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Determination of Thermodynamic and Transport Properties of Humid Air for Power-Cycle Calculations

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EU Project AA-CAES

AA-CAES Cycle

Working Fluid: Humid Air
- at pressures from ambient to 150 bar,
- at temperatures from ambient to 550 °C,
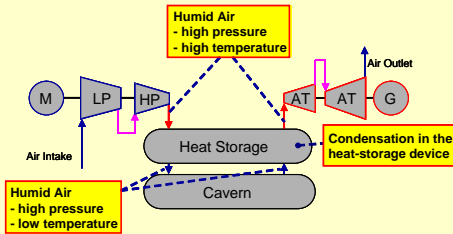- at water content up to 10 ... 20% (mass).

Figure 1 The basic AA-CAES process using compressed humid air as working fluid. The important components of this cycle are the compressor (Motor (M) driven LP – compressor under low pressure and HP – compressor under high pressure), the heat storage, the cavern, and the air turbines (AT) which drive a Generator (G).

Investigated Models

Table 1 Models for calculating thermodynamic properties of humid air used for comparisons.

Abbreviation	Model	Author(s)
IdGas	Ideal mixture of ideal gases	VDI-Guideline 4670 [1]
HuAir	Ideal mixture of the real fluids dry air and water	Hellriegel [2]
HuGas	Ideal mixture of the real fluids N_2, O_2, Ar, and water	Kleemann, Seibt [3]
KTH	Modified Redlich-Kwong equation of state for the mixture	Ji, Yan [4]
RB	Virial equation for the mixture	Rabinovich, Beketov [5]
NEL	Virial equation for the mixture	Nelson, Sauer [6]
HyW	Virial equation for the mixture	Hyland, Wexler [7]

Add-In FluidEXL *Graphics* for Excel®

Abstract

The task of this work has been initiated by the European Commission in whose AA-CAES project's work package 4 the Zittau/Goerlitz University of Applied Sciences participated to investigate and to develop the state-of-the-art model for the calculation of the thermodynamic properties for humid air.

In this work, seven different models for the calculation of humid air have been analysed. The models, which were taken into consideration, treat humid air as an ideal mixture, using a modified Redlich-Kwong equation of state, and virial equations of state.

Except for one model all calculation procedures have been programmed in this work or were available at the Department of Technical Thermodynamics of the Zittau/Goerlitz University of Applied Sciences. In order to determine the accuracy of all models, comparison calculations were carried out within new experimental data for the density and the speed of sound of dry air and unsaturated humid air, and for the saturated composition of humid air, measured by co-workers of the AA-CAES project.

From the results of these comparisons, it could be stated, that the recommended model is a combination of the ideal mixture of the real fluids dry air and water for the unsaturated state of humid air in combination with the virial equation of state from Nelson and Sauer for the saturated composition.

According to the previous investigation, the algorithms of the recommended model are described. The ideal mixture model consists of the most accurate equation for the thermodynamic properties of dry air from Lemmon *et al.* and the scientific formulation IAPWS-95 for water and steam.

In addition, this work presents an algorithm for calculating the thermodynamic properties in case of liquid fog and ice fog. For the solid state, the equation from the new ice IAPWS standard of 2006 is used.

As a final result of this work, the property library LibAirWa has been developed. The program code is programmed in FORTRAN 77 and for the use in software applications a dynamic link library (DLL) was built. The property library LibAirWa contains functions for the calculation of the thermodynamic properties of humid air from the recommended model in this work and functions for the calculation of the transport properties of humid air, developed at the University of Rostock. Backward functions are implemented into the property library, which are needed especially in power plant process calculations. Furthermore, an Add-In for the use in Excel® and one for the use in Mathcad® have been prepared.

Comparison of the Models

Comparison of models with the experimental data of density from PTB 05
$\psi_w = 0.0126, 0.0420, 0.0445, and 0.0446 mol/mol$
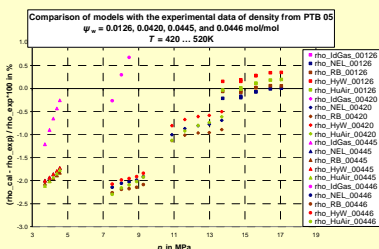$T = 420 \ldots 520K$

Figure 2 Relative deviations for the density of humid air calculated for models listed in Table 1 from the experimental data of Klingenberg & Ulbig [8] as a function of pressure.
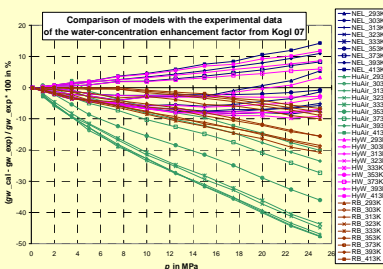

Comparison of models with the experimental data of the water-concentration enhancement factor from Kogl 07

Figure 3 Relative deviations of the water concentration enhancement factor g_w for the saturated composition of humid air calculated for the models listed in Table 1 from the experimental data of Koglbauer & Wendland [9] as a function of pressure.

The comparison calculations show a similar behaviour of all investigated models for density values (e.g. Fig. 1). In the case of the saturated composition, significant differences occurred between the different models (e.g. Fig. 2).

The comparison calculations were restricted by the lack of experimental data for the thermodynamic properties of humid air available in the literature.

The developed property library LibAirWa contains the calculation procedures for the thermodynamic properties of humid air from the proposed model as well as the calculation algorithms for the transport properties of humid air which were prepared by the Department of Physical Chemistry at the University of Rostock.

Proposed Calculation Model

The following mixing rules, e.g. for density and enthalpy, are implemented in the proposed calculation model for the thermodynamic properties of humid air.

Mass Density

$$\rho = \rho_a(p_a, T) + \rho_w(p_w, T)$$

where the partial density of dry air is iteratively calculated from the very accurate fundamental equation for dry air given by Lemmon *et al.* [10]

$$p_a = \rho_a T R_a \left[1 + \delta_a \alpha_{\delta,a}^r(\delta_a, \tau_a) \right]$$

and the partial density of steam is iteratively calculated from a reduced Helmholtz free-energy equation of the scientific formulation for water IAPWS-95 [11]

$$p_w = \rho_w T R_w \left[1 + \delta_w \alpha_{\delta,w}^r(\delta_w, \tau_w) \right].$$

Molar Enthalpy

$$h = \psi_a h_a(\rho_a, T) + \psi_w h_w(\rho_w, T) + \Delta h_{dis}(p, T, \Psi)$$

where the dry air contribution is calculated from Lemmon *et al.* [10]

$$h_a(\rho_a, T) = RT \left[1 + \tau_a \left(\alpha_{\tau,a}^o + \alpha_\tau^r \right) + \delta_a \alpha_\delta^r \right],$$

the steam contribution is calculated from IAPWS-95 [11]

$$h_w(\rho_w, T) = RT \left[1 + \tau_w \left(\alpha_{\tau,w}^o + \alpha_\tau^r \right) + \delta_w \alpha_\delta^r \right], \text{ and}$$

Δh_{dis} consider the influence of the dissociation at temperatures greater than 1200 K.

Saturated Composition

The mole fraction of water in saturated humid air is

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

where f is the enhancement factor, $p_{s,w}$ is the saturation pressure of pure water, and p is the ambient pressure. The enhancement factor f considering the non-ideal behaviour of the mixture at the saturated state is given as a function of p and T and can be derived iteratively from the isothermal compressibility of liquid water, from Henry's constant, and from the virial coefficients of air, of water, and of the mixture air-water using the following relationship. The calculation of f is obtained from the model of Nelson and Sauer [6] with modifications from this work.

$$\ln(f) = \left[\frac{\left(1 + \kappa_T \, p_{s,w}\right)\left(p - p_{s,w}\right) - \kappa_T \frac{\left(p^2 - p_{s,w}^2\right)}{2}}{RT} v_{w,liq} + \ln\left(1 - \beta_H \psi_{s,a} \, p\right) + \right.$$

$$\frac{\psi_{s,a}^2 \, p}{RT} B_{aa} - \left[\frac{2\psi_{s,a}^2 \, p}{RT} \right] B_{aw} - \left[\frac{p - p_{s,w} - \psi_{s,a}^2 \, p}{RT} \right] B_{ww} +$$

$$\frac{\psi_{s,a}^3 \, p^2}{\left(RT\right)^2} C_{aaa} + \left[\frac{3\psi_{s,a}^2 \left(1 - 2\psi_{s,a}\right) p^2}{2\left(RT\right)^2} \right] C_{aaw} -$$

$$\frac{3\psi_{s,a}^2 \left(1 - \psi_{s,a}\right) p^2}{\left(RT\right)^2} C_{aww} - \left[\frac{\left(1 + 2\psi_{s,a}\right)\left(1 - \psi_{s,a}\right)^2 p^2 - p_{s,w}^2}{2\left(RT\right)^2} \right] C_{www} -$$

$$\frac{\psi_{s,a}^2 \left(1 - 3\psi_{s,a}\right)\left(1 - \psi_{s,a}\right) p^2}{\left(RT\right)^2} B_{aa} B_{ww} - \left[\frac{2\psi_{s,a}^3 \left(2 - 3\psi_{s,a}\right) p^2}{\left(RT\right)^2} \right] B_{aa} B_{aw} +$$

$$\frac{6\psi_{s,a}^2 \left(1 - \psi_{s,a}\right) p^2}{\left(RT\right)^2} B_{ww} B_{aw} - \left[\frac{3\psi_{s,a}^4 \, p^2}{2\left(RT\right)^2} \right] B_{aa}^2 -$$

$$\left. \frac{2\psi_{s,a}^2 \left(1 - \psi_{s,a}\right)\left(1 - 3\psi_{s,a}\right) p^2}{\left(RT\right)^2} B_{aw}^2 - \left[\frac{p_{s,w}^2 - \left(1 + 3\psi_{s,a}\right)\left(1 - \psi_{s,a}\right)^3 p^2}{2\left(RT\right)^2} \right] B_{ww}^2 \right]$$

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