Thermodynamic Properties of Real Moist Air

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Abstract

The calculation of the thermodynamic properties for humid air as a real gas mixture using the virial equation of state is presented. The investigations include the Hyland and Wexler model (1983) and consider the Nelson and Sauer model (2001). All of the latest NIST standards for the properties of dry air and virial coefficients and formulations of the International Association for the Properties of Water and Steam (IAPWS) for the properties of ice, for sublimation pressure, and for Henry's constant have been incorporated. The range of validity of the proposed model is in pressure from 0.01 kPa to 10 MPa, in temperature from 130 to 623.15 K, and in humidity ratio from 0 to 10 kg(water)/kg(dry air). This model deviates only slightly from the Hyland-Wexler and Nelson-Sauer models at ambient pressure, the differences increase with increasing pressure and temperature. The developed algorithms have been implemented in a property library for practical use. In addition to thermodynamic properties and derivatives, backward functions on various sets of independent variables and transport properties can be calculated. The property library can be used for calculating air-conditioning processes, compressed air storage processes and other thermal processes having the working fluid humid air.

Methodology

The properties of humid air are calculated from the modified Hyland-Wexler model. The modifications consist in:

- Value for the universal molar gas constant $\bar{R}$ from the CODATA standard by Mohr and Taylor (2005)
- Value for the molar mass of dry air M_a from Gatley et al. (2008) and that of water M_w from IAPWS-95 (IAPWS 2008c)
- Calculation of the ideal-gas parts of the heat capacity $c_{p,a}^{\circ}$, enthalpy h_a°, and entropy s_a° for dry air from the fundamental equation of Lemmon et al. (2000)
- Calculation of the ideal-gas parts of the heat capacity $c_{p,w}^{\circ}$, enthalpy h_w°, and entropy s_w° for water and steam from IAPWS-IF97 (IAPWS 2008a; Wagner and Kretzschmar 2008; Parry et al. 2000) for $T \geq 273.15$ K and from IAPWS-95 (IAPWS 2008c) for $T \leq 273.15$ K (see Fig. 1)
- Calculation of the vapor-pressure enhancement factor f from the equation given by the models of Hyland and Wexler (1973, 1983a, 1983b)
- Calculation of the second and third molar virial coefficients B_{aa} and C_{aaa} for dry air from the fundamental equation of Lemmon et al. (2000)
- Calculation of the second and third molar virial coefficients B_{ww} and C_{www} for water and steam from IAPWS-95 (IAPWS 2008c)
- Calculation of the air-water second molar cross-virial coefficient B_{aw} from Harvey and Huang (2007)
- Calculation of the air-water third molar cross-virial coefficients C_{aaw} and C_{aww} from Nelson and Sauer (2002; Gatley 2005)
- Calculation of the saturation pressure of water $p_{w,s}$ from IAPWS-IF97 (IAPWS 2008a; Wagner and Kretzschmar 2008; Parry et al. 2000) for $T \geq 273.15$ K and of the sublimation pressure of water $p_{w,sub}$ from IAPWS-08 (IAPWS 2008c) for $T \leq 273.15$ K (see Fig. 1)
- Calculation of the isothermal compressibility of liquid water κ_T from IAPWS-IF97 (IAPWS 2008a; Wagner and Kretzschmar 2008; Parry et al. 2000) for $T \geq 273.15$ K and that of ice from IAPWS-06 (IAPWS 2006) for $T \leq 273.15$ K in the determination of the vapor-pressure enhancement factor (see Fig. 1)
- Calculation of Henry's constant β_H from the IAPWS Guideline 2004 (IAPWS 2004) in the determination of the vapor-pressure enhancement factor. The mole fractions for the three main components of dry air were taken from Lemmon et al. (2000). Argon was not considered in the former research projects, but it is now the third component of dry air.
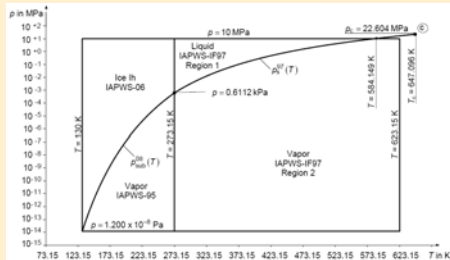

Figure 1: Pressure-temperature diagram with application ranges of the formulations for steam, water, and ice.
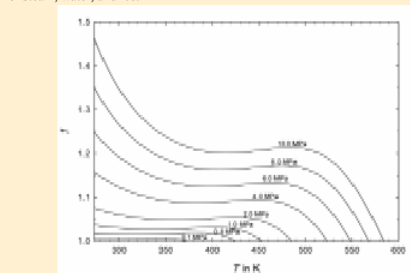

Figure 2: Values of the vapor-pressure enhancement factor f calculated from the shown equation for several total pressures plotted over temperature T.

Proposed Algorithms

Virial Equation of State

The mixture humid air is calculated using the following mixing virial equation of state. The equation contains virial coefficients up to the third virial coefficient. The virial equation of state reads:

$$\frac{p\bar{v}}{\bar{R}T} = 1 + \frac{B_m}{\bar{v}} + \frac{C_m}{\bar{v}^2}$$

with

$$B_m = (1-\psi_w)^2 B_{aa} + 2(1-\psi_w)\psi_w B_{aw} + \psi_w^2 B_{ww} \quad \text{and}$$

$$C_m = (1-\psi_w)^3 C_{aaa} + 3(1-\psi_w)^2 \psi_w C_{aaw} + 3(1-\psi_w)\psi_w^2 C_{aww} + \psi_w^3 C_{www},$$

where ψ_w is the mole fraction of water vapor obtained from the humidity ratio W via

$$\psi_w = \frac{W}{\left(\frac{M_w}{M_a} + W\right)}.$$

Molar Volume

The molar volume $\bar{v}$ for humid air can be calculated iteratively from the expression

$$p(\bar{v}, T, \psi_w) = \frac{\bar{R}T}{\bar{v}}\left(1 + \frac{B_m}{\bar{v}} + \frac{C_m}{\bar{v}^2}\right)$$

where $\bar{R}$ is the universal molar gas constant, B_m is the second molar virial coefficient of the mixture, and C_m is the third molar virial coefficient of the mixture.

Molar Enthalpy

$$\bar{h}(T, \bar{v}, \psi_w) = \bar{h}_0 + (1-\psi_w)\bar{h}_a^{\circ} + \psi_w \bar{h}_w^{\circ} + \bar{R}T\left[\left(B_m - T\frac{dB_m}{dT}\right)\frac{1}{\bar{v}} + \left(C_m - \frac{T}{2}\frac{dC_m}{dT}\right)\frac{1}{\bar{v}^2}\right],$$

where the dry air contribution is calculated from Lemmon et al. (2000)

$$\bar{h}_a^{\circ} = \bar{h}_0^{Lem} + \bar{R}^{Lem}T\left[1 + \tau\left(\frac{\partial\alpha^{\circ}}{\partial\tau}\right)_{\delta}\right]$$

and the steam contribution is calculated from IAPWS-IF97 for $T \geq 273.15$ K

$$\bar{h}_w^{\circ} = \bar{h}_0^{97} + \bar{R}^{97}T\tau\left(\frac{\partial\gamma_2^{\circ}}{\partial\tau}\right)_{\pi}$$

and from IAPWS-95 for $T \leq 273.15$ K

$$\bar{h}_w^{\circ} = \bar{h}_0^{95} + \bar{R}^{95}T\left[1 + \tau\left(\frac{\partial\alpha^{\circ}}{\partial\tau}\right)_{\delta}\right].$$

Molar Entropy

$$\bar{s}(p, T, \psi_w) = \bar{s}_0 + (1-\psi_w)\bar{s}_a^{\circ} + \psi_w \bar{s}_w^{\circ} - \bar{R}\left[\left(B_m + T\frac{dB_m}{dT}\right)\frac{1}{\bar{v}} + \left(C_m + T\frac{dC_m}{dT}\right)\frac{1}{2\bar{v}^2} + (1-\psi_w)\ln(1-\psi_w) + \psi_w\ln(\psi_w)\right],$$

where the dry air contribution is calculated from Lemmon et al. (2000)

$$\bar{s}_a^{\circ} = \bar{s}_0^{Lem} + \bar{R}^{Lem}\left[\tau\left(\frac{\partial\alpha^{\circ}}{\partial\tau}\right)_{\delta} - \alpha^{\circ}\right] + \bar{R}^{Lem}\ln\left(\frac{\bar{v}_a}{\bar{v}_a^{\circ}}\right)$$

and the steam contribution is calculated from IAPWS-IF97 for $T \geq 273.15$ K

$$\bar{s}_w^{\circ} = \bar{R}^{97}\left[\tau\left(\frac{\partial\gamma_2^{\circ}}{\partial\tau}\right)_{\pi} - \gamma_2^{\circ}\right]$$

and from IAPWS-95 for $T \leq 273.15$ K

$$\bar{s}_w^{\circ} = \bar{R}^{95}\left[\tau\left(\frac{\partial\alpha^{\circ}}{\partial\tau}\right)_{\delta} - \alpha^{\circ}\right].$$

Saturation Composition

The mole fraction of water in saturated humid air is

$$\psi_{s,w} = \frac{f\, p_{s,w}}{p}$$

where f is the vapor-pressure enhancement factor, $p_{s,w}$ is the saturation pressure of pure water, and p is the ambient pressure. The vapor-pressure enhancement factor f describes the enhancement of the saturation pressure of water in the air atmosphere under elevated total pressure (see Fig. 2). The calculation of the enhancement factor as a function of total pressure p and temperature T is given by the equation:

$$\ln(f) = (\bar{R}T)^{-1}\left[\left(1 + \kappa_T\, p_{w,s}\right)(p - p_{w,s}) - 0.5\kappa_T\left(p^2 - p_{w,s}^2\right)\right]\bar{v}_{w,s} + \ln\left[1 - \beta_H\left(1-\psi_{w,s}\right)p\right] +$$
$$(\bar{R}T)^{-1}\left\{(1-\psi_{w,s})^2 p\, B_{aa} - 2(1-\psi_{w,s})^2 p\, B_{aw} - \left[p - p_{w,s} - (1-\psi_{w,s})^2\right]p\, B_{ww}\right\} +$$
$$(\bar{R}T)^{-2}\left\{(1-\psi_{w,s})^3 p^2 C_{aaa} + 3\left[0.5 - (1-\psi_{w,s})\right](1-\psi_{w,s})^2 p^2 C_{aaw} -\right.$$
$$3\psi_{w,s}(1-\psi_{w,s})^2 p^2 C_{aww} - 0.5\left[(3-2\psi_{w,s})\psi_{w,s}^2 p^2 - p_{w,s}^2\right]C_{www} -$$
$$\psi_{w,s}(-2+3\psi_{w,s})(1-\psi_{w,s})^2 p^2 B_{aa}B_{ww} - 2(-1+3\psi_{w,s})(1-\psi_{w,s})^3 p^2 B_{aa}B_{aw} +$$
$$6\psi_{w,s}^2(1-\psi_{w,s})^2 p^2 B_{aw}B_{ww} - 1.5(1-\psi_{w,s})^4 p^2 B_{aa}^2 -$$
$$\left.2\psi_{w,s}(-2+3\psi_{w,s})(1-\psi_{w,s})^2 p^2 B_{aw}^2 - 0.5\left[p_{w,s}^2 - (4-3\psi_{w,s})\psi_{w,s}^3 p^2\right]B_{ww}^2\right\}.$$

Range of Validity

The proposed algorithms, which are included into the property library LibHuAirProp, can be used in the following ranges of temperature and pressure:

$$T = 130 \text{ K} \ldots 623.15 \text{ K} \quad \text{and} \quad p = 0.01 \text{ kPa} \ldots 10 \text{ MPa},$$

with the limitation that the partial pressure of steam is restricted to 16 MPa and some small restrictions for transport-property calculations. The humidity ratio of humid air can range from $W = 0$ (dry air) to $W = 10$ kg$_w$/kg$_a$.

Functions of the Property Library

The algorithms for the properties of humid air described in this paper have been implemented into the property library LibHuAirProp (Kretzschmar et al. 2009), which can be received from the authors by request (hj.kretzschmar@hs-zigr.de).

Table 1 comprises the property functions of the property library LibHuAirProp. The input variables for the computation of all thermophysical properties are pressure p in MPa, temperature T in K, and humidity ratio W in kg$_w$/kg$_a$. Furthermore, backward functions of the input variables (p,h,W), (p,s,W), (T,s,W), and (h,s,W) which are required in process modeling are available.

Table 1: Property functions of the property library LibHuAirProp.

Functional Dependence	Property or Function	Functional Dependence	Property or Function
$a = f(p,T,W)$	Thermal diffusivity	$\psi_w = f(W)$	Mole fraction of water
$c_p = f(p,T,W)$	Specific isobaric heat capacity	$\rho = f(p,T,W)$	Density
$c_v = f(p,T,W)$	Specific isochoric heat capacity	$s = f(p,T,W)$	Air-specific entropy
$\eta = f(p,T,W)$	Dynamic viscosity	$\sigma = f(T)$	Surface tension of water
$h = f(p,T,W)$	Air-specific enthalpy	$T = f(h,s,W)$	Backward function: Temperature from air-specific enthalpy and entropy
$\kappa = f(p,T,W)$	Isentropic exponent	$T = f(p,h,W)$	Backward function: Temperature from pressure and air-specific enthalpy
$\lambda = f(p,T,W)$	Thermal conductivity	$T = f(p,s,W)$	Backward function: Temperature from pressure and air-specific entropy
$\nu = f(p,T,W)$	Kinematic viscosity	$T_{wb} = f(p,T,W)$	Wet bulb temperature
$p = f(h,s,W)$	Backward function: Total pressure from air-specific enthalpy and entropy	$T_d = f(p,W)$	Dew point temperature
$p = f(T,s,W)$	Backward function: Total pressure from temperature and air-specific entropy	$u = f(p,T,W)$	Air-specific internal energy
$p_w = f(p,T,W)$	Partial pressure of water vapor	$v = f(p,T,W)$	Air-specific volume
$p_s = f(p,T)$	Saturation partial pressure of water	$w = f(p,T,W)$	Isentropic speed of sound
$\varphi = f(p,T,W)$	Relative humidity	$W = f(p,T,p_w)$	Humidity ratio from temperature and partial pressure of water vapor
$Pr = f(p,T,W)$	Prandtl-number	$W = f(p,T,\varphi)$	Humidity ratio from temperature and relative humidity
Region $= f(h,s,W)$		$W = f(p,T_d)$	Humidity ratio from dew-point temperature
Region $= f(p,h,W)$		$W = f(p,T,T_{wb})$	Humidity ratio from (dry-bulb) temperature and wet-bulb temperature
Region $= f(p,s,W)$	Region (dry air, unsaturated and saturated humid air, liquid fog, ice fog)	$W = f(p,T,v)$	Humidity ratio from temperature and air-specific volume
Region $= f(p,T,W)$		$W_s = f(p,T)$	Humidity ratio of saturated humid air
Region $= f(T,s,W)$			

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