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Thermodynamic Properties Of Air Water Mixtures - 100 to 100° C and 50 to 5000 kPa



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All refrigeration engineers, particularly those dealing in industrial plants have known ammonia as a refrigerant of choice due to its excellent thermodynamic properties. It is almost nearly a perfect refrigerant.

Humidification and dehumidification load calculations require thermodynamic and psychrometric properties of moist air. Formulations are given for the thermodynamic properties of dry and moist air for pressures between 50 to 5000 kPa. The required virial and enthalpy coefficients, and the enhancement factor for saturated moist air are given. A computer program is developed to calculate the properties of air for a given temperature, pressure and relative humidity. The thermodynamic and psychrometric property values generated using the program are plotted in the form of 101.325 kPa (147 psia) and 1000 kPa. The application of the 50 kPa, chart may be for vacuum drying, 1000 kPa chart may be used for compressed air drying and the atmospheric pressure chart would be useful for air conditioning applications at sea level.

Introduction

The design of Heating, Ventilating and Air Conditioning (HVAC) systems start with load estimation. This has a bearing on the capacity of the equipment and the energy required for its operation. Energy conservation has started playing an important role in selection and design of air conditioning equipment. In order to come up with good solutions to a particular air conditioning situation, it is very important to visualize the various steps involved. Access to good psychrometric charts and property data will help in improving the understanding of the processes and will bring forth novel solutions. Barometric pressure charts, in the temperature

range of 0 to 50°C, are readily available. However, they may not be useful for computing air conditioning loads for localities at higher altitudes. Charts and properties are not readily available in a single source for a range of pressures from sub atmospheric to high pressures, and temperatures ranging from sub zero to 100°C.

In this article moist air property correlations are compiled and presented applicable in temperature range of -100 to 100°C for a pressure range of 50 to 5000 kPa. Three charts have also been included to show the general trend in properties over the range of temperature and pressure.

The amount of water vapour in moist air is critical in industrial processes like dehydration plants for compressed natural gases, hygrometry, power processing, pharmaceutical and textile industries. In manufacturing operations, compressed air for powering tools, machinery and for painting require varying amounts of conditioning.

Thus, a need arises to calculate the properties of air at varying pressures depending on the application. The thermodynamic properties of moist air at atmospheric pressure in the temperature range of $-60^{\circ}\text{C} < t < 90^{\circ}\text{C}$ is given in the ASHRAE Handbook - 1997 Fundamentals which is based on Hyland and Wexler formulations. Air behaves as an ideal gas at low pressures and high temperatures. At higher pressure and temperatures in the range of - 100 to 100°C the deviation from ideal gas law should be taken into account while calculating the properties of air with a reasonable degree of accuracy. This is because the water vapour content of air, saturated under these pressure and temperature conditions is not predicted accurately by gas laws. Thus, the real gas behaviour of moist air needs be considered for accurate calculations of thermodynamic properties. This leads to the accurate calculation of heat duties in various HVAC applications.

Utility of Computer Program

With the advent of high speed computers, it is convenient to use the properties of air in the form of equations programmed in a software, rather than interpolating from tables or charts. The authors have developed a computer program which can calculate the properties of air at any given relative humidity, pressure between 50 to 5000 kPa and temperature from - 100 to 200°C for dry air and - 100 to 100°C for moist air. The program is written using version 7 of Math CAD software. Psychrometric charts have been plotted using the values generated by the program. Three psychrometric charts of 50 kPa, 101.325 kPa and 1000 kPa are plotted and given in **Figure 1, 2 and 3** respectively.

In this article formulations are given for the thermodynamic properties like volume, enthalpy and entropy of air. Relationships for saturated moist air per unit mass of dry air are also listed at the end of the article. Psychrometric properties calculated in the program include humidity ratio, humidity ratio at saturation, degree of saturation, dew point temperature, partial pressures of water vapour and dry air and mole fractions of water vapour and dry air.

General Considerations and Assumptions

Youngmoo (1996) calculated the thermodynamic properties of ideal gas at low pressure by means of statistical thermodynamics using the molecular, physical and spectroscopic data. According to Keenan et al. (1980), the accuracy of the experimentally found property values is less than that obtained by theoretical calculation. Stewart et al. (1983 a) describes the calculation used in the preparation of ASHRAE psychrometric charts. Hyland and Wexler (1983 a) gave formulations and sample calculations for the molar and specific volume, enthalpy, and entropy of dry and moist air, along with formulations for the properties of moist air per unit mass of dry air. Estimates of uncertainties are also given by the authors.

The composition of atmospheric air is variable, particularly with regards to amount of water vapour and particulate matter. Dry air assumed to be a homogeneous, single component gas with molecular weight (based on the carbon 12 scale) taken as 28.9645 g/mol. Moist air is treated as a mixture of two real gases and the components are designated by the subscripts 'a' or 'w' for dry air or water vapour respectively. The molecular weight for water is 18.01528 g/mol. The reference state of temperature is 0°C and pressure is 101.325 kPa. The molar enthalpy and entropy, of dry air and liquid water, are set to zero at the reference point. The properties enthalpy, internal energy, specific heat at constant pressure and constant volume are functions of temperature, while the entropy is a function of both temperature and pressure. The real gas behaviour of moist air is described by a virial equation of state for mixtures which includes the second and third virial coefficients for dry air and for water vapour and the second and third cross virial coefficients for air water vapour mixtures.

Dry Air

The P-V-T behaviour of each component of air when acting alone, as well as for the mixture is described by a virial equation of state, Equation 1 where $I = 'a'$ for air or $'w'$ for water.

Formulations for specific enthalpy is given by Equation 2, and specific entropy can be derived from Equation 1 through the use of appropriate identical relations of thermodynamics. The coefficients B and C in Equation 2 are the second and third virial coefficients for enthalpy. For the ranges of pressure and temperature considered, the higher order virial coefficients are ignored.

Virial Equation of State for a Gas

The ideal gas is a model fluid that is useful because it is described by simple equations frequently applicable as good approximations for real gases. In engineering calculations, gases at pressures upto a few bars may be considered ideal. For a real gas, molecular interaction do exist, and exert an influence on the observed behaviour of the gas. Many analytic equations of state, including the Van der Waals equation of state describing the real gas behaviour have been suggested. The virial equation of state was first used by H Kammerlingh Onnes in 1901. It is of theoretical interest since it can be derived from Statistical Mechanics with explicit expressions obtained for the virial coefficients in terms of the potential function between molecules.

The virial coefficients, functions only of temperature, provide a convenient method of describing gas imperfection. They are related to the intermolecular potential energy function of

the molecules concerned. The compressibility data and P-V-T measurements are used to calculate the density series second and third virial coefficients. The data are weighed, then fitted by the least squares method to obtain the second virial coefficient considered to express the effect of interactions between two molecules given by Equation 3. The third virial coefficient may be considered to express the effects of interactions among three molecules given by Equation 4.

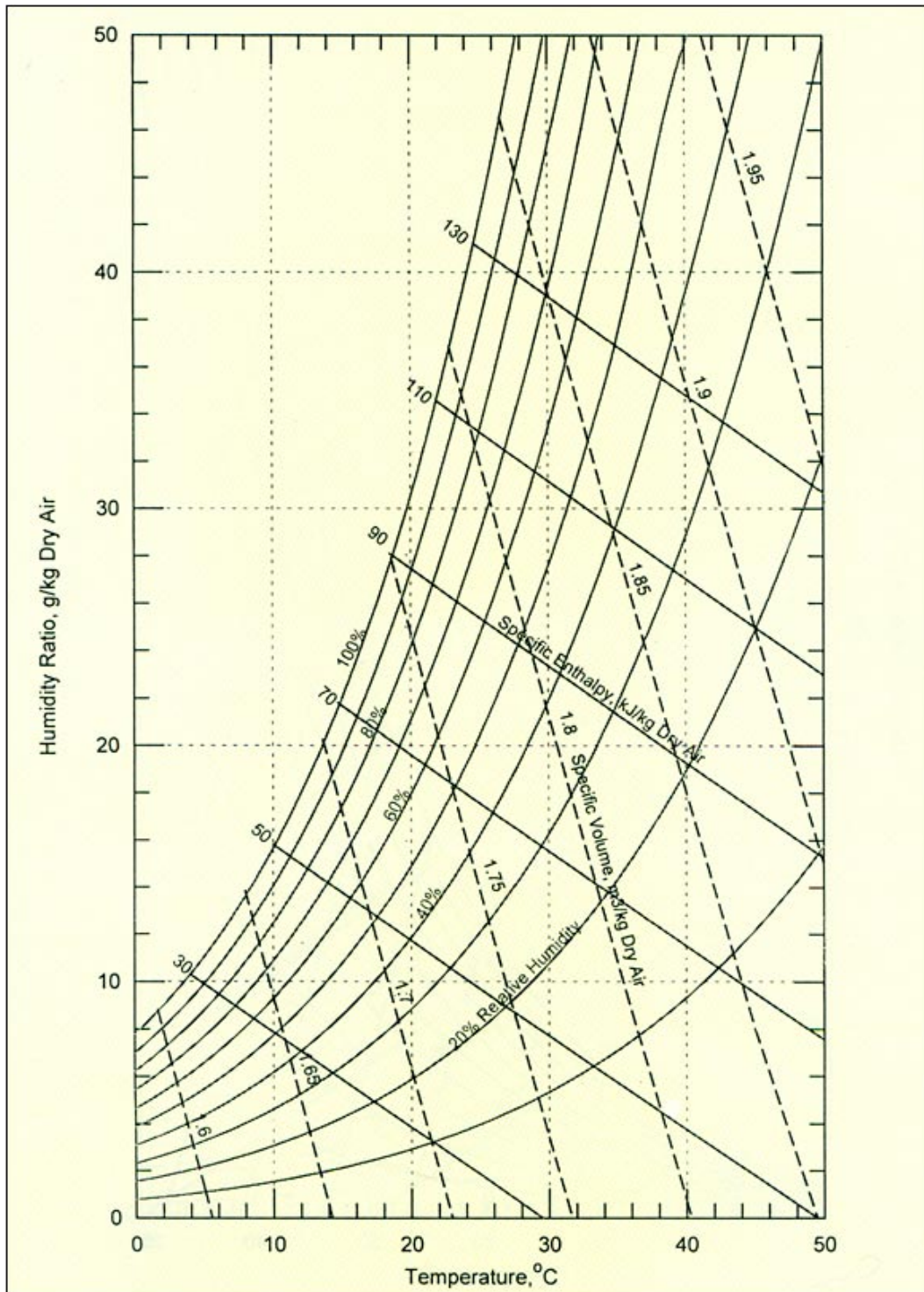


Fig. 1: Psychrometric Chart for Pressure of 50 kPa.

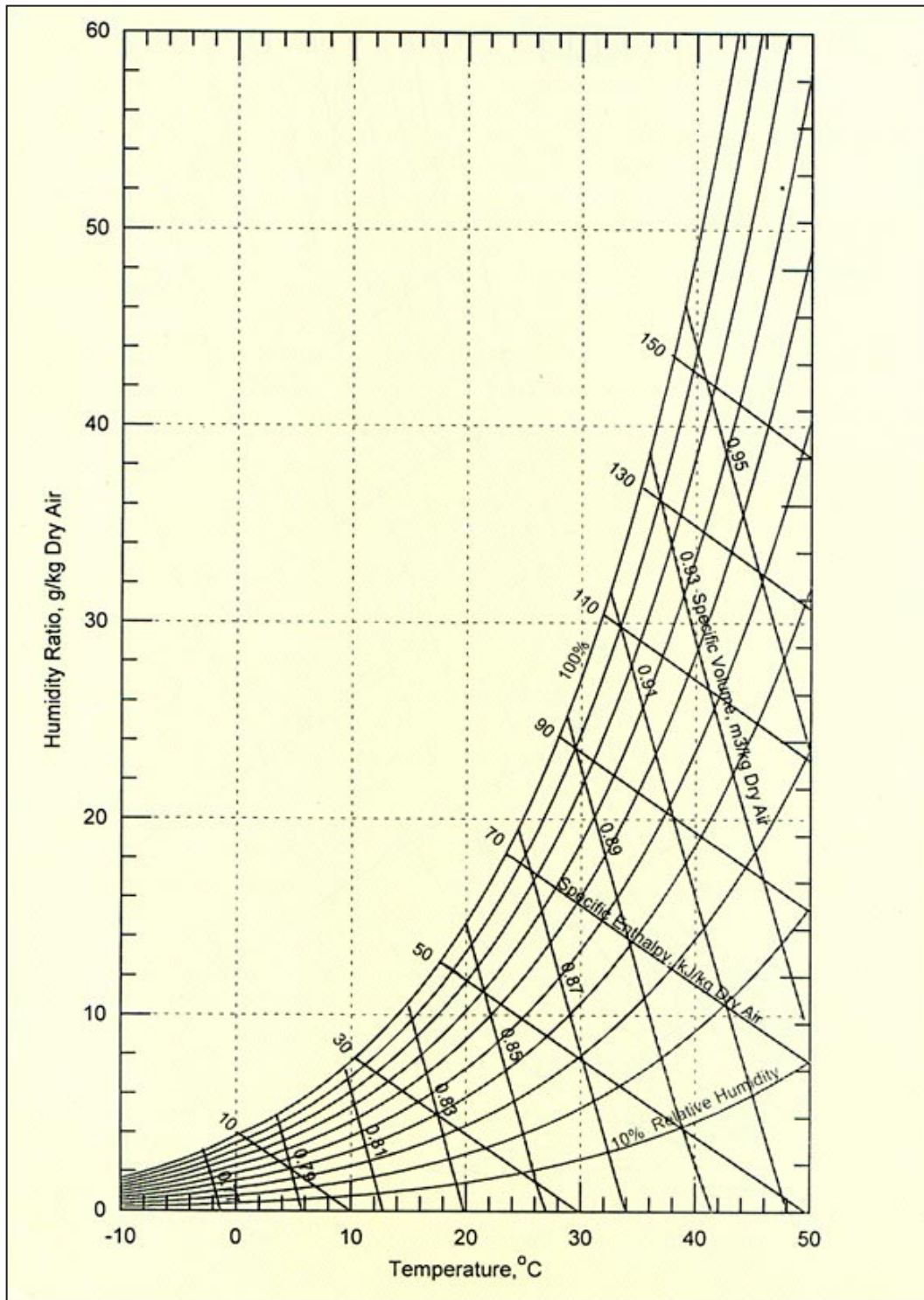


Fig. 2: Psychrometric Chart for Pressure of 101.325 kPa.

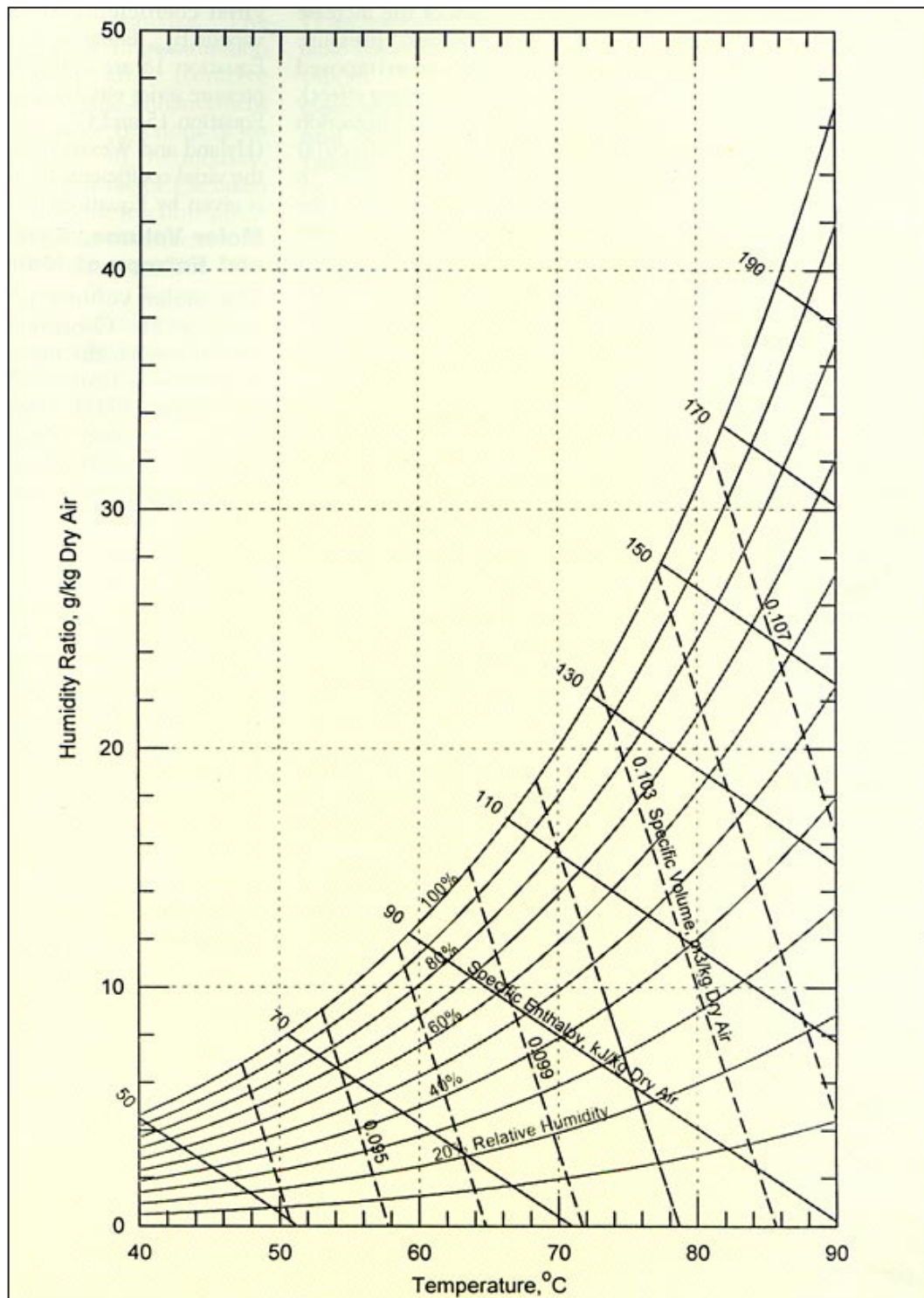


Fig. 3: Psychrometric Chart for Pressure of 1000 kPa.

Molar Volume, Enthalpy and Entropy of Dry Air

From Equation 1, the molar volume of dry air is obtained and is given by Equation 8 (Hyland and Wexler, 1983). Consistent with the choice of reference states, the molar enthalpy of dry air is given by Equation 9 and the molar entropy of dry air by Equation 10. The molar quantities of volume, enthalpy and entropy of dry air are converted into specific quantities by dividing the computed value of each property by the molecular mass of dry air, 28.9645.

Moist Air

The water vapour content of air, saturated under known conditions of pressure and temperature is not predicted adequately by ideal gas laws. The deviation from ideality must be accounted for in orders to obtain accuracies better than 0.5% at pressures as low as 90 kPa. For example, at 0°C and 20000 kPa, the water vapour partial pressure in air is about twice the vapour pressure of pure water at 0°C.

On any isotherm, the saturated water vapour content increases with pressure. The increase in water vapour content with pressure is the algebraic sum of the increase in apparent vapour pressure because of the superimposed pressure of air (the Poynting effect), the Vander Waals type interaction between different molecular species, and the decrease in apparent vapour pressure due to the solution of air in the liquid water (the Henry's law effect). The largest is due to the non ideality of the gas phase, Van der Waals type interaction (Hyland and Wexler, 1973). Given a real gas equation of state of a water vapour air mixture, expressed in virial form, it is possible to derive theoretically an expression for the saturation water vapour content, volume, enthalpy and entropy of the gas mixture, as a function of the mole fraction of the constituents, the parameters of state and the virial coefficients.

The water vapour in moist air is assumed to have the same composition as naturally occurring liquid water. The saturation pressure of vapour over liquid water is obtained by the integration of the Clapyron equation $dp/dT = \Delta h/T\Delta v$ and data fitting to yield an equation implicit in P_w (Hyland and Wexler, 1983). A formulation for the saturation pressure of vapour over liquid water is given by Equations 11, 13 and 14 (ASHRAE Handbook, 1997).

The cross virial coefficients for air water vapour mixture can be written in terms of the mole fractions of the pure components, and quantities called cross interaction virial coefficients. For air water vapour mixture from statistical mechanics we get Equation 12. The virial equations of air water mixtures Equation 5, 6, and 7, where the virial coefficients are as define in the nomenclature. The volume series virial coefficients for pure water vapour B_{ww} , Equation 17 and C_{www} , pressure series virial coefficient B'_{ww} , Equation 15 and C'_{www} , Equation 16 (Hyland and Wexler, 1983). Hence the virial coefficients for the mixture is given by Equations 19 and 20.

Molar Volume, Enthalpy and Entropy of Moist Air

The molar volume is given by Equation 21. Consistent with the reference state, the molar enthalpy of moist air is Equation 22 (Hyland and Wexler, 1983). The constants to adjust reference states for molar enthalpies of dry air h_a is -7914.1982 J/mol and for water vapour h_w is 35994.17 J/mol.

The molar entropy of moist air is Equation 23 (Hyland and Wexler, 1983) and the constants to adjust reference states for molar entropy of dry air S_a is -63.31449 J/mol K. To obtain the specific properties of moist air per mass of dry air and at saturation, the molar quantities are divided by the product of mole fraction of air in moist air and the molecular mass of dry air.

Properties of Moist Air at Saturation

Moist air is said to be saturated when it coexists in neutral equilibrium with an associated condensed phase of water. The associated condensed phase is not pure water, but water containing small concentrations of dissolved gases. At any given temperature the increase in the saturation concentration of the water vapour may be expressed as a ratio of the vapour concentration at the total system pressure in the presence of the second gas to the vapour concentration of the pure phase. This ratio is called the enhancement factor f , a dimensionless quantity. The properties of moist air at saturation depend on an iterative determination of the enhancement factor ' f ' and mole fractions of air and water vapour in the mixture. The enhancement factor f is taken as 1 and the mole fraction of air and water vapour at saturation is calculated by Equation 25. The values obtained from Equation 25 are used in the calculation of new values of the enhancement factor ' f ' and the corresponding mole fraction of air for comparison with the original values. The calculation continues until the incremental change in the enhancement factor is smaller than a predetermined convergence parameter. The equation for the enhancement factor is given by Equation 26 (Hyland and Wexler, 1983).

There is a decrease in vapour pressure caused by the solution of air in water that is in equilibrium with the gas mixture, the Henry's Law effect. The Henry's law constant ' L ' for an inert gas dissolved in liquid water is represented by the parabolic function 24 (Hyland and Wexler, 1983). The isothermal compressibility of saturated liquid water over the range 0 to 200°C is given as Equation 27 (Hyland and Wexler, 1983). The isothermal compressibility of ice is given by Equation 28. If air is considered a mixture solely of oxygen and nitrogen, an approximation adequate for this purpose, then the Henry's law constant for air k_A , can be determined from the Henry's law constant for oxygen and nitrogen k_o and k_N by the relationship 29, where $x_o = 0.22$ and $x_N = 0.78$ are the mole fractions of oxygen and nitrogen. Equation 26 may now be solved for x_{as} and f by iteration. At saturation, Equation 14, 16, and 17 are used with Equation 18 for the mole fractions of dry air and water vapour.

Comparisons with ASHRAE and Hyland and Wexler Tables

The values for volume, enthalpy and entropy of dry air at atmospheric pressure generated using the computer program match with the ASHRAE Tables (ASHRAE, 1997) for the given temperature range. For moist air the specific volume show variations of 0.03% outside of ASHRAE Tables above 70°C. The thermodynamic properties of moist air at pressures lower than atmospheric have not been validated as published data is unavailable.

The values of properties at pressures 50, 1000 and 5000 kPa is found to lie within the error bounds of 0.03% for 0°C < t < 99°C of Hyland and Wexler (1983) Tables (Hyland and Wexler, 1983). At higher pressures, larger disparities with the actual values are expected as the higher order virial and cross-virial coefficients are neglected in the formulations.

Psychrometric Charts

The properties of dry and moist air, calculated in the computer program are used in the construction of psychrometric charts with specific humidity along the ordinate and dry bulb temperature along the abscissa. Psychrometric charts at pressures of 50, 101.3325 and 5000 kPa

are shown in **Figures 1, 2 and 3** respectively. The constant relative humidity, constant specific volume and constant enthalpy lines are drawn in the charts. These charts can have applications in vacuum drying, air conditioning and compressed air drying respectively. The psychrometric chart at 101.325 kPa given in **Figure 2** extends beyond the temperature range of the chart in ASHRAE 197. The temperature range is from -10 to 50°C and the humidity ratio from 0 to 60 g/kg Dry Air. Psychrometric charts at other pressures can also be plotted from the values generated by the computer program.

Conclusion

Computing air conditioning loads for localities at higher altitudes, vacuum drying, land compressed air drying require the use of thermodynamic properties at higher pressure. Formulations for the thermodynamic properties like volume, enthalpy and entropy of dry air from -100 to 200°C and moist air from -100 to 100°C are given for pressures between 50 to 5000 kPa. Relationships for the volume, enthalpy and entropy of saturated moist air per unit mass of dry air are also included. Psychrometric properties calculated include humidity ratio, humidity ratio at saturation, degree of saturation, dew point temperature, partial pressure of water vapour and dry air and mole fraction of water vapour and dry air. The thermodynamic and psychrometric properties were calculated in a computer program using Math CAD V 7.0 for a given temperature, pressure and relative humidity. The values predicted by these equations at atmospheric pressure were compared with ASHRAE tables. At higher pressures upto 5000 kPa the values obtained from the program is found to lie within the error bounds of 0.03% for 0°C < t < 99°C of Hyland and Wexler (1983) Tables. Psychrometric charts at pressures of 50, 101.325 and 1000 kPa are included.

Acknowledgement

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Nomenclature

B,C - Virial Coefficients for air

f - Enhancement factor

h - Specific Enthalpy, kJ/kg

h - Molar specific enthalpy, kJ/kg

p - Pressure, Pa

s - Specific Entropy, kJ/kg

t - temperature, °C

s - Molar specific entropy kJ/kg

v - Specific volume of gas, m³

x - Mole fraction

k - Henry's law constant

Subscripts

a - dry air

w - water vapour

m - mixture

as - air in saturated mixture

aw - water vapour in saturated mixture

aa - second virial coefficient for dry air

aaa - third virial coefficient for dry air

ww - second virial coefficient for water vapour

www - third virial coefficient for water vapour

aw - second interaction (cross) virial coefficient

aww, aaw - third interaction (cross) virial coefficient

O - Oxygen

N - Nitrogen

A - Air

Greek

K - Isothermal compressibility of ice or water

Formulations for Thermodynamic Properties of Air

$$\frac{p \cdot v}{R \cdot t} := 1 + \frac{B_{ii}}{v} + \frac{C_{ii}}{v^2} \quad (1)$$

$$h := h_o + B \cdot p + C \cdot p^2 + \dots \quad (2)$$

$$B_{aa} := \left[0.349568 \cdot 10^{-2} - 0.668772 \cdot 10^{-4} \cdot \left(\frac{t}{K}\right)^{-1} - 0.210141 \cdot 10^{-7} \cdot \left(\frac{t}{K}\right)^{-2} + 0.924746 \cdot 10^{-8} \cdot \left(\frac{t}{K}\right)^{-3} \right] \frac{\text{cm}^3}{\text{mol}} \quad (3)$$

$$C_{aaa} := \left[0.125975 \cdot 10^{-4} - 0.190905 \cdot 10^{-6} \cdot \left(\frac{t}{K}\right)^{-1} + 0.632467 \cdot 10^{-8} \cdot \left(\frac{t}{K}\right)^{-2} \right] \frac{\text{cm}^6}{\text{mol}^2} \quad (4)$$

$$B_{aw} := \left[0.32366097 \cdot 10^{-2} - 0.1411138 \cdot 10^{-5} \cdot \left(\frac{t}{K}\right)^{-1} - 0.1244535 \cdot 10^{-7} \cdot \left(\frac{t}{K}\right)^{-2} - 0.2348789 \cdot 10^{-10} \cdot \left(\frac{t}{K}\right)^{-4} \right] \frac{\text{cm}^3}{\text{mol}} \quad (5)$$

$$C_{aaw} := \left[0.482737 \cdot 10^{-3} + 0.105678 \cdot 10^{-6} \cdot \left(\frac{t}{K}\right)^{-1} - 0.656394 \cdot 10^{-8} \cdot \left(\frac{t}{K}\right)^{-2} + 0.294442 \cdot 10^{-11} \cdot \left(\frac{t}{K}\right)^{-3} \dots \right] \frac{\text{cm}^6}{\text{mol}^2} \quad (6)$$

$$\left[-0.319317 \cdot 10^{-13} \cdot \left(\frac{t}{K}\right)^{-4} \right]$$

$$C_{aww} := \left[-1 \cdot 10^{-6} \cdot \exp \left[-0.10728876 \cdot 10^{-2} + 0.347802 \cdot 10^{-4} \cdot \left(\frac{t}{K}\right)^{-1} - 0.383383 \cdot 10^{-6} \cdot \left(\frac{t}{K}\right)^{-2} + 0.33406 \cdot 10^{-8} \cdot \left(\frac{t}{K}\right)^{-3} \right] \right] \frac{\text{cm}^6}{\text{mol}^2} \quad (7)$$

Formulations for Thermodynamic Properties of Air

$$v := \frac{R \cdot g \cdot t}{p} \cdot \left(1 + \frac{B_{aa}(t)}{v} + \frac{C_{aaa}(t)}{v^2} \right) \quad (8)$$

$$h := \left[\begin{array}{l} -0.79078691 \cdot 10^{-4} + 0.28709015 \cdot 10^{-2} \cdot \left(\frac{t}{K}\right)^1 + 0.26431805 \cdot 10^{-2} \cdot \left(\frac{t}{K}\right)^2 \dots \\ + 0.10405863 \cdot 10^{-4} \cdot \left(\frac{t}{K}\right)^3 + 0.18660410 \cdot 10^{-7} \cdot \left(\frac{t}{K}\right)^4 - 0.97843331 \cdot 10^{-11} \cdot \left(\frac{t}{K}\right)^5 \dots \\ + R \cdot g \cdot t \cdot \left[\left(B_{aa} - t \cdot \frac{d}{dt} B_{aa} \right) \frac{1}{v} + \left(C_{aaa} - \frac{1}{2} t \cdot \frac{d}{dt} C_{aaa} \right) \frac{1}{v^2} \right] \end{array} \right] \frac{\text{joule}}{\text{mol}} \quad (9)$$

$$s := \left[\begin{array}{l} -0.16175159 \cdot 10^{-3} + 0.52863609 \cdot 10^{-2} \cdot \left(\frac{t}{K}\right)^1 - \left[0.15608795 \cdot 10^{-4} \cdot \left(\frac{t}{K}\right)^2 \right] \dots \\ + 0.24880547 \cdot 10^{-7} \cdot \left(\frac{t}{K}\right)^3 \dots \\ + 0.12230416 \cdot 10^{-10} \cdot \left(\frac{t}{K}\right)^4 + 0.28709015 \cdot 10^{-2} \cdot \ln \left(\frac{t}{K}\right) \\ + \left[-R \cdot g \cdot \ln \left(\frac{p}{101325 \cdot \text{Pa}} \right) + R \cdot g \cdot \ln \left(\frac{p \cdot v}{R \cdot g \cdot t} \right) \dots \right. \\ \left. + R \cdot g \cdot \left[\left(B_{aa} + t \cdot \frac{d}{dt} B_{aa} \right) \frac{1}{v} + \frac{1}{2} \left(C_{aaa} + t \cdot \frac{d}{dt} C_{aaa} \right) \frac{1}{v^2} \right] \right] \right] \frac{\text{joule}}{\text{mol} \cdot \text{K}} \quad (10)$$

for 173.15 K < t < 273.15

$$p_{ws1} := \exp \left[\begin{array}{l} -5674.5359 \\ \frac{t}{K} + 6.3925247 - 0.9677843 \cdot 10^{-2} \cdot \frac{t}{K} + 0.62215701 \cdot 10^{-6} \cdot \left(\frac{t}{K}\right)^2 + 0.20747825 \cdot 10^{-8} \cdot \left(\frac{t}{K}\right)^3 \dots \\ + 0.9484024 \cdot 10^{-12} \cdot \left(\frac{t}{K}\right)^4 + 4.1635019 \cdot \ln \left(\frac{t}{K}\right) \end{array} \right] \quad (11)$$

$$p_v := R \cdot t \cdot \left[\left(x_a^2 \cdot B_{aa} + 2 \cdot x_a \cdot x_w \cdot B_{aw} + x_w^2 \cdot B_{ww} \right) p - \left(x_a^3 \cdot C_{aaa} + 3 \cdot x_a \cdot x_w^2 \cdot C_{aaw} + 3 \cdot x_a^2 \cdot x_w \cdot C_{aaw} + x_w^3 \cdot C_{www} \right) p^2 \right] \quad (12)$$

for 273.15 K < t < 370

$$p_{ws2} := \left[\begin{array}{l} \exp \left[153.5411 + 0.066953 \cdot \frac{t}{K} - 5.05796 \cdot 10^{-5} \cdot \left(\frac{t}{K}\right)^2 \dots \right] \dots \\ + 2.183911 \cdot 10^{-8} \cdot \left(\frac{t}{K}\right)^3 - 8990.134 \cdot \left(\frac{t}{K}\right)^{-1} \\ + 25.07797 \cdot \ln \left(\frac{t}{K}\right) \end{array} \right] \text{bar} \quad (13)$$

for 370 K < t < 473.15

$$p_{ws3} := \left[\begin{array}{l} \exp \left[\frac{-5800.2206}{\frac{t}{K}} + 1.3914993 - 0.04860239 \cdot \frac{t}{K} + 0.41764768 \cdot 10^{-4} \cdot \left(\frac{t}{K}\right)^2 - 0.14452093 \cdot 10^{-7} \cdot \left(\frac{t}{K}\right)^3 \dots \right] \dots \\ + 6.5459673 \cdot \ln \left(\frac{t}{K}\right) \end{array} \right] \text{Pa} \quad (14)$$

$$B_{x_{ww}} := \left[0.70 \cdot 10^{-8} - \left[0.147184 \cdot 10^{-8} \cdot \exp \left[1734.29 \cdot \left(\frac{t}{K}\right)^{-1} \right] \right] \right] \text{Pa}^{-1} \quad (15)$$

$$C_{x_{ww}} := \left[0.104 \cdot 10^{-14} - \left[0.335297 \cdot 10^{-17} \exp \left[3645.09 \cdot \left(\frac{1}{K} \right) \right] \right] \right] \cdot \text{Pa}^{-2} \quad (16)$$

$$B_{ww} := (R_g \cdot t \cdot B_{x_{ww}}) \quad (17)$$

Formulations for Thermodynamic Properties of Air

$$C_{www} := (R_g t)^2 [C_{x_{www}} + (B_{x_{ww}})^2] \tag{18}$$

$$B_m := x_a^2 B_{aa} + 2 x_a x_w B_{aw} + x_w^2 B_{ww} \tag{19}$$

$$C_m := x_a^3 C_{aaa} + 3 x_a^2 x_w C_{aaw} + (3 x_a x_w^2 C_{aww}) + x_w^3 C_{www} \tag{20}$$

$$v_{ma} := \frac{R_g t}{p} \left(1 + \frac{B_m}{v} + \frac{C_m}{v^2} \right) \tag{21}$$

$$h_{ma} := \left[x_a \left[0.63290874 \cdot 10^1 + 0.28709015 \cdot 10^2 \cdot \left(\frac{t}{K}\right)^1 + 0.26431805 \cdot 10^{-2} \cdot \left(\frac{t}{K}\right)^2 \dots \right] \right. \\ \left. + x_w \left[-0.5008 \cdot 10^{-2} + 0.32491829 \cdot 10^2 \cdot \left(\frac{t}{K}\right)^1 + 0.65576345 \cdot 10^{-2} \cdot \left(\frac{t}{K}\right)^2 \dots \right] \right] \frac{\text{joule}}{\text{mol}} \tag{22}$$

$$+ R_g t \left[\left(B_m - t \frac{d}{dt} B_m \right) \frac{1}{v_{ma}} + \left[C_m - \left(\frac{1}{2} t \frac{d}{dt} C_m \right) \right] \frac{1}{v_{ma}^2} \right]$$

$$s_{ma} := \left[x_a \left[0.34373874 \cdot 10^2 + 0.52863609 \cdot 10^{-2} \cdot \left(\frac{t}{K}\right)^1 - 0.15608795 \cdot 10^{-4} \cdot \left(\frac{t}{K}\right)^2 \dots \right] \right. \\ \left. + x_w \left[0.2196603 \cdot 10^1 + 0.19743819 \cdot 10^{-1} \cdot \left(\frac{t}{K}\right)^1 - 0.70128225 \cdot 10^{-4} \cdot \left(\frac{t}{K}\right)^2 \dots \right] \right] \frac{\text{joule}}{\text{mol} \cdot K} \tag{23}$$

$$+ R_g \ln \left(\frac{p}{101325 \text{ Pa}} \right) + \left(x_a R_g \ln \left(\frac{p \cdot v_{ma}}{x_a R_g t} \right) \right) + \left(x_w R_g \ln \left(\frac{p \cdot v_{ma}}{x_w R_g t} \right) \right) \dots$$

$$+ \left[R_g \left[\left(B_m + t \frac{d}{dt} B_m \right) \frac{1}{v_{ma}} + \left[\frac{1}{2} \left(C_m + t \frac{d}{dt} C_m \right) \right] \frac{1}{v_{ma}^2} \right] \right]$$

$$\alpha (\log_{10} k)^2 + (\gamma\tau + \delta) \cdot (\log_{10} k) + (\beta\tau^2 + \epsilon\tau - 1) = 0 \tag{24}$$

coefficients for Henry's law constant 'k' for the inert gas

$\alpha_O := -0.0005943$	$\alpha_N := -0.1021$
$\beta_O := -0.1470$	$\beta_N := 0.1482$
$\gamma_O := -0.05120$	$\gamma_N := -0.01900$
$\delta_O := -0.1076$	$\delta_N := 0.03741$
$\epsilon_O := 0.8447$	$\epsilon_N := 0.8510$
$x_O := 0.22$	$x_N := 0.78$

Formulations for Thermodynamic Properties of Air

$$x_{as} := \frac{p - f_{ws}}{p} \quad x_{ws} := \frac{p - f_{ws}}{p} \tag{25}$$

$$\ln(f) := \begin{cases} a1 \leftarrow \left[\frac{(1 + \kappa_{ws})(p - p_{ws}) - \left[\frac{1}{2} \kappa_{ws} (p^2 - p_{ws}^2) \right]}{R_g t} \right] \cdot v_c + \ln(1 - \kappa_{as} p) + \frac{x_{as}^2 p}{R_g t} B_{aa} \\ a2 \leftarrow \left[\frac{2 x_{as}^2 p}{R_g t} \right] B_{aw} - \left[\frac{p - p_{ws} - x_{as}^2 p}{R_g t} \right] B_{ww} + \left[\frac{x_{as}^3 p^2}{(R_g t)^2} \right] C_{aaa}(t) + \frac{3 x_{as}^2 (1 - 2 x_{as}) p^2}{2 (R_g t)^2} C_{aaw} \\ a3 \leftarrow \left[\frac{3 x_{as}^2 (1 - x_{as}) p^2}{(R_g t)^2} \right] C_{aww} - \frac{(1 + 2 x_{as})(1 - x_{as})^2 p^2 - p_{ws}^2}{2 (R_g t)^2} C_{www} \\ a4 \leftarrow \left[\frac{x_{as}^2 (1 - 3 x_{as})(1 - x_{as}) p^2}{(R_g t)^2} \right] B_{aa} B_{ww} \\ a5 \leftarrow \left[\frac{2 x_{as}^3 (2 - 3 x_{as}) p^2}{(R_g t)^2} \right] B_{aa} B_{aw} + \left[\frac{6 x_{as}^2 (1 - x_{as})^2 p^2}{(R_g t)^2} \right] B_{ww} B_{aw} \\ a6 \leftarrow \left[\frac{3 x_{as}^4 p^2}{2 (R_g t)^2} \right] B_{aa}^2 - \left[\frac{2 x_{as}^2 (1 - x_{as})(1 - 3 x_{as}) p^2}{(R_g t)^2} \right] B_{aw}^2 - \left[\frac{p_{ws}(t)^2 - (1 + 3 x_{as})(1 - x_{as})^3 p^2}{2 (R_g t)^2} \right] B_{ww}^2 \\ f \leftarrow (a1 + a2 + a3 + a4 + a5 + a6) \end{cases} \tag{26}$$

$$\kappa(t) := \begin{cases} \left(\frac{ic3}{1 + ic4 \frac{t}{K}} \right) \cdot 10^{-11} Pa^{-1} & \text{if } 373.15 K < t \leq 473.15 K \\ \left(\frac{ic1}{1 + ic2 \frac{t}{K}} \right) \cdot 10^{-11} Pa^{-1} & \text{if } 273.15 K \leq t \leq 373.15 K \end{cases} \tag{27}$$

$$ic1 := \left[\begin{aligned} &0.5088496 \cdot 10^{-2} + 0.6163813 \cdot \left(\frac{t}{K} \right) + 0.1459187 \cdot 10^{-2} \cdot \left(\frac{t}{K} \right)^2 + 0.2008438 \cdot 10^{-4} \cdot \left(\frac{t}{K} \right)^3 \dots \\ &+ -0.5847727 \cdot 10^{-7} \cdot \left(\frac{t}{K} \right)^4 + 0.4104110 \cdot 10^{-9} \cdot \left(\frac{t}{K} \right)^5 \end{aligned} \right]$$

$$ic2 := 0.1967348 \cdot 10^{-1} \quad ic4 := 0.19859983 \cdot 10^{-1}$$

$$ic3 := \left[\begin{aligned} &0.50884917 \cdot 10^{-2} + 0.62590623 \cdot \left(\frac{t}{K} \right) + 0.13848668 \cdot 10^{-2} \cdot \left(\frac{t}{K} \right)^2 + 0.21603427 \cdot 10^{-4} \cdot \left(\frac{t}{K} \right)^3 \dots \\ &+ -0.72087667 \cdot 10^{-7} \cdot \left(\frac{t}{K} \right)^4 + 0.46545054 \cdot 10^{-9} \cdot \left(\frac{t}{K} \right)^5 \end{aligned} \right]$$

$$\kappa := \left(8.875 + 0.0165 \frac{t}{K} \right) \cdot 10^{-11} Pa^{-1} \quad \text{if } t < 273.15 K \tag{28}$$

$$\frac{1}{x_A} := \frac{x_O}{k_O} + \frac{x_N}{k_N} \tag{29}$$