

Principles of Humidity – Dalton's law

Air is a mixture of different gases. The main gas components are:

Gas component	volume [%]	weight [%]
Nitrogen N ₂	78,03	75,47
Oxygen O ₂	20,99	23,20
Argon Ar	0,93	1,28
Carbon dioxide CO ₂	0,03	0,04
Rest: H ₂ , Ne, He, Kr	0,02	0,01

On normal physical conditions these gases behave ideal which means that the gas molecules act independent from each other which leads to **Dalton's law** :

”The total pressure of a gas is the sum of the pressures of each component”

The pressure of a single component is called **partial pressure**, so the total pressure of air is the sum of the partial pressures of its components i.e.

$$p = p_{N_2} + p_{O_2} + p_{Ar} + \dots$$

dimension of p: [mbar] or [hPa]

Water in its gaseous phase (vapour) is an additional ideal gas component of air which appears in Dalton's law :

$$p = p_{N_2} + p_{O_2} + p_{Ar} + \dots + e = p_{da} + e$$

e partial pressure of (water) vapour [mbar]
 p_{da} partial pressure of dry air

Principles of Humidity - Vapour pressure

Vapour pressure above water

Vapour pressure cannot take on any value in air. There is a maximum partial pressure of vapour which depends only on air temperature. At high temperatures air can hold more vapour than at low temperatures.

This behaviour can be explained in the following way :

The molecules, bounded in a liquid like water, are moving with different velocities and the average kinetic energy is proportional to the temperature of the liquid. The energy distribution of the molecules is statistical as shown in Fig.1.

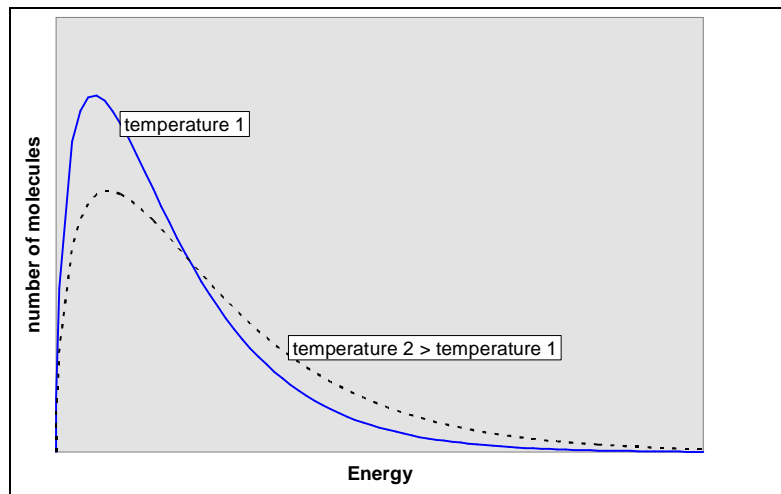


Fig. 1: Statistical energy distribution of molecules in a liquid at different temperatures.

The overall average kinetic energy of the molecules is depending on temperature whereas the energy of a single molecule can be lower or higher with a statistical probability. Molecules with energies below the binding energy of the liquid cannot leave the water surface, but some have enough energy to exceed the binding force. These molecules can leave the liquid, they evaporate from the water surface and increase the vapour concentration in the room above the water surface.

The molecules in the vapour behave similar but for them the case to have less energy than the binding energy of water is exceptional: they are absorbed from the water surface by condensation and decrease the vapour concentration.

A closed box partly filled with water at temperature t (Fig.2) will stabilize in equilibrium between evaporation and condensation. If there is a lack of water molecules in the moist region, more evaporation will occur and the vapour concentration will increase. In the opposite case more molecules will condense than evaporate and the vapour concentration will decrease.

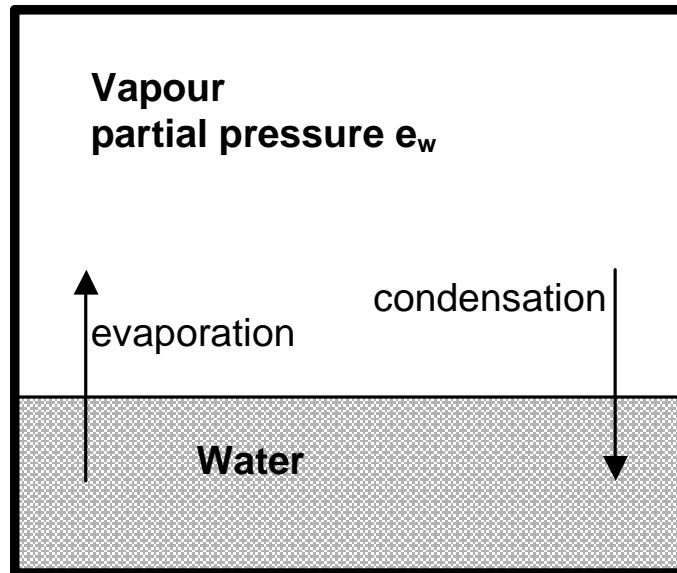


Fig. 2 : Box partly filled with water at constant temperature

The balance between evaporation and condensation leads to a vapour pressure, which depends only on temperature. Increasing the temperature more molecules have higher energies (see Fig.1), will leave the water surface and shift the equilibrium to higher vapour concentrations.

On normal environmental conditions vapour is an ideal gas with no interaction with other present ideal gases. So the vapour concentration is practically independent from other existing gases in the region above the water surface.

In the box at temperature t the balanced vapour pressure is a maximum at this temperature and is called

“saturation vapour pressure” above water e_w at temperature t .

The saturation pressure above water e_w depends approximately exponential on temperature t . Values for e_w for different temperatures are given in Tab.1^[1].

t [degC]	e _w [mbar]	t [degC]	e _w [mbar]
100	1014.19	0	6.112
90	701.82	-10	2.8652
80	474.16	-20	1.2559
70	312.02	-30	0.5103
60	199.48	-40	0.1903
50	123.53	-50	0.0644
40	73.853	-60	0.0195
30	42.470	-70	5.187E-03
20	23.392	-80	1.190E-03
10	12.281	-90	2.298E-04
0.01	6.117	-100	3.622E-05

Tab. 1: Saturation vapour pressure values e_w above water

Vapour pressure above ice

Below t=0.01 degC (triple point of water) water can exist in the liquid phase as well as in the solid phase (ice) but the liquid phase is usually not stable. The physical interpretation of evaporation above ice is equal to water.

t [degC]	e _i [mbar]
0.01	6.117
0	6.112
-10	2.5989
-20	1.0324
-30	0.3800
-40	0.1284
-50	0.0394
-60	0.0108
-70	2.615E-03
-80	5.472E-04
-90	9.670E-05
-100	1.402E-05

Tab. 2 : Saturation vapour pressure values e_i above ice

According to the existence of a solid and liquid phase there are two saturation curves below $t=0.01$ degC as shown in Fig.3 on a logarithmic scale. Mind that between -100 degC and 100 degC the saturation vapour pressure is changing over 8 orders of magnitude !

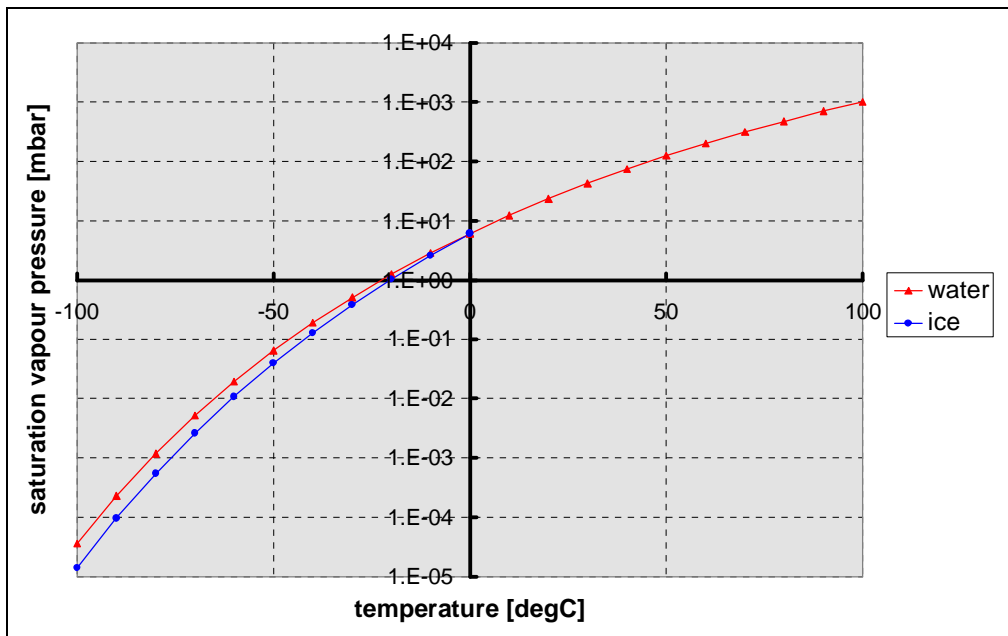


Fig. 3 : Vapour saturation curves above ice and water. Below the triple point ($t=0.01$ degC) the curve splits into two graphs.

Real gas correction

As so far water vapour was treated as an ideal gas i.e. water molecules act independent from the surrounding air. In reality there is an interaction between water molecules and the air which leads to a small increase of saturation vapour pressure under presence of air. This fact is taken into account by the enhancement factor $f(p,t)$.

The saturation vapour pressure under presence of air e'_w is given by

$$e'_w = e_w(t) \cdot f(p,t)$$

At normal pressure ($p < 1100$ mbar) the enhancement factor is close to one and can usually be neglected. This means that water vapour mostly behaves like an ideal gas.

If you wish higher accuracies you should correct the saturation water pressure using the enhancement factor f , which depends on air pressure p and temperature t (for values see Tab.3^[2]).

t [degC]	-40	-20	0	10	20	30	40	60	80
p [bar]									
0.25	1.0013	1.0012	1.00131	1.00148	1.00173	1.00202	1.00223	1.00111	
0.5	1.0026	1.0022	1.00217	1.00229	1.00251	1.00284	1.00323	1.00362	1.00051
1	1.0052	1.0044	1.0039	1.00388	1.004	1.00426	1.00467	1.00571	1.00564
1.5	1.0078	1.0065	1.0056	1.0055	1.00547	1.00564	1.00599	1.00713	1.00801
2	1.0104	1.0086	1.0074	1.0071	1.0069	1.00701	1.00728	1.00839	1.00968
2.5	1.013	1.0108	1.0091	1.0087	1.0084	1.0084	1.0086	1.00959	1.01108
3	1.0156	1.0129	1.0108	1.0103	1.0099	1.0097	1.0098	1.0108	1.01234
3.5	1.0183	1.015	1.0126	1.0119	1.0114	1.0111	1.0111	1.0119	1.01351
4	1.0209	1.0172	1.0144	1.0135	1.0128	1.0125	1.0124	1.013	1.0146
4.5	1.0236	1.0194	1.0161	1.0151	1.0143	1.0138	1.0136	1.0142	1.0157
5	1.0262	1.0215	1.0179	1.0167	1.0158	1.0152	1.0149	1.0153	1.0168
10	1.0533	1.0435	1.0356	1.033	1.0308	1.029	1.0277	1.0265	1.0271
20	1.11	1.089	1.072	1.066	1.0615	1.0573	1.0539	1.0493	1.0474
30	1.171	1.138	1.111	1.101	1.093	1.087	1.081	1.073	1.068
40	1.237	1.189	1.151	1.138	1.126	1.117	1.109	1.096	1.089
50	1.307	1.243	1.193	1.175	1.161	1.148	1.137	1.121	1.111
60	1.38	1.3	1.237	1.215	1.196	1.18	1.167	1.146	1.133
70	1.46	1.36	1.282	1.256	1.233	1.213	1.197	1.172	1.155
80	1.55	1.42	1.33	1.298	1.271	1.248	1.228	1.198	1.178
90	1.64	1.49	1.381	1.343	1.311	1.284	1.261	1.226	1.202
100	1.75	1.56	1.43	1.389	1.352	1.32	1.294	1.254	1.226

Tab. 3 : Enhancement factor $f(p,t)$

Principles of Humidity - Magnus formula

The saturation vapour pressure above ice and water can be calculated with good accuracy with the Magnus formula ^[1]:

$$e_{w,i} = A \exp\left(\frac{m \cdot t}{T_n + t}\right)$$

The parameters A, m, T_n are different for ice and water and are given in Tab. 4.

Temperature range t [degC]	A	m	T _n
above ice : -80 to 0.01	6.112	22.46	272.62
above water : -45 to 50	6.112	17.62	243.12

Tab. 4 : Magnus formula parameter ^[1]

Principles of Humidity – Relative humidity

Relative humidity U_w [%]

Table 1 and 2 (in section “Vapour pressure”) give values for the saturation water vapour pressure as a function of temperature. These values are maximum values, in practice partial vapour pressures are usually lower.

Relative humidity U_w is defined as the ratio between the actual partial vapour pressure e and the saturation vapour pressure above water e_w

$$U_w = \frac{e}{e_w} \cdot 100 \quad [\%]$$

Since the partial vapour pressure cannot exceed the saturation vapour pressure, the maximum value of relative humidity is $U_w=100\%$.

Relative humidity below the triple point

The definition of relative humidity below the triple point of water $t < 0.01$ degC refers again to the saturation pressure above water. In this exceptional temperature regime you can either have water with saturation vapour pressure e_w or ice with a smaller value $e_i < e_w$. In most applications however you will find ice since this is the stable state for temperatures $t < 0.01$ degC. So the case $e=e_i$ gives you an upper limit for the relative humidity:

$$t < 0.01^\circ\text{C}: U_{w,\max} = \frac{e_i}{e_w} \cdot 100 \quad [\%]$$

t [degC]	0	-5	-10	-15	-20	-25	-30	-35	-40
e_i [mbar]	6.108	4.015	2.597	1.652	1.032	0.633	0.380	0.223	0.128
e_w [mbar]	6.108	4.212	2.857	1.905	1.246	0.799	0.502	0.308	0.184
U_{\max} [%]	100%	95%	91%	87%	83%	79%	76%	73%	70%

Tab. 5 : Maximum relative humidity values above ice

Principles of Humidity - Dew Point, Frost Point

When you cool down air containing vapour below the saturation concentration the actual partial pressure e initially stays constant while the relative humidity is increasing due to the decrease of the saturation vapour pressure with temperature t .

$$U_w = \frac{e}{e_w} \cdot 100 \quad [\%]$$

t decreasing $\rightarrow e_w(t)$ decreasing $\rightarrow U_w$ increasing

At the “**dew point temperature t_d** ” the saturation vapour pressure equals the actual vapour pressure i.e. $e_w(t_d)=e$ and the relative humidity reaches its maximum value of $U_w=100\%$.

The dew point temperature t_d is therefore the temperature to which you have to cool down moist air at constant pressure for beginning condensation. It can be calculated from the temperature and relative humidity using the Magnus formula :

t [$^{\circ}\text{C}$] \rightarrow saturation vapour pressure e_w

$$e_w[\text{mbar}], U_w [\%] \rightarrow e = \frac{e_w \cdot U_w}{100}$$

$$e \rightarrow t_d = T_n \cdot \frac{\ln\left(\frac{e}{A}\right)}{\left(m - \ln\left(\frac{e}{A}\right)\right)}$$

The Magnus parameters A , m , T_n are given in Table 4 in the section “Magnus Formula”.

Decreasing the temperature below the dew point temperature the partial vapour pressure exceeds the saturation value, so condensation occurs until the balance is reached again.

Below the triple point of water $t < 0.01^{\circ}\text{C}$ you will usually find ice (e_i) in your application instead of water (e_w). The temperature at which the partial vapour pressure e reaches the saturation vapour pressure e_i and frosting starts is called “frost point” $t_f > t_d$.

Principles of Humidity – Absolute Humidity

Absolute humidity d_v [g/m³]

Gives the mass of water in 1 m³ moist air and can be calculated from the temperature t [degC] and the partial vapour pressure e [mbar] :

t [degC] \rightarrow saturation vapour pressure $e_w \rightarrow e = e_w \cdot U_w$

$$d_v = 216.7 \cdot \left(\frac{e}{273.15 + t} \right) \text{ [g/m}^3\text{]}$$

Principles of Humidity – Mixing ratio

Mixing ratio r [g/kg]

Gives the mass of water you have to evaporate and mix with 1 kg dry air to perform a certain relative humidity U_w or partial vapour pressure e

t [degC] \rightarrow saturation vapour pressure $e_w \rightarrow e = e_w \cdot U_w$

$$r = \frac{622 \cdot e}{(p - e)} \quad [g / kg]$$

p air pressure [mbar]

Principles of Humidity – Specific Enthalpy

Specific enthalpy h [kJ/kg]

The specific enthalpy of air with temperature t , relative humidity U_w and corresponding mixing ratio r is the sum of the energies you need to create this state in the following way :

- a) warming up 1 kg dry air from 0 degC to t
- b) evaporating the vapour inside the moist air
- c) warming up the vapour from 0 degC to t

Ⓜ **Specific Enthalpy per 1 kg dry air:**

$$h = [c_{pa} \times t + (l_w + c_{pv} \times t) \times r] \quad [\text{kJ/kg}]$$

$c_{pa} = 1.00545$ kJ/kg specific heat capacity of dry air at constant pressure

$c_{pv} = 1.85894$ kJ/kg specific heat capacity of vapour at constant pressure

$l_w = 2500.827$ kJ/kg latent heat of water

The specific enthalpy is a relative quantity i.e. only differences are significant.

More generally enthalpy gives you the amount of energy which you need to bring moist air from a thermal state 1 into a state 2.

Example 1 :

To warm up air from 20 to 25 degC and humidify the air from 40 to 60 % relative humidity you will need $h=20.2$ kJ/kg.

Example 2 :

Warming up air from 20 to 25 degC and keeping the relative humidity constant dissipates only $h=10.3$ kJ/kg.

Example 3 :

When warming up air from 20 to 25 degC and keeping the partial vapour pressure e constant ($r = \text{constant}$, $t_d = \text{constant}$) the relative humidity decreases down to $U_w=29.5$ % which wastes only $h=5.1$ kJ/kg.

These examples are summarized in Table 6 and are drawn as “process 1, 2, 3” in Fig. 4 in the section “Mollier diagram”.

Example 1	t [degC]	U_w [%]	h [kJ/kg]
state 1	20	40	34.6
state 2	25	29.5	39.7
		<i>difference</i>	5.1
Example 2	t [degC]	U_w [%]	h [kJ/kg]
state 1	20	40	34.6
state 2	25	40	44.9
		<i>difference</i>	10.3
Example 3	t [degC]	U_w [%]	h [kJ/kg]
state 1	20	40	34.6
state 2	25	60	54.8
		<i>difference</i>	20.2

Tab. 6: Enthalpy differences with different changes of state

Principles of Humidity - Mollier diagram

Table 7 summarizes humidity function values at different temperatures. A Mollier diagram serves for solving problems in air conditioning technology graphically. It summarizes different humidity functions in one chart.

Using the mixing ratio r there is a relation between r and temperature t with relative humidity U_w as free parameter :

$$r = \frac{622 \cdot e}{p - e} \rightarrow e = \frac{p \cdot r}{622 + r} = \frac{e_w(t) \cdot U_w}{100}$$

Using the Magnus formula you can draw a band of curves of constant relative humidity U_w as functions $t(r)$ which is called “Mollier diagram”. It is convenient to add curves of constant enthalpy to the Mollier diagram (as in Fig. 4) :

$$h = [c_{pa} \cdot t + (I_w + c_{pv} \cdot t) \cdot r] \rightarrow t = (h - I_w \cdot r) / (c_{pa} + c_{pv} \cdot r)$$

In this way you can describe graphically thermodynamical processes such as examples 1, 2, 3 in the section “Specific Enthalpy”.

In a professional Mollier diagram usually further humidity functions are included.

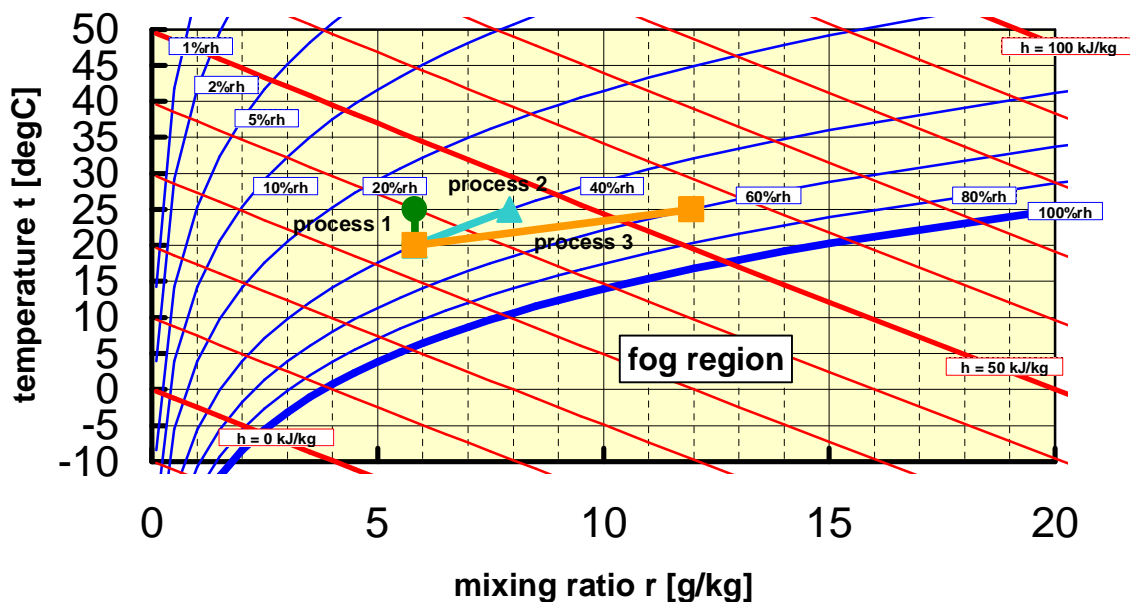


Fig. 4 : Mollier diagram : curves of constant relative humidity and enthalpy. Examples 1, 2, 3 from the section “Specific Enthalpy” are drawn as processes 1, 2, 3.

Tab. 7: Humidity function values at different temperatures
($p = 1013.25$ mbar, real gas corrections are taken into account) :

-20 degC					
U_w [%]	t_d [degC]	e [mbar]	d_v [g/m ³]	r [g/kg]	h [kJ/kg]
80	-22.56	1.013	0.867	0.622	-18.56
70	-24.07	0.886	0.758	0.544	-18.76
60	-25.78	0.759	0.650	0.467	-18.95
50	-27.78	0.633	0.542	0.389	-19.14
40	-30.17	0.506	0.433	0.311	-19.34
30	-33.17	0.380	0.325	0.233	-19.53
20	-37.26	0.253	0.217	0.155	-19.72
10	-43.90	0.127	0.108	0.078	-19.92

0 degC					
U_w [%]	t_d [degC]	e [mbar]	d_v [g/m ³]	r [g/kg]	h [kJ/kg]
100	0.00	6.139	4.870	3.791	9.45
90	-1.45	5.525	4.383	3.410	8.50
80	-3.04	4.911	3.896	3.029	7.55
70	-4.82	4.297	3.409	2.649	6.61
60	-6.85	3.683	2.922	2.269	5.66
50	-9.20	3.069	2.435	1.890	4.72
40	-12.02	2.456	1.948	1.511	3.77
30	-15.55	1.842	1.461	1.133	2.83
20	-20.35	1.228	0.974	0.755	1.89
10	-28.11	0.614	0.487	0.377	0.94
5	-35.34	0.307	0.243	0.188	0.47

20 degC					
U_w [%]	t_a [degC]	e [mbar]	d_v [g/m³]	r [g/kg]	h [kJ/kg]
100	20.00	23.431	17.318	14.723	56.64
90	18.31	21.088	15.586	13.220	52.96
80	16.44	18.745	13.854	11.723	49.28
70	14.36	16.402	12.123	10.234	45.62
60	12.00	14.059	10.391	8.751	41.95
50	9.26	11.715	8.659	7.276	38.30
40	5.98	9.372	6.927	5.807	34.65
30	1.88	7.029	5.195	4.345	31.00
20	-3.67	4.686	3.464	2.890	27.36
10	-12.60	2.343	1.732	1.442	23.73
5	-20.89	1.172	0.866	0.720	21.92

40 degC					
U_w [%]	t_a [degC]	e [mbar]	d_v [g/m³]	r [g/kg]	h [kJ/kg]
100	40.00	74.052	51.237	49.041	158.72
90	38.04	66.647	46.113	43.791	146.57
80	35.89	59.242	40.989	38.623	134.49
70	33.48	51.836	35.866	33.535	122.47
60	30.76	44.431	30.742	28.525	110.52
50	27.61	37.026	25.618	23.590	98.64
40	23.84	29.621	20.495	18.730	86.83
30	19.14	22.216	15.371	13.943	75.08
20	12.79	14.810	10.247	9.226	63.39
10	2.62	7.405	5.124	4.579	51.77
5	-6.78	3.703	2.562	2.281	45.99

60 degC					
U_w [%]	t_a [degC]	e [mbar]	d_v [g/m³]	r [g/kg]	h [kJ/kg]
100	60.00	200.610	130.470	153.543	400.02
90	57.74	180.549	117.423	134.859	363.59
80	55.26	160.488	104.376	117.055	327.75
70	52.50	140.427	91.329	100.069	292.48
60	49.38	120.366	78.282	83.846	257.75
50	45.79	100.305	65.235	68.337	223.57
40	41.51	80.244	52.188	53.494	189.91
30	36.17	60.183	39.141	39.276	156.77
20	28.99	40.122	26.094	25.644	124.14
10	17.51	20.061	13.047	12.563	91.99
5	6.97	10.030	6.523	6.219	76.10

Principles of Humidity - Literature

[1] Sonntag D.: Important New Values of Physical Constants of 1986, Vapour Pressure Formulations based on the ITS-90 and Psychrometer Formulae; *Z.Meteorol.*70 (1990) 5, 340-344

[2] Hyland R.W.: A Correlation for the second Interaction Virial Coefficients and Enhancement Factors for Moist air; *J.Research NBS, A.Physics and Chemistry* 79A (1975) 551-560