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Psychrometric Properties of Humid Air from Multi-Fluid Helmholtz-Energy-Explicit Models [a]

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ABSTRACT

Psychrometric properties of humid air are widely used in the analysis and modeling of thermal systems. In this work we present a method for obtaining these properties from the multi-fluid mixture formulation of the GERG mixture model. This mixture model was originally developed to model the thermodynamics of natural gas mixtures, and now has been extended to model thermodynamic properties relevant for carbon capture and storage. The primary advantage of this formulation is that the dry air composition is not fixed, and can be adjusted to suit the application, for instance in submarines, for Martian atmospheres, etc.

We present an algorithm that can be used to calculate the saturated vapor water composition in vapor-liquid equilibrium, and other properties that arise out of this equilibrium calculation, such as relative humidity and dewpoints. Solid-vapor equilibrium is not considered, and neither is the calculation of wet-bulb temperatures.

1. INTRODUCTION

Psychrometry is the study of mixtures of water and air. In this section, we will discuss the general characteristics of psychrometry and the evaluation of psychrometric properties in a manner that is independent of the underlying thermodynamic model.

There have been a number of formulations of the properties of humid air proposed over the years, with varying levels of complexity and accuracy:

- Wexler *et al.* (1983), Nelson and Sauer (2002)
- ASHRAE Handbook (ASHRAE, 2001)
- ASHRAE RP-1485 (Herrmann et al., 2009a)

The work of Herrmann *et al.* (2009b) (page 53) provides an overview of the models that had been developed as of 2009.

One of the nomenclature-related issues that constantly bedevils the discussion of psychrometric property evaluation is the fact that in most psychrometric evaluations, the thermodynamic properties are used on a per-unit-dry-air basis. Not all works are consistent or clear about their choice of nomenclature, and the distinction between properties defined on a per-unit-dry-air or per-unit-humid-air basis is one of the most frequent sources of confusion. In this work, the mixture model always considers the entire humid air mixture, and never the dry air by itself. Therefore, all properties derived from the mixture model are on a per-unit-humid-air basis.

For the subset of thermodynamic properties considered here, the distinction between per-unit-dry-air or per-unit-humid-air properties does not generally arise. In contrast, in many applications (e.g., the evaluation of cycle efficiency in a Brayton cycle), enthalpies and entropies are required. In that case, it is important to be explicit about whether properties are on a per-unit-dry-air or per-unit-humid-air basis.

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2. AIR

2.1 Dry air composition

The composition of dry air is given on a mole fraction basis. Humid air can be modeled as a pseudo-binary mixture formed of water vapor and a fixed-composition dry air. While the exact composition of dry air varies slightly with time and location, the composition of dry air is dominated by the composition contributions from nitrogen, oxygen, and argon, which form more than 99.95% of the molar composition of dry air. The current international standard for the composition of dry air is that of Picard *et al.* (2008).

In practice, the minor constituents of air can be neglected as they do not contribute significantly to the thermodynamics of the dry air mixture. It is common to keep only the top three or four constituents. In this work, we have decided to use a four-component dry air mixture with the composition as given in Table 1. These values are based on the top four components given by Picard, and evenly distributing the remaining mole fraction of 3×10^{-5} from the minor constituents among the top three components (by adding 1×10^{-5} to each).

Table 1: Composition of dry air using four major components

Component	Variable	Mole fraction
Nitrogen	z_{N_2}	0.780858
Oxygen	z_{O_2}	0.20940
Argon	z_{Ar}	0.009342
Carbon dioxide	z_{CO_2}	0.0004

The molar mass of the dry air is obtained as a mole-fraction-weighted average obtained from the fixed composition of dry air

$$M_{da} = z_{N_2} M_{N_2} + z_{O_2} M_{O_2} + z_{Ar} M_{Ar} + z_{CO_2} M_{CO_2}. \tag{1}$$

2.2 Humid air composition

The humid air mixture can then be treated as a binary mixture of water and dry air. For a given water mole fraction x_{H_2O}, the dry air mole fraction is $x_{da} = 1 - x_{H_2O}$, and the mixture composition array $\boldsymbol{x}$ can then be calculated from

$$x_{N_2} = (1 - x_{H_2O}) z_{N_2} \tag{2}$$
$$x_{O_2} = (1 - x_{H_2O}) z_{O_2} \tag{3}$$
$$x_{Ar} = (1 - x_{H_2O}) z_{Ar} \tag{4}$$
$$x_{CO_2} = (1 - x_{H_2O}) z_{CO_2}, \tag{5}$$

where the values of the mole fractions of the dry air constituents can be found in Table 1. The mole fractions of all the constituents must therefore sum to unity:

$$x_{H_2O} + x_{N_2} + x_{O_2} + x_{Ar} + x_{CO_2} = 1. \tag{6}$$

The molar mass of the humid air is then obtained as a mole-fraction-weighed average of the dry air and water

$$M_{ha} = x_{H_2O} M_{H_2O} + (1 - x_{H_2O}) M_{da}. \tag{7}$$

Unless otherwise specified, the composition of dry air is assumed to be fixed with the composition of Table 1.

3. MIXTURE MODEL

3.1 Model formulation

The GERG (Groupe Européen de Recherches Gazières) mixture model is formulated based on mixing rules combining highly-accurate equations of state for the pure components forming the mixture. This mixture model has been extensively described in the literature (Kunz et al., 2007; Kunz and Wagner, 2012; Gernert et al., 2014; Gernert and

Span, 2016). This model is formulated in terms of the fundamental thermodynamic potential of Helmholtz free energy, which is appealing as all other properties can be obtained as derivatives of the Helmholtz free energy. For instance, the pressure can be evaluated from

$$p = \rho R T \left(1 + \delta \left(\frac{\partial \alpha^r}{\partial \delta} \right)_\tau \right), \tag{8}$$

where the variables are described in the nomenclature. All other properties like molar-specific entropy and molar-specific enthalpy can be obtained in a similar fashion. The non-dimensionalized temperature $\tau = T_r(\boldsymbol{x})/T$ and density $\delta = \rho/\rho_r(\boldsymbol{x})$ are used in the place of the dimensional quantities, where the reducing functions are

$$T_r(\boldsymbol{x}) = \sum_{i=1}^{N} x_i^2 T_{c,i} + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} 2 x_i x_j \beta_{T,ij} \gamma_{T,ij} \frac{x_i + x_j}{\beta_{T,ij}^2 x_i + x_j} (T_{c,i} T_{c,j})^{0.5} \tag{9}$$

$$\rho_r(\boldsymbol{x}) = \left[\sum_{i=1}^{N} x_i^2 \frac{1}{\rho_{c,i}} + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} 2 x_i x_j \beta_{v,ij} \gamma_{v,ij} \frac{x_i + x_j}{\beta_{v,ij}^2 x_i + x_j} \frac{1}{8} \left(\frac{1}{\rho_{c,i}^{1/3}} + \frac{1}{\rho_{c,j}^{1/3}} \right)^3 \right]^{-1} \tag{10}$$

and contain the adjustable binary interaction parameters $\beta_{T,ij}$, $\gamma_{T,ij}$, $\beta_{v,ij}$, and $\gamma_{v,ij}$.

The total non-dimensionalized Helmholtz free energy α is given as the summation of the ideal-gas contribution α^0 (not considered further here) and the residual part α^r. The residual non-dimensionalized Helmholtz free energy α^r is given by the form

$$\alpha^r = \sum_{i=1}^{N} x_i \alpha_{oi}^r (\tau, \delta) + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} x_i x_j F_{ij} \alpha_{ij}^r (\tau, \delta) \tag{11}$$

where α_{oi}^r is the contribution from the i-th pure component evaluated at the mixture τ and δ, α_{ij}^r is a mixture departure function for the ij binary pair, and F_{ij} is a constant weighting factor for the ij binary pair.

3.2 Humidity ratio
The humidity ratio W is defined as the mass of water in the mixture to the mass of dry air, or

$$W \equiv \frac{m_{H_2O}}{m_{da}} = \frac{M_{H_2O}}{M_{da}} \frac{x_{H_2O}}{1 - x_{H_2O}}. \tag{12}$$

If the humidity ratio W is known, the water mole fraction x_{H_2O} can be obtained from

$$x_{H_2O} = \frac{W \dfrac{M_{da}}{M_{H_2O}}}{1 + W \dfrac{M_{da}}{M_{H_2O}}}. \tag{13}$$

3.3 Relative humidity
There are a number of different definitions for the relative humidity of humid air. Lovell-Smith (2016) covers the different definitions that are available in the literature. The most commonly used definition of the relative humidity, and accordingly that employed here, is that it is the ratio of the mole fraction of water to the mole fraction of water at saturation at the same temperature and pressure. As discussed below, an iterative solution is required to obtain the mole fraction of water in the vapor phase at saturation (humid air in equilibrium with liquid water at a given temperature and pressure). Thus we can define the relative humidity φ as

$$\varphi \equiv \frac{x_{H_2O}}{x''_{H_2O,sat}(T,p)} \tag{14}$$

If dry-bulb temperature and pressure are known, $x''_{H_2O,sat}$ can be obtained through the use of the methods presented below, and x_{H_2O} can be obtained from Eq. 14 for the given relative humidity φ.

3.4 Density

If dry-bulb temperature, pressure, and density are known (for instance when constructing psychrometric charts), the mole fraction of water x_{H_2O} must be obtained through the use of an iterative solver, which in this case could be a bounded solver like Brent's method as it is known that the mole fraction of water is between zero and $x''_{H_2O,sat}(T)$ inclusive. The residual function to be driven to zero by the numerical solver could be given by

$$F(x_{H_2O}) = p(T, \rho, x_{H_2O})/p_{given} - 1 \tag{15}$$

If density, pressure and the mole fraction of water are known, the dry-bulb temperature T_{db} must be determined. In the gas phase, it is known that the compressibility factor Z is very nearly unity. Thus, an initial guess for the temperature is $T_{guess} = p/(\rho R)$ (for $Z = 1$), and the residual function could be given by

$$F(T) = p(T, \rho, x_{H_2O})/p_{given} - 1, \tag{16}$$

which can be reliably solved with a secant solver.

3.5 Dewpoint

The dewpoint of humid air is the temperature where the first droplet of liquid water condenses out of a humid air mixture as it is cooled at constant pressure. The algorithm used to obtain the dewpoint temperature and/or molar composition is presented in the following section.

4. SATURATION FLASH ROUTINES

In a classical mixture dewpoint calculation (for instance in natural gas mixtures), the vapor phase composition is fully specified, and then one of either the temperature or pressure is specified and the other is solved for.

While the conventional dewpoint calculation is required for psychrometry, it is also necessary to be able to efficiently carry out the backwards evaluation, where the dewpoint temperature is known, and the composition of the vapor phase must be solved for - in particular, the water mole fraction of the vapor phase must be determined for the specified temperature and pressure at saturation.

The algorithm required for the determination of the vapor-phase composition for a given dewpoint state is somewhat more complex than the conventional dewpoint calculation, and to our knowledge has not been published before.

4.1 Vapor-phase composition calculation

The independent variables are $N - 1$ compositions of the dry air constituents in the liquid phase (x'_1 to x'_{N-1}) and the water mole fraction in the vapor phase x''_{H_2O}. In vector form, the independent variables can be given by

$$X = \begin{pmatrix} x'_1 \\ x'_2 \\ \vdots \\ x'_{N-1} \\ x''_{H_2O} \end{pmatrix} \tag{17}$$

One of the challenges of this formulation has to do with the composition derivatives that will be described further below. In the mixture model and composition derivatives developed by Gernert and co-workers (Gernert et al., 2014; Gernert and Span, 2016), the last component in the mixture is a dependent variable, and is obtained from the summation of the preceding $N - 1$ mole fractions as

$$x_N = 1 - \sum_{i=1}^{N-1} x_i. \tag{18}$$

In this formulation, it is not possible to take derivatives of any property with respect to x_N. The challenge arises in that it is necessary to take derivatives with respect to the mole fractions of all of the dry air constituents in the liquid phase (x'_1 to x'_{N-1}), as well as the mole fraction of water in the vapor phase x''_{H_2O}. In the liquid phase, the water mole fraction must be an independent variable, and in the vapor phase, the water mole fraction must be a dependent variable.

The resolution to this derivative problem is to sort the arrays of components and compositions differently for the liquid and vapor phases. Therefore, we write the liquid composition array as

$$\boldsymbol{x}' = [x_{N_2}, x_{O_2}, x_{Ar}, x_{CO_2}, x_{H_2O}] \tag{19}$$

and the vapor array as

$$\boldsymbol{x}'' = [x_{H_2O}, x_{N_2}, x_{O_2}, x_{Ar}, x_{CO_2}]. \tag{20}$$

In this way we can take the necessary derivatives; the only challenge is associated with some additional bookkeeping in the code to ensure that the indices in the arrays are consistently and correctly used.

The residual functions to be driven to zero are N equalities of fugacities (on a natural logarithm basis) for all the components (dry air and water) given by equations of the form

$$F_i = \ln(f_i') - \ln(f_i'') \tag{21}$$

where, as described above, the implementer must be careful to ensure that the correct indices are being used. The Jacobian matrix is given by

$$\mathbf{J} = \begin{pmatrix} \dfrac{\partial F_1}{\partial x_1'} & \cdots & \dfrac{\partial F_1}{\partial x_{N-1}'} & \dfrac{\partial F_1}{\partial x_{H_2O}''} \\ \dfrac{\partial F_2}{\partial x_1'} & \cdots & \dfrac{\partial F_2}{\partial x_{N-1}'} & \dfrac{\partial F_2}{\partial x_{H_2O}''} \\ \vdots & \ddots & \vdots & \vdots \\ \dfrac{\partial F_N}{\partial x_1'} & \cdots & \dfrac{\partial F_N}{\partial x_{N-1}'} & \dfrac{\partial F_N}{\partial x_{H_2O}''} \end{pmatrix} \tag{22}$$

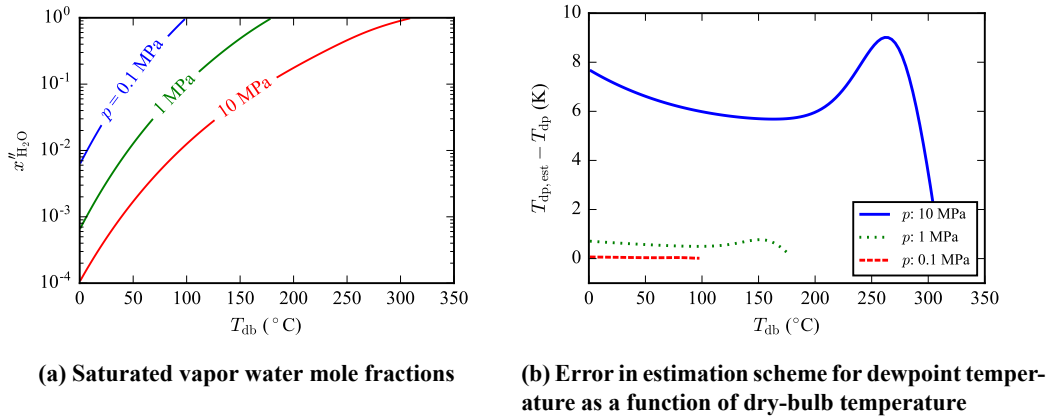where all derivatives are taken with temperature, pressure, and all other mole fractions constant.

Algorithm:

1. The first guess for the water mole fraction is given by $x_{H_2O,0}'' = p_{sat,H_2O,0}(T)/p$ (here assuming an enhancement factor of unity)

2. For given water mole fraction x_{H_2O}'' in the vapor phase, evaluate the vapor-phase composition through the use of Eqs. 2 to 6.

3. In the first iteration, estimate the liquid composition through the use of Henry's law (see next section). In subsequent iterations, skip this step.

4. Calculate $\rho(T,p)$ for the liquid and vapor phases. In the first iteration, estimate the liquid density as being pure water at the specified temperature and pressure, and the vapor phase as being a mixture of ideal gases. Cache calculated densities as initial estimates for the next iteration. In subsequent iterations, use the cached densities as guess densities.

5. Construct the residual matrix from Eq. 21 and the Jacobian matrix from Eq. 22. All necessary derivatives are explained in Gernert *et al.* (2014; 2016); see especially their supplemental information.

6. Solve $\mathbf{J}\Delta\boldsymbol{X} = -\boldsymbol{r}$ for $\Delta\boldsymbol{X}$ and update the vector $\boldsymbol{X}$ from $\boldsymbol{X} = \boldsymbol{X} + \Delta\boldsymbol{X}$. Update the liquid and vapor compositions.

7. Return to step # 2 until convergence is reached (when the maximal mole fraction change is less than the acceptable tolerance).

Figure 1a shows the water mole fractions for a range of pressures for mixtures at saturation. As the temperature approaches the saturation temperature of pure water at the given pressure, the water mole fraction at saturation approaches unity. That is, the vapor phase at equilibrium becomes pure water. The higher the pressure, the greater the range of temperatures and water mole fractions that can be obtained.

4.2 Dew-point calculation

In the calculation for a dewpoint, the pressure and x_{H_2O}'' are given and it is necessary to obtain the dry-bulb temperature T_{db} at saturation. The numerical analysis required to evaluate a dewpoint is quite straightforward. The solver used

(a) Saturated vapor water mole fractions

(b) Error in estimation scheme for dewpoint temperature as a function of dry-bulb temperature

Figure 1: Results for saturation calculations

is nearly identical to the solver for x''_{H_2O} except that the variable x''_{H_2O} is replaced with T in the matrix of independent variables and also in the Jacobian matrix. Thus the vector of independent variables is given by

$$X = \begin{pmatrix} x'_1 \\ x'_2 \\ \vdots \\ x'_{N-1} \\ T \end{pmatrix} \tag{23}$$

and the Jacobian matrix is given by

$$\mathbf{J} = \begin{pmatrix} \left.\dfrac{\partial F_1}{\partial x'_1}\right|_{T,p,x'_j} & \cdots & \left.\dfrac{\partial F_1}{\partial x'_{N-1}}\right|_{T,p,x'_j} & \left.\dfrac{\partial F_1}{\partial T}\right|_{p,\bar{x}} \\ \left.\dfrac{\partial F_2}{\partial x'_1}\right|_{T,p,x'_j} & \cdots & \left.\dfrac{\partial F_2}{\partial x'_{N-1}}\right|_{T,p,x'_j} & \left.\dfrac{\partial F_2}{\partial T}\right|_{p,\bar{x}} \\ \vdots & \ddots & \vdots & \vdots \\ \left.\dfrac{\partial F_N}{\partial x'_1}\right|_{T,p,x'_j} & \cdots & \left.\dfrac{\partial F_N}{\partial x'_{N-1}}\right|_{T,p,x'_j} & \left.\dfrac{\partial F_N}{\partial T}\right|_{p,\bar{x}} \end{pmatrix}, \tag{24}$$

where the same residual functions are used as in Eq. 21.

The initialization and estimation of the liquid-phase composition proceeds in the same fashion as the evaluation of the vapor-phase composition at the dewpoint. We obtain a first guess for the dew-point temperature by assuming a unity enhancement factor, which yields the partial pressure of water from $p_{sat,H_2O,0} = x''_{H_2O} \cdot p$. The vapor pressure curve can be inverted (in some cases, like the IF97 industrial formulation for water (Wagner and Kretzschmar, 2007), without iteration), to yield the estimated dew-point temperature from

$$T_{db,est} = T_{sat,H_2O,0}(x''_{H_2O} \cdot p). \tag{25}$$

Figure 1b shows the error in the prediction of the dew-point temperature from this scheme. The water saturation composition was calculated by the above section to obtain x''_{H_2O} for the given pressure, and $T_{sat,H_2O,0}$ is obtained from the equation of state of Wagner and Pruss (2002). While the errors are up to approximately 9 K, this accuracy is sufficient to yield convergence for pressures from 0.1 MPa to 10 MPa. The liquid-phase composition is then estimated based on Henry's law for the given vapor composition, pressure, and estimated temperature.

4.3 Liquid-phase composition estimates
One of the challenges in the evaluation of the dewpoint is that the conventional means used to estimate the composition of the incipient liquid phase are significantly incorrect. Most commonly, Wilson's method (1968) is used to predict
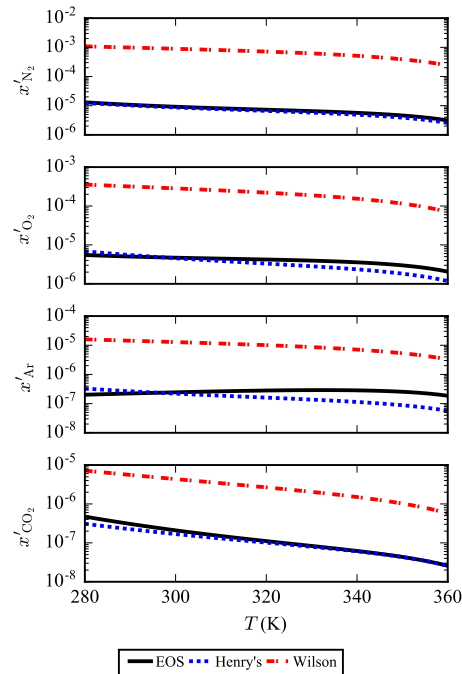
Figure 2: Liquid-phase compositions for dewpoints calculated from the full mixture model, Henry's law, and Wilson's method estimation schemes at 101.325 kPa (1 atmosphere)

the liquid-phase composition. Wilson's equation yields an explicit solution for the liquid-phase composition given the vapor-phase composition and the temperature and pressure. While Wilson's method was originally developed for hydrocarbon mixtures, it remains the default estimation scheme for a wide range of mixtures due to a lack of better alternatives of equivalent simplicity. This lack of accuracy in prediction of the liquid-phase composition means that the numerical solvers commonly applied to this problem suffer from significant challenges.

Thus, reasonable guesses for the liquid-phase composition are important. The liquid-phase composition can be predicted through the use of Henry's law because the liquid phase is very nearly pure water. Henry's law constants for the solubility of component i in pure water are defined as the ratio of the pure component's fugacity in the vapor phase to the mole fraction of that constituent in the liquid phase in the infinite-dilution limit. Mathematically, this can be expressed as

$$k_H \equiv \lim_{x_i' \to 0} \frac{f_i}{x_i'}, \tag{26}$$

and by dropping the limit, the solute mole fraction can be estimated from

$$x_i' = \frac{f_i}{k_H}, \tag{27}$$

where the fugacity f_i and the Henry's law constant k_H are both given in the same unit of pressure. If the vapor phase is furthermore assumed to be a mixture of ideal gases, then the solute mole fraction can be given by

$$x_i' = \frac{x_i'' p}{k_H}, \tag{28}$$

since the fugacity of a component in an ideal gas mixture is simply its mole fraction times the total pressure. In this case, we are only looking to obtain reasonably good estimates for the water phase composition, and the use of the ideal gas assumption for the vapor phase is entirely appropriate. In the work of Fernández-Prini *et al.* (2003), the Henry's law constants for the components of dry air have been fitted to the form proposed by Harvey (1996) in terms of reduced temperatures:

$$\ln\left(\frac{k_H}{p_{sat,H_2O,0}}\right) = \frac{A}{T_R} + \frac{B\tau^{0.355}}{T_R} + C \cdot (T_R)^{-0.41} \exp \tau, \tag{29}$$

where the reduced temperature T_R is given by $T_R = T/T_c$, T_c is the critical temperature of pure water (647.096 K), τ is given by $\tau = 1/T_R$, and $p_{sat,H_2O,0}$ is the saturation pressure of pure water at temperature T. Through the use of this form, the Henry's law constants are evaluated for the components of dry air, and Eq. 28 is used to evaluate the estimate for the liquid-phase composition, with the assumption that the solubility of one air constituent has no impact on the solubility of another dry air constiuent. The water mole fraction in the liquid phase then becomes simply

$$x'_{H_2O} = 1 - \sum_{i=2}^{N} x'_i \tag{30}$$

as the index $i = 1$ is reserved for the water mole fraction.

Figure 2 shows the comparison of the liquid-phase compositions as calculated with the entire mixture model presented in section 4.1 as well as the liquid-phase compositions calculated by Henry's law constants at 101.325 kPa. While the quantitative agreement is not excellent, the qualitative agreement is entirely sufficient to use this model as a preconditioner for the Newton-Raphson solver that is used to solve for the saturation state.

5. RESULTS

The algorithms presented above can be used to construct the psychrometric chart, as seen in Figure 3. This chart represents the links between the thermodynamic variables for a humid air mixture. In this variant of the psychrometric chart, we plot only the lines of constant relative humidity and the lines of constant specific volume (on a per-unit-dry-air basis). The density (on a molar humid air basis) can be obtained from the specific volume per kilogram dry air from

$$\rho = \frac{W + 1}{v_{da} M_{ha}} \tag{31}$$

In this psychrometric chart we have used orthogonal axes for ease of plotting, while the ASHRAE standard psychrometric charts have non-orthogonal axes. The lines of constant relative humidity were constructed by first determining the saturation ($\varphi = 1$) humidity ratio and multiplying by the relative humidity. Lines of constant specific volume were constructed by first interpolating the saturation curve to determine the value of x_{H_2O} corresponding to this specific volume, then evaluating $T(p, v_{da}, x_{H_2O})$ between the saturation water mole fraction and dry air ($x_{H_2O} = 0$).

6. CONCLUSIONS

In this work, we have developed the necessary algorithms to carry out the most important psychrometric calculations for mixtures modeled using the multi-fluid GERG formulation. This framework can be applied to mixtures of arbitrary air composition, and can be applied to the construction of psychrometric charts, amongst other calculations.

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NOMENCLATURE

The formatting of the units in the nomenclature have been selected for consistency with existing literature in the field of psychrometry. They do not strictly follow the unit standards specified in the SI unit system.

Variables

A, B, C	Coefficient for Henry's law
f_i	i-th fugacity (Pa)
f_i'	i-th liquid fugacity (Pa)
f_i''	i-th vapor fugacity (Pa)
F	Residual function
F_{ij}	Binary scaling factor
$\mathbf{J}$	Jacobian matrix
k_H	Henry's law constant (Pa)
m	Slope
m_{H_2O}	Mass of water (kg)
m_{da}	Mass of dry air (kg)
M	Molar mass (kg·mol^{-1})
M_{da}	Molar mass of dry air (kg$_{da}$·mol$_{da}^{-1}$)
M_{ha}	Molar mass of humid air (kg$_{ha}$·mol$_{ha}^{-1}$)
p	Pressure (Pa)
$p_{sat,H_2O,0}$	Sat. pressure of pure water (Pa)
$p_{c,i}$	Crit. press. i-th fluid (Pa)
R	Universal gas constant (J·mol^{-1}·K^{-1})
T	Temperature (K)
T_{db}	Dry-bulb temperature (K)
T_{dp}	Dew-point temperature (K)
$T_{c,i}$	Crit. temp. i-th fluid (K)
T_r	Reducing temperature (K)
$T_{sat,H_2O,0}$	Sat. temp. of pure water (K)
v_{da}	Spec. volume per kg dry air (m^3·kg$_{da}^{-1}$)
W	Humidity ratio (kg$_{H_2O}$·kg$_{da}^{-1}$)
$\mathbf{x}$	Array of mole fraction (-)

X	Vector of independent variables (-)
x	Mole fraction (-)
z	Mole fraction (-)
x''	Mole fraction of vapor (-)
x'	Mole fraction of liquid (-)
α	Non-dimensionalized Helmholtz energy (-)
α^r	Non-dim. residual H.E. (-)
α^r_{oi}	Pure fluid H.E. (-)
α^r_{ij}	Binary departure function (-)
α^0	Non-dim. ideal-gas H.E. (-)
β	Mixture interaction parameter (-)
δ	Reduced density (-)
γ	Mixture interaction parameter (-)
φ	Relative humidity (-)
ω_i	Acentric factor (-)
ρ	Molar density of humid air (mol$_{ha}$·m^{-3})
ρ_r	Reducing density (mol$_{ha}$·m^{-3})
$\rho_{c,i}$	Crit. dens. i-th fluid (mol$_{ha}$·m^{-3})
τ	Reciprocal reduced temperature (-)

Subscripts

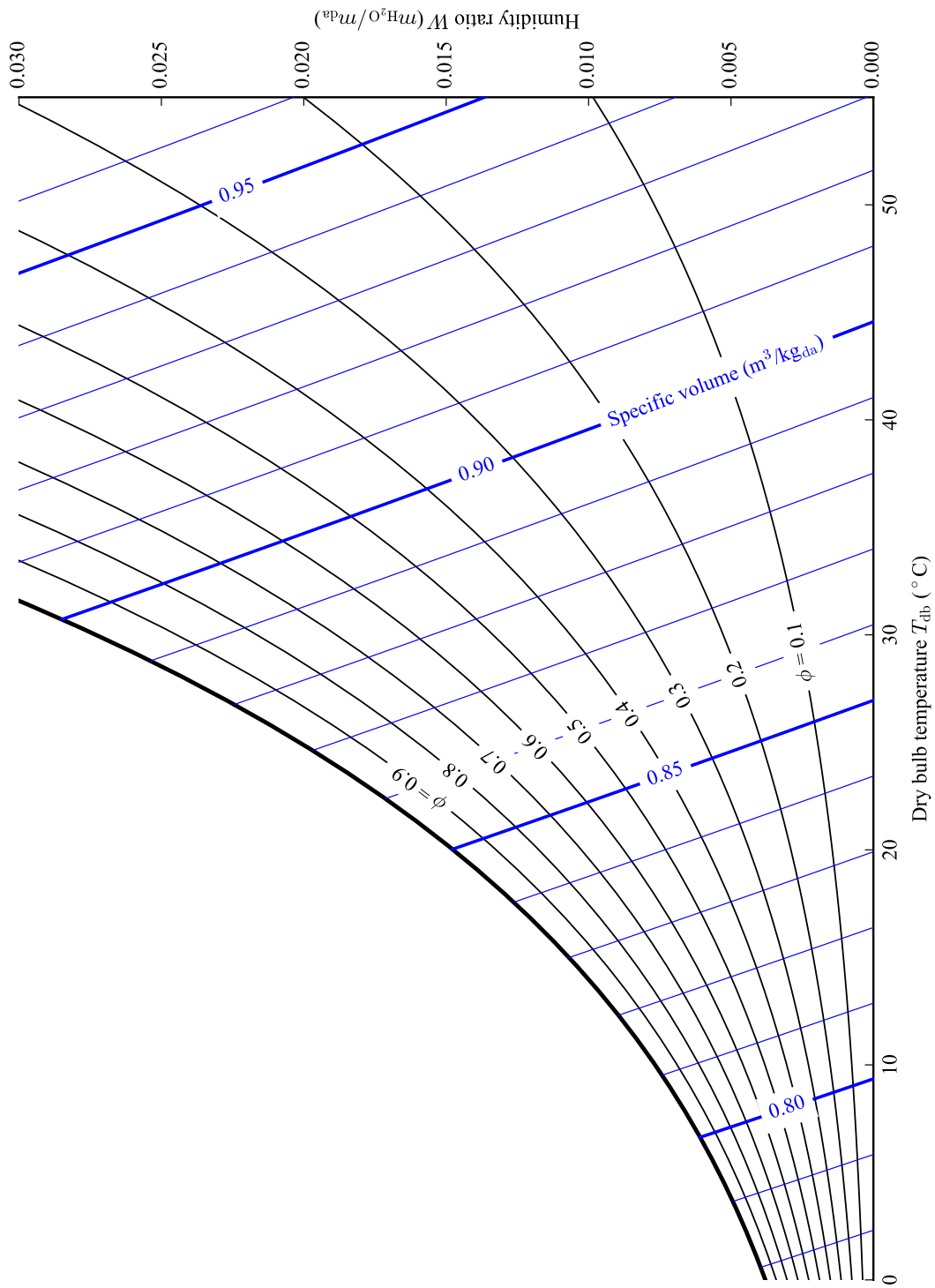|	
da	Dry air
ha	Humid air
i	Index
j	Index
H_2O	Water
Ar	Argon
N_2	Nitrogen
O_2	Oxygen
CO_2	Carbon dioxide

Figure 3: Psychrometric chart at 101.325 kPa (1 atmosphere) as in the work of Zhang and Pate (1988)