]	P_{cr} [ata]
Air	28.9644	1,006	718	287.056	1.40	1.003	132.41	37.25
Ar	39.944	515	310	208	1.67	1.008	150.72	47.996
CO_2	44.011	846	653	188.9	1.304	1.027	304.20	72.90
H_2O	18.016	1,867	1,407	460.6	1.33	1.060	647.27	218.167
N_2	28.016	1,038	741	296.6	1.404	1.005	126.2	33.54
O_2	31.9988	917	653	259.6	1.401	1.004	154.78	50.14

Note: $\Lambda = \frac{c_p - c_v}{R} = \frac{\tilde{c}_p - \tilde{c}_v}{\Re}$

Additionally, many specialized real-gas equations/models of state exist, such as, already mentioned perturbative *virial* equation, *Van der Waals* equation, *Beattie-Bridgman* equation, *Dieterici* equation, two-parameter *Redlich-Kwong* model, *Peng-Robinson* model, etc. Many gases in homogeneous dry air mixture, such as N_2, show that compressibility factor stays almost constant and very close to one for not too high pressures. Unfortunately, that is not the case with water vapor. Non-ideal gas behavior of water vapor (e.g., *Mollier's* steam tables and diagram) is typically taken into account through experimentally obtained correction factors, which are weak functions of pressure and temperature (Alduchov & Eskridge, 1996; Buck, 1981; Hyland, 1975; Hyland & Wexler, 1983a, 1983b). Theoretical water-vapor real-gas models based on modeling of virial coefficients of moist air over liquid and/or ice are given, for example, in Hyland and Wexler (1973), Wexler and Greenspan (1971), and Wexler (1976, 1977).

Properties of Moist Air

Unsaturated moist or humid air is a two-component dilute gas mixture of inert dry air and superheated water vapor (Saad, 1966). Psychrometry is a branch of applied thermodynamics focusing on the properties and behavior of moist air and has many engineering applications, such as, in HVAC systems. We omitted *enhancement factor* for simplicity in this work. *Absolute humidity* of moist air is equal to water vapor mass density in an ideal-gas:

$$\rho_v = \frac{e}{R_v T} \qquad R_v = \frac{\Re}{M_{H_2O}} = \frac{8,314.41}{18.016} \approx 461.5\left[\text{J/kgK}\right] \tag{13}$$

We borrow the terminology mostly from meteorology. Partial pressure of water vapor in moist air e follows *Dalton* and *Amagat-Leduc* ideal-gas mixture laws to large extent (but not fully). The *mixture ratio* for two-component moist air mixture in thermodynamic equilibrium is:

$$r \equiv \frac{m_v}{m_d} = \frac{\rho_v}{\rho_d} = \frac{e}{p_d} \cdot \frac{R_d}{R_v} << 1 \tag{14}$$

The ratio of molar masses of dry air and water vapor is:

$$\varepsilon \equiv \frac{M_v}{M_d} = \frac{R_d}{R_v} \approx \frac{18.016}{28.9644} \approx \frac{287.056}{461.5} \approx 0.622 < 1 \tag{15}$$

Total mass of humid (moist, wet) air is thus:

$$m = m_d + m_v \quad \Rightarrow \quad \frac{m}{m_d} = 1 + r \geq 1 \qquad \frac{m_d}{m} = \frac{1}{1+r} \leq 1 \tag{16}$$

Up to 40 g (0.04 kg) H_2O per kg of dry air or 40 parts-per-thousand (‰) sometimes occur. In mid-latitude this is typically maximum of 15 to 20 g atmospheric H_2O per kg of dry air or 15 to 20 ‰. The *specific humidity* defines the amount of water vapor per unit mass of moist air:

$$\mathrm{q} \equiv \frac{m_v}{m} = \frac{m_v}{m_v + m_d} = \frac{\rho_v}{\rho_m} = \frac{r}{1+r} \approx r - r^2 + r^3 - r^4 + \ldots < r \tag{17}$$

Relative humidity (RH) is temperature dependent and defined as:

$$\varphi = \left(\frac{RH}{100} \right) \equiv \frac{e(T)}{e_s(T)} = \frac{r}{r_s} = \frac{\mathrm{q}}{\mathrm{q}_s} \left[- \right] \qquad RH \left[\% \right] \tag{18}$$

Atmospheric RHs (and other parameters) are measured with radiosondes and rawinsondes (FAA, 2016; Lester, 2007; Saucier, 1989). If we assume water vapor under low partial pressures to behave as an ideal-gas, we can write for thermodynamic equilibrium (T_v=T_d=T):

$$\frac{e}{p_d} = \frac{\rho_v R_v T_v}{\rho_d R_d T_d} \qquad T_v = T_d = T$$

and finally:

$$\frac{e}{p_d} = \frac{\rho_v R_v}{\rho_d R_d} = \frac{r}{\varepsilon} \approx 1.61 \cdot r$$

Now we have for mixture ratio:

$$r = \varepsilon \cdot \frac{e}{p_d} = 0.622 \frac{e}{p_d} = 0.622 \frac{e}{p - e} \approx 0.622 \frac{e}{p} \qquad e << p_d < p \tag{19}$$

Similarly, it can be shown:

$$\mathrm{q} = \frac{\varepsilon \cdot e}{p - (1-\varepsilon) \cdot e} = 0.622 \frac{e}{p - 0.378 \cdot e} \approx 0.622 \frac{e}{p} \qquad e << p_d < p \tag{20}$$

Moist air gas constant is derived from the mixture model:

$$mR_m = m_d R_d + m_v R_v \quad \Rightarrow \quad R_m = \frac{1}{1+r} R_d \left(1 + \frac{r}{\varepsilon}\right) \approx R_d \left(1 + 0.61 \cdot \mathrm{q}\right) \tag{21}$$

On the other hand:

$$\frac{e}{p} = \frac{\rho_v R_v T}{\rho_m R_m T} = \frac{\rho_v R_v}{\rho_m R_m} \approx \frac{\rho_v}{\rho_m} \frac{R_v}{R_d} \left(1 + 0.61 \cdot \mathrm{q}\right)^{-1} \approx \frac{\rho_v}{\rho_m} \frac{R_v}{R_d} \left(1 - 0.61 \cdot \mathrm{q}\right) \tag{22}$$

Mass density of moist air mixture follows directly:

$$\rho_m \approx \rho_d \cdot \left(1 - 0.61 \cdot \mathrm{q}\right) < \rho_d \tag{23}$$

Alternatively, we can write first-order approximation for the moist air mixture mass density using the ideal-gas law and the molar masses of water and non-condensable dry air mixture:

$$\rho_m = \frac{M_v p_v}{\Re T} + \frac{M_d \left(p - p_v\right)}{\Re T} \approx \frac{M_d p}{\Re T} \cdot \left(1 - 0.61 \cdot \frac{e}{p}\right) \approx \rho_d \left(1 - r\right) \tag{24}$$

Clearly, humid air is less dense than dry air occupying the same volume, which directly affects the density altitude (DA). In many cases, *r* is on the order of 10^{-2} and the moist-air gas-constant is only very slightly larger (1-2%) than for dry air, while the moist-air density is about 0.6% lower. In meteorology, it is preferable to keep dry-air gas-constant and use virtual temperatures (T_V) instead (Dutton, 2002; Rogers, 1979; Saucier, 1989; Tsonis, 2007):

$$p = \rho_m R_m T = \rho_m R_d \left(1 + 0.61 \cdot \mathrm{q}\right) T \approx \rho_m R_d T_V \quad \Rightarrow \quad T_V = T\left(1 + 0.61 \cdot \mathrm{q}\right) > T \left[\mathrm{K}\right] \tag{25}$$

In general, $\mathrm{T_{LCL}} < \mathrm{T_{DP}} < \mathrm{T_{WB}} < \mathrm{T} < \mathrm{T_V}$. Specific heats at constant pressure and volume for moist air are (Dutton, 2002):

$$
\begin{aligned}
c_{pm} &= \frac{1}{1+r}c_{pd} + \frac{r}{1+r}c_{pv} = c_{pd}\cdot\left(1+0.86\cdot \mathrm{q}\right) > c_{pd} \\
c_{vm} &= \frac{1}{1+r}c_{vd} + \frac{r}{1+r}c_{vv} = c_{vd}\cdot\left(1+0.96\cdot \mathrm{q}\right) > c_{vd}
\end{aligned}
\tag{26}
$$

Average values of specific heats at constant pressure and constant volume for water vapor and dry air are given in Table 1. Enthalpy of water vapor can be modeled similarly as for dry air using cubic fitting polynomials (Tribus, 1961). The specific enthalpy of moist air is a sum of dry air and water vapor enthalpies:

$$
mh_m = m_d h_d + m_v h_v \quad \Rightarrow \quad \left(1+r\right)h_m = h_d + r\cdot h_v \quad \Rightarrow \quad h_m = \frac{\mathrm{q}}{r}h_d + \mathrm{q}\cdot h_v \tag{27}
$$

The isentropic (and adiabatic) coefficient of expansion/compression of moist air is:

$$
\gamma_m \equiv \frac{c_{pm}}{c_{vm}} \approx \frac{c_{pd}\cdot\left(1+0.86\cdot \mathrm{q}\right)}{c_{vd}\cdot\left(1+0.96\cdot \mathrm{q}\right)} \approx \frac{c_{pd}}{c_{vd}}\left(1+0.86\cdot \mathrm{q}\right)\cdot\left(1-0.96\cdot \mathrm{q}\right) \approx \gamma_d\left(1-0.1\cdot \mathrm{q}\right) \tag{28}
$$

As specific humidity of moist air is approximately 10^{-2}, the reduction of isentropic coefficient for moist air is only about 1‰ of dry air value. It is thus acceptable to use dry air value in many applications. Another coefficient of frequent use in pseudo-adiabatic (saturated adiabats) processes of moist air is:

$$
\frac{c_{pm}}{R_m} = \frac{\gamma_m}{\gamma_m - 1} = \frac{c_{pd}\cdot\left(1+0.86\cdot \mathrm{q}\right)}{R_d\left(1+0.61\cdot \mathrm{q}\right)} \approx \left(\frac{\gamma_d}{\gamma_d - 1}\right)\left(1+0.25\cdot \mathrm{q}\right) \approx \frac{7}{2}\cdot\left(1+0.25\cdot \mathrm{q}\right) \tag{29}
$$

Isentropic process of ideal-gas moist air is described with:

$$
d\left(\ln T\right) = \left(\frac{\gamma_m - 1}{\gamma_m}\right) d\left(\ln p\right) \tag{30}
$$

Clapeyron and Clausius-Clapeyron Equations

Clapeyron (*C*) and the special case *Clausius-Clapeyron* (*C-C*) equation applied to ideal-gases describe phase transitions (Lay, 1963). *C-C* equation is normally used in gas-liquid phase transition computations, but can also be used for gas-solid (deposition/sublimation) transitions. A *C*-equation is used for liquid-solid transitions (solidification, melting, fusion, freezing) since no condensed phase (liquid or solid) behaves as an ideal gas. We will use the *C*-equation to compute the liquid water-ice transition. Sears (1953) provides a very elegant derivation of the *C*-equation, which will be replicated for convenience and importance. We will use two approaches in derivation, one involving *Carnot* process and the other *Gibbs* free-energy thermodynamic functions.

The most efficient thermodynamic cycle is the *Carnot* cycle, which consist of two isotherms during which heat is entering and leaving the system, and two adiabats defining isentropic compression and expansion. The efficiency of the *Carnot* cycle is:

$$\eta_C = \frac{W}{Q_{in}} = \frac{Q_{in} - Q_{out}}{Q_{in}} = \frac{T_2 - T_1}{T_2} = 1 - \frac{T_1}{T_2} \tag{31}$$

If we assume reversible *Carnot*-cycle engine operating in a single-component two-phase gas-liquid (vapor-liquid) phase transition region between two heat reservoirs (source and sink) and differing infinitesimally in temperatures (Sears, 1953), then:

$$\frac{\delta W}{Q} = \frac{dT}{T} \tag{32}$$

The heat entering the system from the source is used for phase change (liquid *v''* to vapor *v'''*) of working fluid of mass *m*, and the infinitesimal (but not a total differential) thermodynamic work obtained by gas-liquid ("gl") phase change and phase-transition expansion, are:

$$Q = L_{gl} = ml_{gl} \qquad \delta W = m\left(v''' - v''\right)dp_{gl} \tag{33}$$

Carnot-cycle efficiency is now:

$$\frac{\delta W}{Q} = \frac{m\left(v''' - v''\right)dp_{gl}}{m \cdot l_{gl}} = \frac{dT}{T} \tag{34}$$

The *C*-equation defining the slope of the *p*-*T* phase transition readily yields:

$$\frac{dp_{gl}}{dT} = \frac{l_{gl}}{T\left(v_{gs} - v_{ls}\right)} = \frac{l_{gl}}{T\left(v''' - v''\right)} \tag{35}$$

The *C*-equation for gas-liquid phase transitions can be extended to other phase transitions such as gas-solid (sublimation, deposition) and liquid-solid (fusion, solidification, melting, freezing, etc.). Another, and perhaps more elegant way to derive the *C*-equation is by using the *Gibbs* (free-energy) function (Saad, 1966; Sears, 1953), and defined in (Holman, 1980; Lay, 1963; Rief, 1965; Saad, 1966; Sears, 1953; Tribus, 1961) as:

$$G \equiv H - T \cdot S \qquad g = \frac{G}{m} = h - T \cdot s \tag{36}$$

According to the First Law-of-Thermodynamics, *Gibbs* function remains constant during liquid-vapor phase transition (Sears, 1953), i.e., $g'' = g'''$. Using the same *Carnot*-cycle process in the liquid-vapor region, we can write *Gibbs* function for a reversible process as:

$$dg = dh - T \cdot ds - s \cdot dT = -s \cdot dT + v \cdot dp \qquad \left(\delta q = T \cdot ds = dh - vdp\right) \tag{37}$$

Since, the *Gibbs* function stays constant for the vapor and liquid phases and temperature and pressure differential are equal in both phases (Sears, 1953), we can write:

$$-s'' \cdot dT + v'' \cdot dp = -s''' \cdot dT + v''' \cdot dp \quad \Rightarrow \quad \left(v''' - v''\right) dp = \left(s''' - s''\right) dT \tag{38}$$

The change of entropy during phase transition is related to the specific latent heat of condensation-evaporation:

$$\Delta s = \left(s''' - s''\right) = \frac{l_{gl}}{T} \tag{39}$$

Finally, the *Clapeyron* equation derived using the *Gibbs* functions becomes:

$$\frac{dp}{dT} = \frac{l_{gl}}{T\left(v''' - v'''\right)} = \frac{l_{gl}}{T\left(v_{gs} - v_{ls}\right)} = \frac{L_{gl}}{T \cdot \Delta V} \tag{40}$$

The *C-C* equation is the special case of the *C*-equation when the working gas/vapor is an ideal-gas. The *C-C* equation can be used for gas-liquid (condensation, evaporation) and gas-solid (deposition, sublimation) phase transitions. Since the specific volume of the gas is normally much larger than the specific volume of the liquid (condensed) phase, we have in the saturation region where the vapor behaves as an ideal gas:

$$\frac{de_s}{dT}=\frac{l_{\mathrm{lg}}}{T\left(v_s'''-v_s''\right)}\approx\frac{l_{\mathrm{lg}}}{T\cdot v_{sv}'''}\approx\frac{l_{\mathrm{lg}}\cdot e_s}{R_v\cdot T^2}\qquad v_s'''>>v_s'' \tag{41}$$

The *C-C* equation now becomes:

$$\frac{de_s}{dT}=\frac{l_{\mathrm{lg}}\cdot e_s}{R_v\cdot T^2} \tag{42}$$

The vapor pressure can also be presented in a modified *p-T* diagram (Lay, 1963):

$$\frac{d\left(\ln e\right)}{d\left(1/T\right)}=-\frac{l_{\mathrm{lg}}}{R_v}=-\frac{l_v}{R_v} \tag{43}$$

Thermodynamic diagrams used in meteorology and aviation weather product will show isobars, isotherms, isochores, dry-adiabats, pseudo-adiabats, isohumes etc. Some popular thermodynamic diagrams used for analysis of moist air are *Emagrams*, *Tephigrams*, *Skew-T log-p* diagrams, *Stüve* diagrams, etc. For more details and methods of construction, consult Saucier (1989), Stull (2016), and Tsonis (2007). In fact, Reichmann (1993) uses *Stüve* diagrams for planning cross-country soaring flights.

Theoretical and Semi-Empirical Models of Phase Transitions

The *Clapeyron* (*C*) equation can be simplified and integrated easily in the case when the working fluid is (or approximately is) an ideal gas. Since the specific volume of saturated gas is normally much larger than of saturated liquid, we can write *C*- and *C-C* equations as:

$$\frac{de_s}{dT}=\frac{l_v}{T\left(v_s'''-v_s''\right)}\quad\Rightarrow\quad\frac{de_s}{dT}=\frac{l_v\cdot e_s}{R_v\cdot T^2}\qquad v_s'''>>v_s'' \tag{44}$$

This differential equation is integrated directly when the latent heat of vaporization l_v is constant:

$$\int_{e_{sTP}}^{e_s} d\left(\ln e_s\right) = -\frac{l_v}{R_v}\int_{T_{TP}}^{T} d\left(\frac{1}{T}\right) \quad \Rightarrow \quad \ln\frac{e_s}{e_{sTP}} = \frac{l_v}{R_v}\left(\frac{1}{T_{TP}} - \frac{1}{T}\right) = \frac{l_v}{R_v T_{TP}}\left(1 - \frac{T_{TP}}{T}\right)$$

$$\Rightarrow \quad e_s\left(T\right) = e_{sTP}\cdot\exp\left[\frac{l_v}{R_v T_{TP}}\left(1 - \frac{T_{TP}}{T}\right)\right] = \underbrace{\left[e_{sTP}\cdot\exp\left(\frac{l_v}{R_v T_{TP}}\right)\right]}_{=\text{const}}\cdot\exp\left(-\frac{l_v}{R_v T}\right) \tag{45}$$

As the temperature increases so does the average molecular kinetic energy and less energy is required for phase transition. In condensation process, the latent heat is released (less energy is needed to keep molecules close together in condensed state than in a gas). However, in the first approximation and for limited temperature range of interest in meteorology and aviation sciences, we assumed that the latent heat of phase transition is constant in Eq. (45). The reference point in *C-C* equation is based on the well-defined triple-point (TP) of water (all three phases coexisting) with the equilibrium pressure of about 611.657 Pa or 6.11657 mbar or hPa (Guildner et al., 1976) and water TP-temperature of 273.16 K (0.01^{o}C). Hence, for vaporization (vapor-liquid) transition:

$$e_s\left(T\right) = 611.657\cdot\exp\left[\frac{l_v}{R_v}\left(\frac{1}{273.16} - \frac{1}{T}\right)\right] = 611.657\cdot\exp\left(19.831 - \frac{5417.12}{T}\right)\left[\text{Pa}\right]$$
$$l_v \approx 2,500\ \text{kJ/kg} \qquad R_v \approx 461.5\ \text{J/kgK} \qquad \text{T}\in\left[-50^o\text{C}, +40^0\text{C}\right] \tag{46}$$

Sears (1953) provides derivation of the TP conditions and shows by analytical considerations that its temperature is about *0.01* K higher than the ice-point temperature. For a vapor-solid transition (sublimation, deposition) and constant latent-heat of phase transition, we have similarly:

$$e_S\left(T\right) = 611.657\cdot\exp\left[\frac{l_{sg}}{R_v}\left(\frac{1}{273.16} - \frac{1}{T}\right)\right] = 611.657\cdot\exp\left(22.50 - \frac{6145.18}{T}\right)\left[\text{Pa}\right] \tag{47}$$

where:

$$l_{sg} = 2,836\ \text{kJ/kg, T}\in\left[-50^o\text{C}, 0^o\text{C}\right]$$

In the case of liquid-solid transition, we have to use *C*-equation. Interestingly, water is just one of the very few substances in nature, which has solid phase (ordinary ice) with a larger specific volume (lower density) than the corresponding liquid phase. Water expands upon freezing resulting in a negative melting/fusion slope, which is so important in nature:

$$\begin{aligned} de_{sm} &= \frac{l_{sl}}{\left(v_{sl}-v_{sm}\right)}\frac{dT}{T} \\ \Rightarrow \quad e_m &= e_0-\left(\frac{l_{sl}}{\Delta v}\right)\cdot\ln\left(\frac{T}{T_0}\right)=611.657-\left(36.8\times10^{8}\right)\cdot\ln\left(\frac{T}{273.16}\right) \end{aligned} \tag{48}$$

So far, we have assumed latent heat to be constant in given temperatures zone. That may be acceptable for vapor-solid water transition, but not sufficiently accurate for vapor-liquid transition. Indeed, latent heat of vaporization is function of temperature. Dutton (2012) delivers temperature-dependent linear fit of the latent heat of evaporation in terms of cal/g (1 cal/g=4.186 kJ/kg) as:

$$l_v = 597-0.57\cdot\left(T-273\right)\left[\text{cal/g}\right] \qquad \frac{dl_v}{dT}=-0.57<0 \qquad T\in\left[233,313\right] \tag{49}$$

or in SI units

$$l_v = 2,499-2.386\cdot\left(T-273\right)\left[\text{kJ/kg}\right] \qquad \frac{dl_v}{dT}=-2.386<0 \qquad T\in\left[233,313\right] \tag{50}$$

Based on thermodynamic considerations and varying enthalpies and specific heat capacities of saturated liquid and saturated vapor, Tsonis (2007) shows that approximately:

$$\begin{aligned} &l_v = l_{v0}+\left(c_{pv}-c_{pw}\right)\left(T-T_0\right)=2,500-2.368\cdot\left(T-273\right)\left[\text{kJ/kg}\right] \\ &l_{v0}=2.50\times10^{6}\ \text{J/kg}, \quad c_{pv}=1.850\times10^{3}\ \text{J/kgK}, \quad c_{pw}=4.218\times10^{3}\ \text{J/kgK} \end{aligned} \tag{51}$$

Dutton’s (2002) linear approximation agrees well with the tabulated water vapor saturation pressures provided in Rogers (1979), Saucier (1989) and Stull (2016). The *C-C* integral with temperature-dependent latent heat of condensation results in:

$$\int_{p_{TP}}^{p_s} d\left(\ln e_{vs}\right)=\frac{l_{v0}}{R_v}\int_{T_{TP}}^{T}\frac{\left[1-a\cdot\left(T-273\right)\right]dT}{T^2} \qquad a=\frac{2.386}{2,499}=9.548\times10^{-4}\left[\text{K}^{-1}\right] \tag{52}$$

The integration (temperature in K) yields:

$$\ln\frac{e_s}{e_{TP}}=\frac{l_{v0}}{R_v}\cdot\left[(1+a\cdot 273)\cdot\left(\frac{1}{T_{TP}}-\frac{1}{T}\right)-a\cdot\ln\left(\frac{T}{T_{TP}}\right)\right]$$
$$\Rightarrow\quad e_s\left(T\right)=611.657\cdot\exp\left(54.015-\frac{6829.36}{T}-5.1723\cdot\ln T\right)\left[\mathrm{Pa}\right]\tag{53}$$

We could have also used more accurate higher-order polynomial representation of the latent heat as a function of temperature. However, the fact remains that *C-C* equation is only an approximation of phase transition thermodynamics for ideal gases. Water vapor does not behave exactly as an ideal gas and the presence of the non-condensable dry-air component complicates the situation a bit. More accurate water vapor saturation pressure correlations exist. They are semi-empirical based on measurements and have been continuously refined over the last 200 years. We will only mention relatively simple, yet reasonably accurate *Magnus*-type equations.

The *Clausius-Clapeyron* equation was derived based on an existence of pure substance, e.g., water vapor and liquid in equilibrium. However, most air contains dry non-condensable or inert fraction and the variable water content in all three phases. The question arises on how does pressure of inert gas components affect the vapor pressure. In fact, Sears (1953) and Saad (1966), provide answer to that question. Utilizing *Gibbs* function equality in the presence of the inert gas component. In moist air, the water vapor changes phases in the presence of dry air. The pressure of the inert (indifferent) dry air affects the equilibrium vapor pressure in moist air mixture to a small degree. True, the effect is small, but has been included in many other studies for higher accuracy. For example, Buck (1981) and Alduchov and Eskridge (1996) provide equations for the *enhancement factor f*, which is defined as the ratio of the saturation water vapor pressure of moist air to that of pure water vapor and solid water, i.e., ice:

$$f_v=\frac{e_v'}{e_v}\qquad f_i=\frac{e_i'}{e_i}\tag{54}$$

While the equilibrium (saturation) vapor pressure is a function of temperature only, the enhancement factor is a weak function of both, pressure and temperature (Alduchov & Eskridge, 1996; Buck, 1981). This can be observed from the virial equation of state given by Eq. (12).

Dew Point and Relative Humidity Computations

DP is temperature achieved by isobaric cooling of moist air until equilibrium vapor pressure is reached (so-called "saturation" vapor pressure). This process can be observed in the *p-T* diagram shown in Fig. 1. While not the most suitable diagram to show atmospheric thermodynamic processes, it will suffice for our purpose. Using definition of RH from Eq. (18), we write:

$$\ln\varphi(T)=\ln e(T)-\ln e_s(T) \tag{55}$$

For example, RH can increase by increasing vapor pressure (adding water vapor or humidifying to air) as it is done in HVAC applications and occurs in some meteorological phenomena or by cooling air parcels at constant pressures (e.g., radiation fog or advection fog). As seen in Fig. 1, isobaric cooling of air parcel moves the state from the starting point **A** to the point **C** located on the saturation line. Since the process is isobaric and we have closed material system, the vapor pressure at point **A** with temperature T has the same vapor pressure as the point **C** or the DP. There is no exchange of mass/matter with the surroundings, but there is energy/heat exchange (cooling) and thus it is not an adiabatic process. Following the isoenthalpy line from point **A** we arrive at point **D** on the liquid-vapor equilibrium curve. Point **D** defines the WB-temperature of state **A**. Accordingly, for unsaturated region (e.g. point A), the relation DB > WB > DP is valid. RH can be calculated from DB and WB temperature measurements (ASHRAE, 2001). Additionally, DPs are related to RH:

$$e(T)=e_s(T_{DP}) \quad\Rightarrow\quad \varphi=\frac{RH}{100}=\frac{e_s(T_{DP})}{e_s(T)} \tag{56}$$

Using the *C-C* equation derived in Appendix D, we may write:

$$e_s(T)=e_{sTP}(T_{TP})\cdot\exp\left[\frac{l_v}{R_v}\left(\frac{1}{T_{TP}}-\frac{1}{T}\right)\right]=C_1\cdot\exp\left(-\frac{l_v/R_v}{T}\right)\qquad C_1=e_{sTP}(T_{TP})\cdot\exp\left(\frac{l_v/R_v}{T_{TP}}\right)$$

(57)

Eq. (57) defines DP at constant DB air temperature T and is designated in Fig. 1 with point **B**. The saturation pressure at point **B** (isothermal heating) is higher than the saturation pressure at point **C** (T_{DP}) achieved by isobaric cooling of an air parcel. Hence, RH is less than one at point **A** (with associated mixture ratio and specific humidity). The vapor pressure at point **A** with unsaturated air and the saturation pressure at DP for condition **C** are equal:

$$e_s\left(T_{DP}\right)=e_{sTP}\left(T_{TP}\right)\cdot\exp\left[\frac{l_v}{R_v}\left(\frac{1}{T_{TP}}-\frac{1}{T_{DP}}\right)\right]=C_1\cdot\exp\left(-\frac{l_v/R_v}{T_{DP}}\right) \tag{58}$$

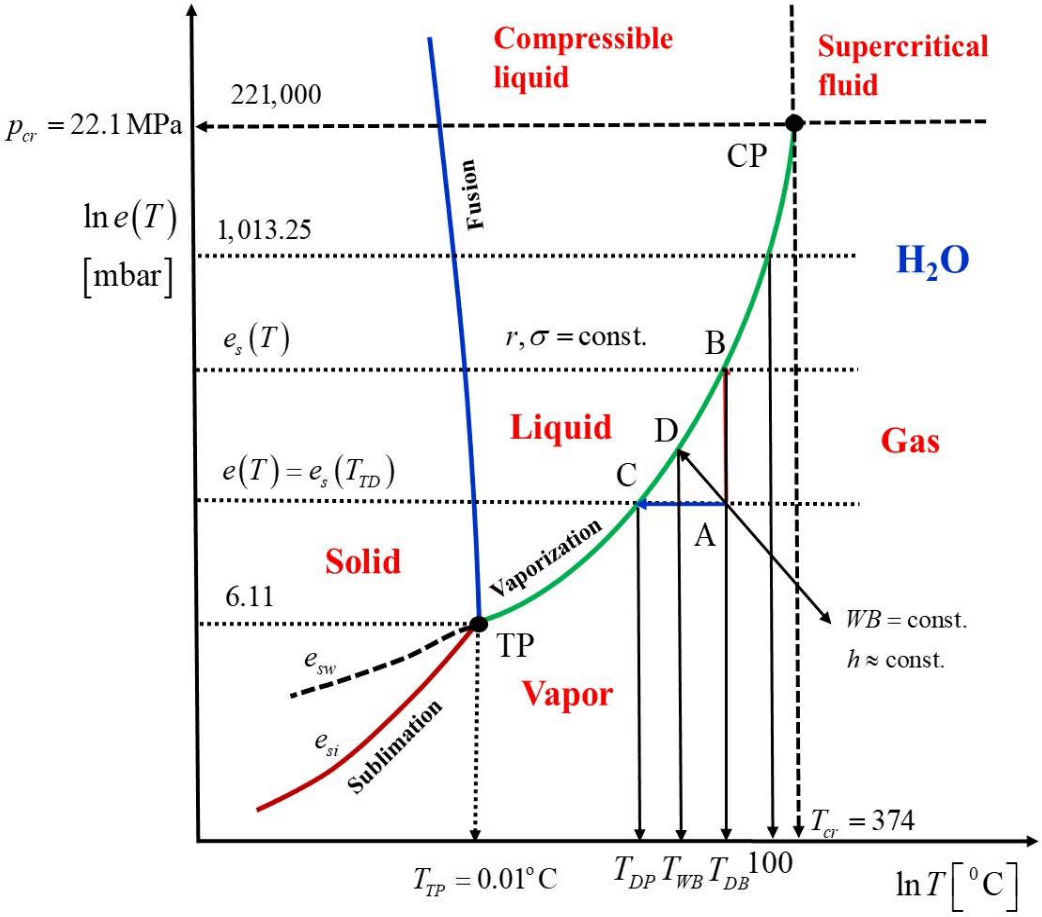

Figure 1. Schematic of the thermodynamic *p-T* phase diagram for pure water. (Not to scale).

If DPs and air temperatures are known, RH is computed as:

$$\varphi=\exp\left[\frac{l_v}{R_v}\left(\frac{1}{T}-\frac{1}{T_{DP}}\right)\right]\approx\exp\left[-5417\cdot\left(\frac{T-T_{DP}}{T\cdot T_{DP}}\right)\right] \tag{59}$$

Assuming all pseudo-constants remain unchanged during the isobaric cooling, we obtain:

$$T_{DP}\left(T,RH\right)=T\left[1-\frac{T}{5417}\cdot\ln\left(\frac{RH}{100}\right)\right]^{-1}=T\left(1-\frac{T}{5417}\cdot\ln\varphi\right)^{-1} \tag{60}$$

This is the same result as obtained by Lawrence (2005). Related but not identical to DP is the WB-temperature (ASHRAE, 2001). RH of air can be computed or by DB and WB temperatures using psychrometer (with some corrections) or by dry-bulb (DB) air temperature and hygrometers (e.g., chilled-mirror dew point hygrometer) measuring DPs directly. Using DP depression, we obtain for RH directly from Eq. (59):

$$RH\left(T,T_{DP},D\right)=100\cdot\exp\left(-\frac{5417\cdot D}{T\cdot T_{DP}}\right) \tag{61}$$

While usually easiest to measure using common (DB) thermometers, in case DP and RH are only known, the air temperature estimate is:

$$T\left(T_{DP},RH\right)=T_{DP}\left[1+\frac{T_{DP}}{5417}\cdot\ln\left(\frac{RH}{100}\right)\right]^{-1} \tag{62}$$

As reported by Buck (1981), Alduchov and Eskridge (1996), and Lawrence (2005) among many other authors, a large number of expressions for computation of water and ice saturation vapor pressures, DPs, and RH exist. Of many models, we will only mention popular *Magnus*-type formulas for saturation vapor pressures for water and ice (Alduchov & Eskridge, 1996; Buck, 1981; Lawrence, 2005). Lawrence (2005) refers to *Magnus*-formulas as more appropriately *August-Roche-Magnus* type of formulas. Essentially, the same form of the expression was used with ever improving coefficients based on more accurate water vapor pressure measurements. Even more accurate correlations for the region of interest in meteorology exist, but will not be addressed here. For more details on various models, the reader is encouraged to consult Buck (1981) and Alduchov and Eskridge (1996). An *August-Roche-Magnus* empirical formula for water saturation vapor pressure is (Buck 1981; Lawrence, 2005) yields:

$$e_s(\theta) = C \cdot \exp\left(\frac{A \cdot \theta}{B+\theta}\right)[\mathrm{Pa}] \qquad -40^{\mathrm{o}}\mathrm{C} \le \theta \le 50^{\mathrm{o}}\mathrm{C}$$
$$A = 17.625\,[-] \quad B = 243.04\left[{}^{\mathrm{o}}\mathrm{C}\right] \quad C = 610.94\,[\mathrm{Pa}] \tag{63}$$

The coefficients are from Alduchov and Eskridge (1996). DPs are now:

$$\theta_{DP} = \frac{B \cdot \ln\left(\frac{e}{C}\right)}{A - \ln\left(\frac{e}{C}\right)} = \frac{B \cdot \left[\ln\left(\frac{RH}{100}\right) + \frac{A \cdot \theta}{B+\theta}\right]}{A - \ln\left(\frac{RH}{100}\right) - \frac{A \cdot \theta}{B+\theta}} \quad \left[{}^{\mathrm{o}}\mathrm{C}\right] \tag{64}$$

Linearized expression for DPs when RH > 50%, was proposed by Lawrence (2005):

$$\theta_{DP} = \theta_{AIR} - \frac{(100 - \mathrm{RH})}{5}\left[{}^{o}\mathrm{C}\right] \qquad RH \ge 50\% \tag{65}$$

Lawrence (2005) also provides simple estimate of RH from air and DP temperatures:

$$\mathrm{RH} = 100 - 5 \cdot \left(\theta_{AIR} - \theta_{DP}\right) \qquad RH \ge 50\% \tag{66}$$

Results and Discussion

Numerical values of saturated water vapor pressure in equilibrium with liquid water is shown in Fig. 2 on semi-logarithmic plot. The *C-C* equation solutions using constant latent heat of evaporation (Eq. 46) and linearly varying latent heat of evaporation (Eq. 53) in the range of interest are plotted against the experimental data from the Smithsonian Meteorological Tables as reported in Rogers (1979) and Saucier (1989). More accurate measurements of the saturation vapor pressure (over liquid and ice) are given, for example, in ASHRAE (2001) and Buck (1981). Those data are actually based on the measurements and correlations from Wexler (1976, 1977) and Hyland and Wexler (1983a, 1983b). Additionally, we used *Magnus*-type semi-empirical correlation with the constant coefficients coming from Alduchov and Eskridge (1996) as given in Eq. (63). This semi-empirical correlation provides no real advantage over theoretical *C-C* relationships for the given temperature range. In fact, the *C-C* model using linearly changing latent heat of evaporation provides best fit to experimental/measured data.

Water saturated vapor pressures in equilibrium with super-cooled liquid water and solid water (ice) is shown in Fig. 3. We used *C-C* theoretical models in both cases. The latent heat of sublimation for water vapor-ice is fairly constant over the temperature range. For the vapor-liquid equilibrium, we also used *C-C* model with latent heat of evaporation changing linearly for the given temperature range. The experimental data over ice are taken from ASHRAE (2001), Buck (1981), Wexler (1977), and Bielska et al. (2013). The experimental data from Buck (1981), Rogers (1979) and Saucier (1989) were used for vapor-liquid equilibrium in super-cooled (metastable) region. All these comparisons were also used to verify vapor pressure models for subsequent analysis of LCL.

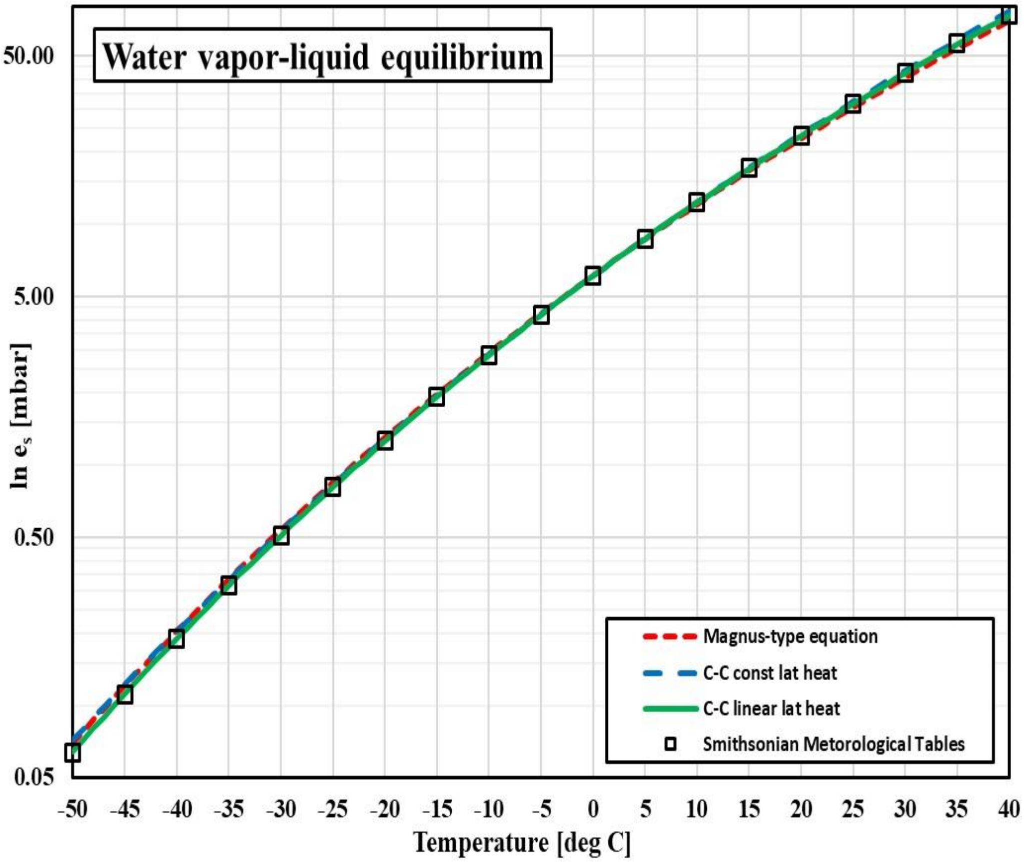

Figure 2. Saturated vapor pressure over liquid water in equilibrium using *Clausius-Clapeyron* theoretical model, *Magnus*-type semi-empirical correlation and experimental data.

Saturation values for mixture ratio (green squares) and specific humidity (red solid line) are shown in Fig. 4 together with the vapor mass as a function of air temperature (black solid line). Note rapid increase in water vapor amount with higher air temperatures (above about 10^{o}C). The difference between the mixture ratio and specific humidity is small indeed and barely observable until high air temperatures. Highest recorded DPs were around 36^{o}C. That corresponds to about maximum amounts of 40-gram water per kg of dry air. Apparently, small amount, but the energy released per kg of dry air in condensation is very significant.

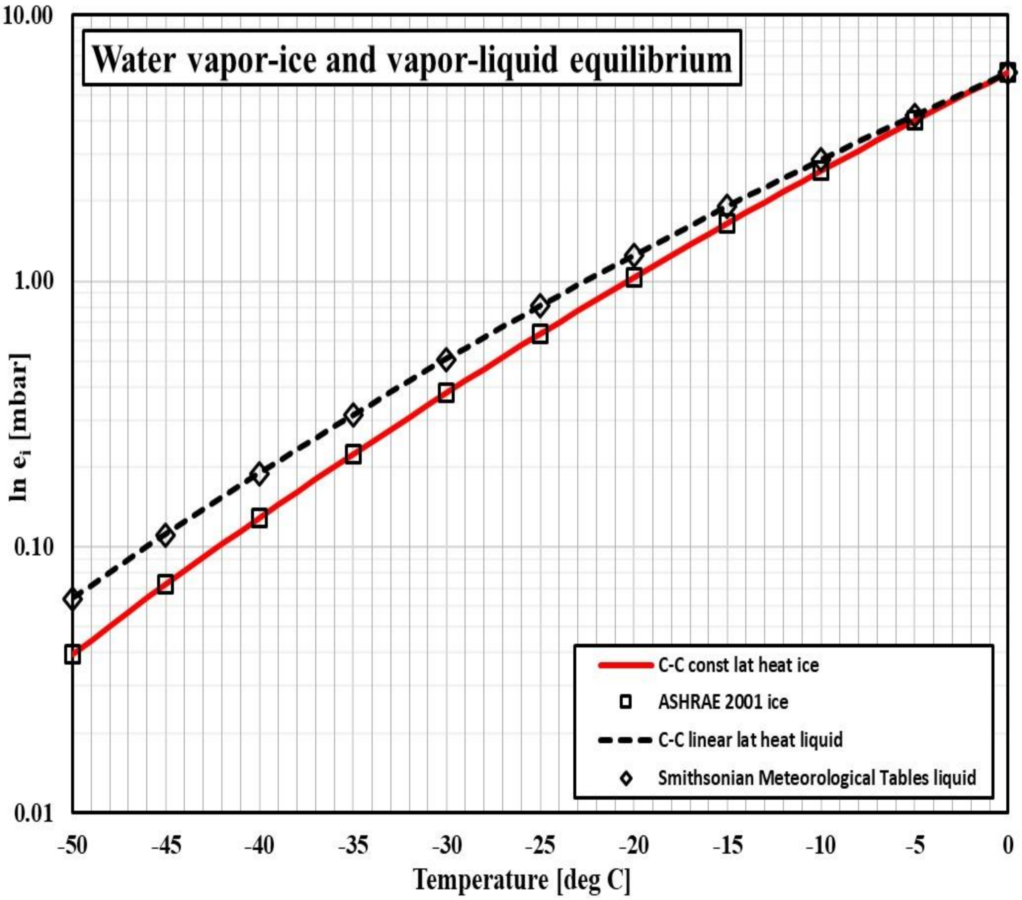

Figure 3. Equilibrium vapor pressure over solid water (ice). Equilibrium vapor-liquid pressures in super-cooled region are given as well.

Computations of DPs versus DB air temperatures for constant parametric RHs (40-100%) is shown in Fig. 5. Besides results from model used (Eq. 60), we also presented DP computations based on Magnus-type formula given with Eq. (63)

and Lawrence's estimate from Eq. (65). Computations of DPs using simple Magnus-type formulas with optimized Alduchov and Eskridge (1996) coefficients does not deviate much from computations based on simple *C-C* model. Errors using Lawrence's model (2005) are large below RH of 50% and increase somewhat with higher air temperatures for any RH at and above 50%. Computations of RHs from known DB air temperatures and DP depressions is shown in Fig. 6. Again, we added Lawrence's (2005) simple model given with Eq. (66). Clearly, errors are large in Lawrence's model for RH < 50%, which the author clearly stated. We also observe that in Lawrence's model RH, while on average is a decent approximation for higher RHs, is a constant over the entire range of temperatures for constant DP depressions. Hence, it can serve as a good first approximation or as a rule-of-thumb only. For more accurate computations of RH we recommend using Eq. (61).

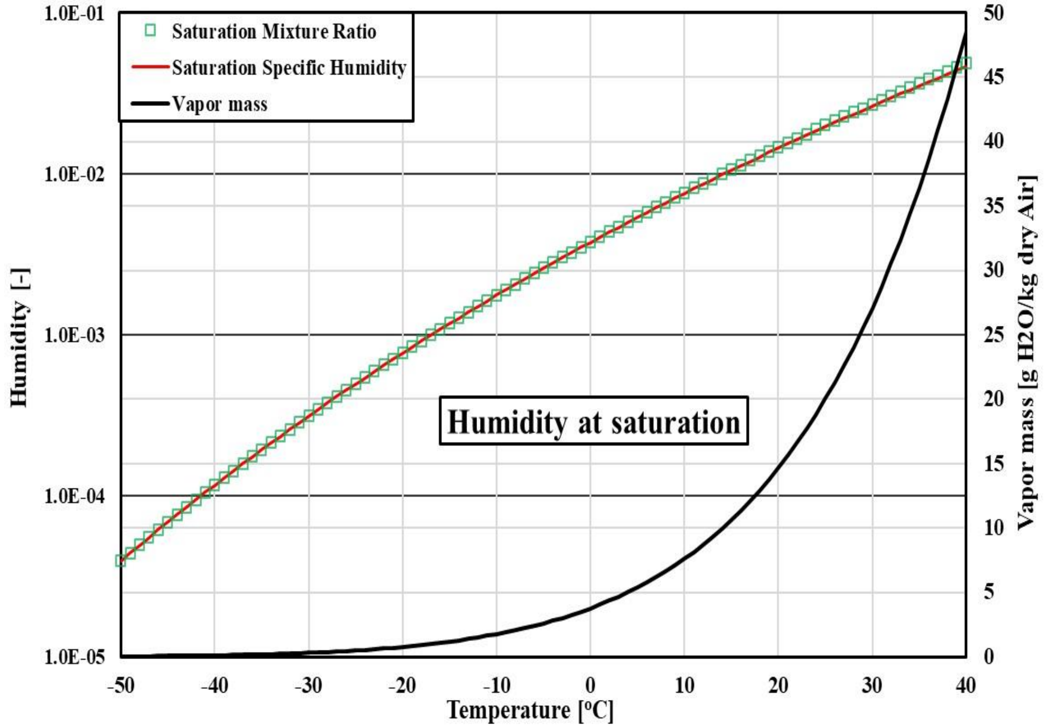

Figure 4. Mixture ratio, specific humidity and water vapor mass (g/kg dry air) at saturation.

The largest source of uncertainties in our model comes from the deviations of moist air from the ideal-gas law and by assuming that thermodynamic parameters remain constant in a given temperature region. Simultaneously tackling all these additional variables would considerably complicate the analysis and would require much more space and effort. Additionally, the effects of Henry's and Raoult's laws (Bohren, 2001; Lay, 1963; Pauling, 1988) were not considered in phase transitions. In fact, atmospheric air will dissolve into liquid water (precipitation) as governed by the Henry's law.

As we have seen, relatively small amount of water vapor co-exists with atmospheric dry air circulating primarily in troposphere. However, latent heat of vapor-liquid phase transition is relatively large (about 2,500 kJ/kg). A typical mid-latitude T-storm (CB) can contain at any moment about 10 million kg of water vapor, which upon condensation would release about 10 TJ of energy. That would be equivalent to about metric 2.4 kiloton (TNT) energy release. Of course, T-storms are extremely complex and dynamic thermal-fluid phenomenon and moist air (T-storm's "fuel") is entrained for the significant part of their lifetime, so the total energy released can be significantly higher. Luckily, all that energy is released over relatively long time (temporal scale on the order of an hour) and large space (spatial scale of a km or a mile). Nevertheless, CBs are violent and present real hazard in commercial and personal air transportation.

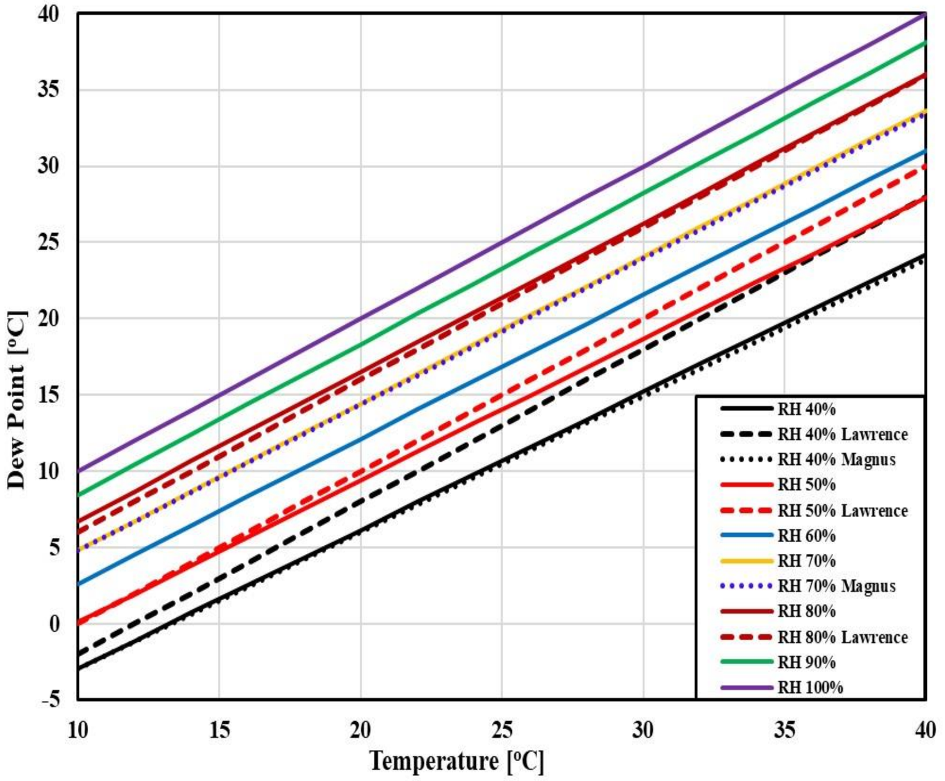

Figure 5. DP change versus air temperature for various RHs.

One of the persistent common misconceptions is that air somehow “holds” or “contains” variable amount of water vapor depending on its own temperature and that upon reaching certain limit it cannot “hold” more water vapor – and the excess must condense. Such notion is false and is also repeatedly stated in some aviation weather texts. Such misconception has been rebutted often. For example, Bohren (2001) gives an eloquent no-formula explanation of the “air-absorbing-water-vapor” fallacy. Explanations of the actual physics can be found in many expert references cited here. In ideal gas, the molecules of dry air and water vapor co-exist in the entire volume being practically “ignorant” of each other. Dry air cannot “count” and “manage” water-vapor molecules. Hence, dry air has no “knowledge” how much water molecules are there and therefore cannot control it. This issue has been stated long time ago by the English chemist and meteorologist John Dalton. Dalton was indeed conducting phase transitions experiment. He is most famous for introducing atomic theory in chemistry and research in gas laws.

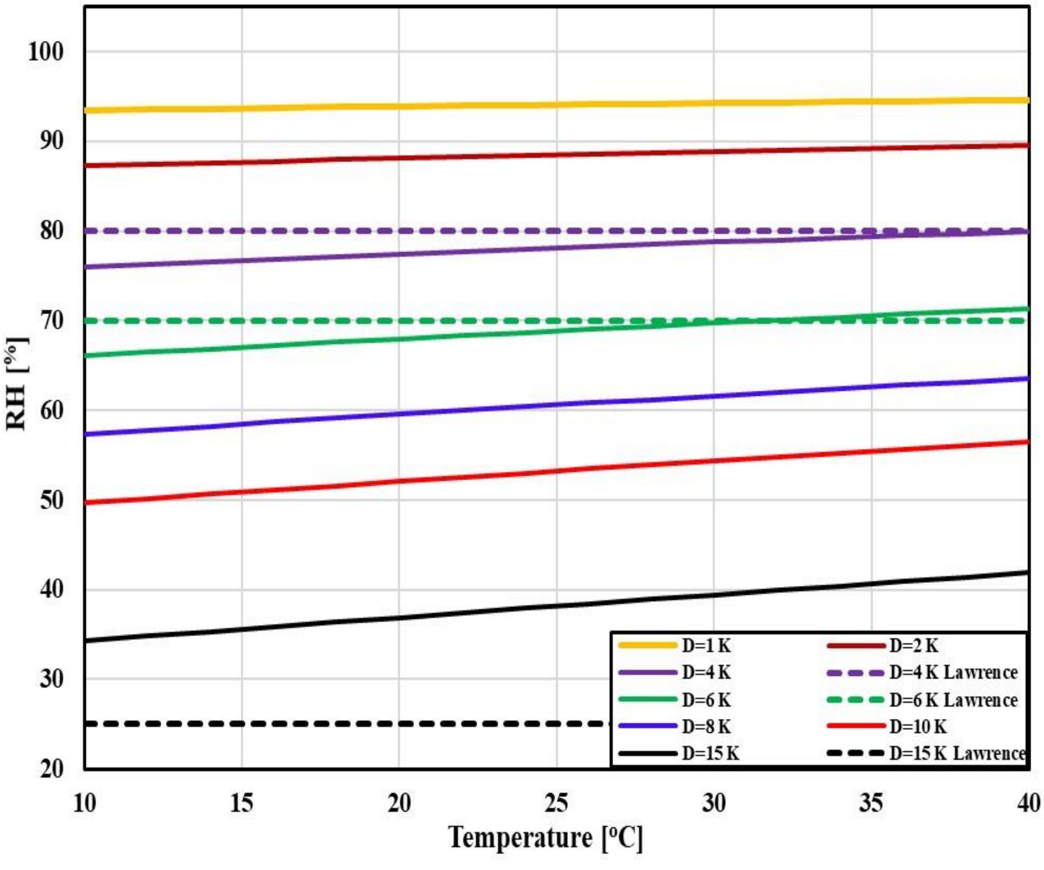

Figure 6. RH change versus air temperature for various DP depressions.

Interestingly, the term "*Daltonism*" was given to *color blindness* condition honoring Dalton's original research in that area. Moist air thermodynamics is necessary ingredient in development of complex atmospheric models, cloud–resolving physics, and detailed energy budgets as given, for example, in Romps (2008).

The maximum amount of water vapor and the saturation of equilibrium between vapor and liquid phases is governed by the *Clapeyron* equation. True, the presence of non-condensable (inert) dry air mixture does affect the water vapor equilibrium pressure, but to a very small degree. For example, Sears (1953) and Saad (1966) show that increase in the partial pressure of inert gas (dry air) does affect the saturation (phase equilibrium) pressure of the condensable component by increasing the pressure in the liquid phase which then increases evaporation rate thus increasing vapor saturation pressure and vapor content. However, this effect is very small. Thermodynamic equilibrium is assumed to take place instantly. The effect is stronger as the equilibrium temperatures and pressures increase. In addition, one has to consider that water vapor does not follow the ideal-gas law faithfully. For example, Saucier (1989) includes a deviation from the ideal-gas law factor in defining moist air parameters. Hence, combined effects due to non-ideal gas behavior and the presence of non-condensable dry air component is taken into account through, the so called, *enhancement factor "f"*, which is a very weak function of temperature and pressure. In a sense, the *enhancement factor* is an inverse of the *compressibility factor* Z (≤ 1) from the virial equation, which is a function of pressure and temperature and different for every gas or vapor (Holman, 1980; Hyland, 1975; Lay 1963; Wexler, 1976, 1977; Wexler and Greenspan, 1971). While *Clapeyron* equation is exact, the *Clausius-Clapeyron* equation is only an approximation of the *Clapeyron* equation when condensable component (e.g., water vapor in air) mimics ideal gas in its gaseous phase. Hence, the equilibrium liquid-vapor pressure values are not truly exact using *C-C* equation. Therefore, many empirical correlations have been developed for water vapor pressure in the past 200 years or so.

Conclusions

The basic thermodynamic theories of dry and moist air are summarized and most important relationships were derived for clarity and better understanding. Atmospheric water vapor-liquid, vapor-ice and liquid-ice phase transitions described by the Clapeyron and Clausius-Clapeyron equations are also presented. While moist air exhibits real-gas behavior for many practical applications not requiring very high accuracies, it can be regarded as an ideal-gas. Some common misconception regarding moist air have been addressed. Basic theory and several original practical expressions to compute dew points and/or relative humidity are given and compared to existing ones. Density altitude corrected for humidity can be easily computed from presented moist air thermodynamic relationships, but that has not been presented in this article. Understanding thermodynamics and dynamics of atmospheric moist air and phase transitions is of fundamental importance for safety, economy, and performance of flight operations.

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Nomenclature

Greek

$\gamma\left[-\right]$	Isentropic coefficient.
$\varepsilon\left[-\right]$	Ratio of molecular masses for humid air.
$\varphi\left[-\right]$	Relative humidity.
$\lambda\left[\mathrm{m}\right]$	Mean free path (MFP).
$\rho\left[\mathrm{kg/m^3}\right]$	Density (mass).
$\sigma\left[\mathrm{m^2}\right]$	Molecular cross-section area.

Alphabetic

$c\left[\mathrm{kJ/kg\ K}\right]$	Specific heat capacity.
$e\left[\mathrm{Pa}\right]$	Water vapor pressure.
$f\left[-\right]$	Enhancement factor or molal/volume fractions.
$g\left[\mathrm{m/s^2}\right]$	Terrestrial gravitational acceleration.
$h\left[\mathrm{kJ/kg}\right]$	Enthalpy.
$l\left[\mathrm{J/kg}\right]$	Mass specific latent heat (vaporization, fusion, etc.).
$p\left[\mathrm{Pa}\right]$	Pressure (thermodynamic).
$\mathrm{q}\left[-\right]$	Specific humidity.
$q\left[\mathrm{J/kg}\right]$	Specific heat.
$r\left[-\right]$	Mixture ratio.
$s\left[\mathrm{kJ/kg\ K}\right]$	Entropy.
$v\left[\mathrm{m^3/kg}\right]$	Specific volume.
$z\left[\mathrm{m}\right]$	Height (Orthometric).
$D\left[\mathrm{K}\right]$	Dew point depression (spread).
$H\left[\mathrm{m}\right]$	Height (Geopotential).
$L\left[\mathrm{J}\right]$	Latent heat (vaporization, fusion, etc.).
$M\left[\mathrm{kg/kg\text{-}mol}\right]$	Molar Mass.

$N_0\ [\text{molecl/mol}]$	Avogadro number.
$Q\ [\text{J}]$	Heat.
$R_0\ [\text{m}]$	Radius (average) of spherical Earth approximation.
$R\ [\text{J/kg K}]$	Gas constant (gas specific).
$\Re\ [\text{J/kg K}]$	Ideal-gas constant.
$T\ [\text{K}]$	Temperature.
$V\ [\text{m}^3]$	Volume.
$W\ [\text{J}]$	Work (thermodynamic or technical).
$Z\ [-]$	Compressibility factor (real gases).

Subscripts

d	Dry.
i	Ice (water).
m	Mixture.
p	Constant pressure process.
s	Saturated.
v	Vapor, wet.
v	Constant volume process.

DP	Dew point.
M	Moist (humid).
TP	Triple point.

Abbreviations

ASHRAE	American Society of Heating, Refrigerating and Air-Conditioning Engineers.
CB	Cumulonimbus cloud (T-Storm).
C-C	Clausius-Clapeyron (equation).
CN	Condensation Nuclei.
D	Dew point depression (spread) [K].
DA	Density Altitude [m, ft].
DB	Dry Bulb
DP	Dew Point [K].
ECS	Environmental Control Systems.
ELR	Environmental Lapse Rate.

FP	Frost Point.
HLS	Human Life Support Systems.
HVAC	Heating Ventilation Air-Conditioning.
LCL	Lifting Condensation Level.
LR	Lapse Rate [K/m].
MALR	(unsaturated) Moist Air Adiabatic Lapse Rate.
RH	Relative humidity [%].
WB	Wet Bulb.

References

Alduchov, O. A. & Eskridge, R. E. (1996). Improved Magnus form approximation of saturation vapor pressure. *Journal of Applied Meteorology, 35*, 601-609. doi: 10.2172/548871.

ASHRAE. (2001). *Fundamentals handbook* (SI). Atlanta, GA: Author.

Bielska, K., Havey, D. K., Scace, G. E., Lisak, D., Harvey, A. H., & Hodges J. T. (2013). High-accuracy measurements of the vapor pressure of ice referenced to the triple point. *Geophysical Research Letters*, *40*, 6303-6307, doi:10.1002/2013GL058474

Bohren, C. F., & Albrecht, B. A. (1998). *Atmospheric thermodynamics*. Oxford, UK: Oxford University Press.

Bohren, C. F. (2001). *Clouds in a glass of beer: Simple experiments in atmospheric physics*. Mineola, NY: Dover.

Bolton, D. (1980). The computation of equivalent potential temperature. *Monthly Weather Review*, *108*, 1046–1053, doi:10.1175/1520-0493(1980)108,1046:TCOEPT.2.0.CO;2.

Buck, A. (1981). New equations for computing vapor pressure and enhancement factor. *Journal of Applied Meteorology*, *20*, 1527-1532. doi:10.1175/1520-0450(1981)020<1527:NEFCVP>2.0.CO;2.

Daidzic, N. E. (2015a). Efficient general computational method for estimation of standard atmosphere parameters. *International Journal of Aviation Aeronautics and Aerospace, 2*(1), 1-37. doi:10.15394/ijaaa.2015.1053

Dutton, J. A. (2002). *The ceaseless wind: An introduction to the theory of atmospheric motion*. Mineola, NY: Dover.

Federal Aviation Administration (2016). *Aviation weather* (AC 00-6B). Department of Transportation (DOT), Washington, DC: Author.

Fleagle, R. G., & Businger, J. A. (1980). *An introduction to atmospheric physics* (2nd ed.). New York, NY: Academic Press.

Forrester, F. H. (1981). *1001 questions answered about the weather*. New York, NY: Dover.

Guildner, L. A., Johnson, D. P., & Jones, F. E. (1976). Vapor pressure of water at its triple point. *Journal of Research of the Natural Bureau of Standards, 80A*(3), 505–521, doi:10.6028/jres.080A.054.

de Groot, S. R., & Mazur, P. (1984). *Non-equilibrium thermodynamics*. Mineola, NY: Dover.

Hansen, C. F. (1976). *Molecular physics of equilibrium gases* (NASA SP-3096). Washington, DC: National Aeronautics and Space Administration.

Hill, T. L. (1987). *Statistical mechanics: Principles and selected applications*. Mineola, NY: Dover.

Holman, J. P. (1980). *Thermodynamics* (3rd ed.). Singapore, Singapore: McGraw-Hill.

Houghton, J. (2002). *The physics of atmosphere* (3rd ed.). Cambridge, United Kingdom: University Press.

Hyland, R. W. (1975). A correlation for the second interaction virial coefficients and enhancement factors for moist air. *Journal of Research of the National Bureau of Standards, 79A*(4), 551–560. doi:10.6028/jres.079a.017.

Hyland, R. W., & Wexler, A. (1973). The Second Interaction (Cross) Virial Coefficient for Moist Air. *Journal of Research of the National Bureau of Standards, 77A*(1), 133–147. doi:10.6028/jres. 077a.007

Hyland, R. W., & Wexler, A. (1983a). Formulations for the thermodynamic properties of the saturated phases of H_2O from 173.15 K to 473.15 K. *ASHRAE Transactions*, *89*(2A), 500-519.

Hyland, R. W., & Wexler, A. (1983b). Formulations for the thermodynamic properties of dry air from 173.15 K to 473.15 K, and of saturated moist air from 173.15 K to 372.15 K, at pressures to 5 MPa. *ASHRAE Transactions, 89*(2A), 520-35.

International Civil Aviation Organization (1993). *Manual of the ICAO standard atmosphere* (Doc 7488-CD, 3rd ed.). Montreal, Canada: Author.

International Organization for Standardization (1975). *Standard atmosphere* (ISO 2533:1975/Add. 2: 1997(en)). Geneva, Switzerland: Author.

Iribarne, J. V., & Cho, H.-R. (1980). *Atmospheric physics.* Dordrecht, Holland: D. Reidel Publishing Company.

Iribarne, J. V., & Godson, W. L. (1981). *Atmospheric thermodynamics* (2nd ed.). Dordrecht, Holland: D. Reidel Publishing Company.

Kennard, E. H. (1938). *Kinetic theory of gases, with an introduction to statistical mechanics*. New York, NY: McGraw-Hill.

Lawrence, M. G. (2005). The relationship between relative humidity and the dewpoint temperature in moist air: A simple conversion and applications. *Bulletin of the American Meteorology Society, 86,* 225–233. doi:10.1175/BAMS-86-2-225

Lay, J. E. (1963). *Thermodynamics: A macroscopic-microscopic treatment*. Columbus, OH: Charles E. Merill Books.

National Atmospheric and Oceanic Administration. (1976). *U.S. standard atmosphere, 1976* (NOAA-S/T 76-1562). Washington, D.C.: U.S. Government Printing Office.

Pauling, L. (1988). *General chemistry*. Mineola, NY: Dover.

Reif, F. (1965). *Fundamentals of statistical and thermal physics*. New York, NY: McGraw-Hill.

Reichmann, H. (1993). *Cross-country soaring* (7th ed.). Stuttgart, Germany: Motorbuchverlag (English translation by the Soaring Society of America (SSA).

Rogers, R. R. (1979). *A short course in cloud physics* (2nd ed.). Oxford, UK: Pergamon Press.

Romps, D. M. (2008). The dry-entropy budget of a moist atmosphere. *Journal of Atmospheric Science, 65,* 3779-3799, doi:10.1175/2008JAS2679.1

Saad, M. A. (1966). *Thermodynamics for engineers*. Englewood Cliffs, NJ: Prentice Hall.

Saucier, W. J. (1989). *Principles of meteorological analysis*. Mineola, NY: Dover.

Sears, F. W. (1953). *Thermodynamics, the kinetic theory of gases, and statistical mechanics* (2nd ed., 5th printing 1964). Reading, MA: Addison-Wesley.

Stull, R. (2016). *Practical meteorology: An algebra-based survey of atmospheric science*. http://www.eos.ubc.ca/books/Practical_Meteorology/

Tribus, M. (1961). *Thermostatics and thermodynamics*. Princeton, NJ: Van Nostrand.

Tsonis, A. A. (2007). *An introduction to atmospheric thermodynamics* (2nd ed.). Cambridge, UK: University Press.

Tufty, B. (1987). *1001 questions answered about hurricanes, tornadoes and other natural disasters*. New York, NY: Dover.

Wallace, J. M., & Hobbs, P. V. (2006). *Atmospheric science: An introductory survey* (2nd ed.). Burlington, MA: Academic Press.

Wannier, G. H. (1987). *Statistical physics*. Mineola, NY: Dover.

Wexler, A., & Greenspan, L. (1971).Vapor pressure equation for water in the range 0 to 100°C. *Journal of Research of the National Bureau of Standards, 75A*(3), 213–230. doi:10.6028/jres.075a.022.

Wexler, A. (1976). Vapor pressure formulation for water in range 0 to 100°C. A revision. *Journal of Research of the National Bureau of Standards, 80A*(5 and 6), 775–785. doi: 10.6028/jres.080a.071.

Wexler, A. (1977). Vapor pressure formulation for ice. *Journal of Research of the National Bureau of Standards, 81A*(1), 5–20. doi:10.6028/jres.081a.003