Equations describing the physical properties of moist air

This appendix covers these topics:

Saturation vapour pressure
Definition of the Pascal
Concentration of water vapour in space
Relative humidity
Dew point
Concentration of water vapour in air
Enthalpy
The psychrometer

Water vapour pressure

In a closed container partly filled with water there will be some water vapour in the space above the water. The concentration of water vapour depends only on the temperature. It is not dependent on the amount of water and is only very slightly influenced by the presence of air in the container.

The water vapour exerts a pressure on the walls of the container. The empirical equations given below give a good approximation to the saturation water vapour pressure at temperatures within the limits of the earth's climate.

Saturation vapour pressure, $p_s$, in pascals:

$$p_s = 610.78 \times \exp\left( \frac{t}{(t + 238.3) \times 17.2694} \right)$$

where $t$ is the temperature in degrees Celsius

Thesvp below freezing can be corrected after using the equation above, thus:

$$p_{s, \text{ice}} = -0.00486 + 0.85471 \times p_s + 0.2441 \times p_s^2$$

The next formula gives a direct result for the saturation vapour pressure over ice:

$$p_{s, \text{ice}} = \exp\left( \frac{-6140.4}{(273 + t)} + 28.916 \right)$$

The pascal is the SI unit of pressure = newtons / m². Atmospheric pressure is about 100,000 Pa (standard atmospheric pressure is defined as 101,300 Pa).

Water vapour concentration

The relationship between vapour pressure and concentration is defined for any gas by the equation:

$$p = nRT/V$$

$p$ is the pressure in Pa, $V$ is the volume in cubic metres, $T$ is the temperature in degrees Kelvin (degrees Celsius + 273.16), $n$ is the quantity of gas expressed in molar mass (0.018 kg in the case of water), $R$ is the gas constant: 8.31 Joules/mol/m³
To convert the water vapour pressure to concentration in kg/m³: \((\frac{\text{Kg}}{0.018})/V = \frac{p}{RT}\)

\[\text{kg/m}³ = 0.002166 \times \frac{p}{(t + 273.16)}\] where \(p\) is the actual vapour pressure

Relative Humidity

The Relative Humidity (RH) is the ratio of the actual water vapour pressure to the saturation water vapour pressure at the prevailing temperature.

\[\text{RH} = \frac{p}{p_s}\]

RH is usually expressed as a percentage rather than as a fraction.

The RH is a ratio. It does not define the water content of the air unless the temperature is given. The reason RH is so much used in conservation is that most organic materials have an equilibrium water content that is mainly determined by the RH and is only slightly influenced by temperature.

Notice that air is not involved in the definition of RH. Airless space can have a RH. Air is the transporter of water vapour in the atmosphere and in air conditioning systems, so the phrase "RH of the air" is commonly used, and only occasionally misleading. The independence of RH from atmospheric pressure is not important on the ground, but it does have some relevance to calculations concerning air transport of works of art and conservation by freeze drying.

The Dew Point

The water vapour content of air is often quoted as dew point. This is the temperature to which the air must be cooled before dew condenses from it. At this temperature the actual water vapour content of the air is equal to the saturation water vapour pressure. The dew point is usually calculated from the RH. First one calculates \(p_s\), the saturation vapour pressure at the ambient temperature. The actual water vapour pressure, \(p_a\), is:

\[p_a = p_s \times \frac{\text{RH} \%}{100}\]

The next step is to calculate the temperature at which \(p_s\) would be the saturation vapour pressure. This means running backwards the equation given above for deriving saturation vapour pressure from temperature:

Let \(w = \ln \left( \frac{p_s}{610.78} \right)\)

\[\text{Dew point} = w \times 238.3 \div (17.294 - w)\]

This calculation is often used to judge the probability of condensation on windows and within walls and roofs of humidified buildings.

The dew point can also be measured directly by cooling a mirror until it fogs. The RH is then given by the ratio

\[\text{RH} = 100 \times \frac{p_{dew\text{point}}}{p_{ambient}}\]
Concentration of water vapour in air

It is sometimes convenient to quote water vapour concentration as kg/kg of dry air. This is used in air conditioning calculations and is quoted on psychrometric charts. The following calculations for water vapour concentration in air apply at ground level.

Dry air has a molar mass of 0.029 kg. It is denser than water vapour, which has a molar mass of 0.018 kg. Therefore, humid air is lighter than dry air. If the total atmospheric pressure is \( P \) and the water vapour pressure is \( p \), the partial pressure of the dry air component is \( P - p \). The weight ratio of the two components, water vapour and dry air is:

\[
\frac{\text{kg water vapour}}{\text{kg dry air}} = \frac{0.018 \times p}{0.029 \times (P - p)} = 0.62 \frac{p}{(P - p)}
\]

At room temperature \( P - p \) is nearly equal to \( P \), which at ground level is close to 100,000 Pa, so, approximately:

\[
\frac{\text{kg water vapour}}{\text{kg dry air}} = 0.62 \times 10^{-5} \times p
\]

Thermal properties of damp air

The heat content, usually called the enthalpy, of air rises with increasing water content. This hidden heat, called latent heat by air conditioning engineers, has to be supplied or removed in order to change the relative humidity of air, even at a constant temperature. This is relevant to conservators. The transfer of heat from an air stream to a wet surface, which releases water vapour to the air stream at the same time as it cools it, is the basis for psychrometry and many other microclimatic phenomena. Control of heat transfer can be used to control the drying and wetting of materials during conservation treatment.

The enthalpy of dry air is not known. Air at zero degrees celsius is defined to have zero enthalpy. The enthalpy, in kJ/kg, at any temperature, \( t \), between 0 and 60°C is approximately:

\[
h = 1.007t - 0.026 \quad \text{below zero: } h = 1.005t
\]

The enthalpy of liquid water is also defined to be zero at zero degrees celsius. To turn liquid water to vapour at the same temperature requires a very considerable amount of heat energy: 2501 kJ/kg at 0°C

At temperature \( t \) the heat content of water vapour is:

\[
h_w = 2501 + 1.84t
\]

Notice that water vapour, once generated, also requires more heat than dry air to raise its temperature further: 1.84 kJ/kg°C against about 1 kJ/kg°C for dry air.
The enthalpy of moist air, in kJ/kg, is therefore:

\[ h = (1.007t - 0.026) + g(2501 + 1.84t) \]

*\( g \) is the water content in kg/kg of dry air

### The Psychrometer

The final formula in this collection is the **psychrometric equation**. The psychrometer is the nearest to an absolute method of measuring RH that most people ever need. It is more reliable than electronic devices, because it depends on the calibration of thermometers or temperature sensors, which are much more reliable than electrical RH sensors. The only limitation to the psychrometer is that it is difficult to use in confined spaces (not because it needs to be whirled around but because it releases water vapour).

The psychrometer, or wet and dry bulb thermometer, responds to the RH of the air in this way:

Unsaturated air evaporates water from the wet wick. The heat required to evaporate the water into the air stream is taken from the air stream, which cools in contact with the wet surface, thus cooling the thermometer beneath it. An equilibrium wet surface temperature is reached which is very roughly half way between ambient temperature and dew point temperature.

The air's potential to absorb water is proportional to the difference between the mole fraction, \( m_w \), of water vapour in the ambient air and the mole fraction, \( m_{wa} \), of water vapour in the saturated air at the wet surface. It is this capacity to carry away water vapour which drives the temperature down to \( t_w \), the wet thermometer temperature, from the ambient temperature \( t_a \):

\[
( m_w - m_{wa} ) = B(t_a - t_w)
\]

*\( B \) is a constant, whose numerical value can be derived theoretically by some rather complicated physics (see the reference below).

The water vapour concentration is expressed here as mole fraction in air, rather than as vapour pressure. Air is involved in the psychrometric equation, because it brings the heat required to evaporate water from the wet surface. The constant \( B \) is therefore dependent on total air pressure, \( P \). However the mole fraction, \( m \), is simply the ratio of vapour pressure \( p \) to total pressure \( P \): \( p/P \). The air pressure is the same for both ambient air and air in contact with the wet surface, so the constant \( B \) can be modified to a new value, \( A \), which incorporates the pressure, allowing the molar fractions to be replaced by the corresponding vapour pressures:

\[
p_w - p_{wa} = A( t_a - t_w)
\]

The relative humidity (as already defined) is the ratio of \( p_w \), the actual water vapour pressure of the air, to \( p_s \), the saturation water vapour pressure at ambient temperature.

\[
\text{RH}\% = 100 \times \frac{p_a}{p_s} = 100 \times \frac{p_w - (t_a - t_w) \times 63}{p_s}
\]

*When the wet thermometer is frozen the constant changes to 56*
The psychrometric constant is taken from: R.G. Wylie & T. Lalas, "Accurate
psychrometer coefficients for wet and ice covered cylinders in laminar transverse air
streams", in Moisture and Humidity 1985, published by the Instrument Society of
America, pp 37 - 56. These values are slightly lower than those in general use.

 Doing the calculations

There are tables and slide rules for calculating RH from the psychrometer and other
climatic variables that are not measured directly, but a programmable calculator is very
handy for this job. There is also a downloadable calculator in javascript:

www.natmus.dk/cons/tp/atmcalc/atmocalc.htm

It uses the equations listed here. The file can be used in a web browser even when it is
not online. Psychrometric, or Mollier, charts provide graphical versions of all these
formulæ and don't need electricity.

A list of the formulæ used in this article, in spreadsheet and calculator notation

The following functions are the equations described above, rewritten in a format which
can be further altered to suit the peculiarities of any particular spreadsheet or
programmable pocket calculator. I don't recommend using a simple pocket calculator.

\[
\begin{align*}
\text{function } & \text{TtoSVP}(t) \; // \text{saturation vapour pressure (svp)} \\
\text{svp} &= 610.78 \times \exp\left(\frac{t}{(t+238.3) \times 17.2694}\right); \\
\text{function } & \text{SVPtoT}(vp) \; // \text{dew point temperature (dp) from vapour pressure (vp)} \\
w &= \log\left(\frac{vp}{610.78}\right); \\
dp &= \frac{w \times 238.3}{(17.294 - w)}; \\
\text{function } & \text{VPtoKGM3}(vp, t) \; // \text{kg water/cubic metre from vapour pressure and temperature} \\
\text{kgm} &= 0.002167 \times \frac{vp}{(t+273.16)}; \\
\text{function } & \text{WBtoRH}(t, wb) \; // \text{RH from dry (t) and wet (wb) temperatures} \\
rh &= \frac{(TtoSVP(wb) - (t-wb) \times 66.7)}{TtoSVP(t) \times 100}; \\
\text{function } & \text{VPtoKGKG}(vp) \; // \text{approx. vapour pressure to kg water/kg air at ground level} \\
kprkg &= 0.622 \times \frac{vp}{(101300 - vp)};
\end{align*}
\]

To check your program, take air at 20C and 15.7C wet bulb temperature. The RH is
65%. The water vapour pressure is 1500 Pa. The water vapour concentration in kg/m3
is 0.011, in kg/kg it is 0.009. The dew point is 13C.
Weighed air conditioner

General view, showing details of the main frame and weighing system. Other diagrams show details of the two cooling systems.
Thermoelectric cooler
The first cooling stage

Perspective sketch
of the first stage cooling plate with flexible silicone membrane

The heat sink is normally forced up against the screws by water pressure under the flexible membrane

The heat sink and the thermoelectrically cooled reservoir that is fixed to it are weighed periodically after the water pressure is removed, so that the membrane sinks clear of the heat sink.

The heat sink assembly then puts its entire weight on the cantilever weighing beam.

Heat sink for thermoelectric second stage cooler
Frame clamps silicone membrane to baseplate
Silicone membrane, 1 mm thick, is forced up by water pressure to touch the heat sink
An approximately 2 mm gap opens up when the water pump is stopped and the membrane collapses
Brass wire spiral prevents the collapsed membrane from blocking the water pipes when the pump is stopped. This is important in preventing air accumulating under the membrane
Outlet pipe is narrower than inlet, to give overpressure under membrane
Weighing beam
Beam springs up when water pressure takes the load, so that the fulcrum is always in contact
Water pressure forces the heat sink up against the screws

100 mm
Cover for climate chamber

Tim Podfield, 27/7/97

Square base frame in 3 x 20mm stainless steel. Flat on underside to seal to base plate.

Four sides in two sizes 0.5mm stainless steel. One edge bent out at 90 degrees.

Inside dimensions 810 x 770 x 860 high

Sides fit outside upright part of base frame.

Top in 0.5mm stainless steel. All sides bent up at 90 degrees.

Top has inspection hole covered with polycarbonate.

Spot weld just for rigidity: airtightness is by sealing with silicone.

Hole at each bottom corner for mounting lifting cords, 4mm dia., 10mm from base.
Appendices on the CD-ROM (in html format):

Electrical circuit diagrams
Data logger program
Java code for the modelling program