

## C. Saturation pressure of water vapor



In 1824 a French engineer, Sady Nicolas Léonard Carnot (1796-1832), published the only work in his lifetime: A book dealing with the maximum efficiency that could be obtained from a steam machine, equivalent to the efficiency of the "Carnot cycle". In this book, an equation for the saturation pressure of water vapor was given:

$$p_s = p_{s0} e^{\frac{h_{fg}}{R} \left( \frac{1}{T_0} - \frac{1}{T} \right)} = 4.58 e^{5210 \left( \frac{1}{273.15} - \frac{1}{273.15+t^{\circ}\text{C}} \right)}$$

where:

$p_s$  = saturation pressure of water vapor in mmHg @  $t$  °C

$T_0 = 273.15$  °K

$p_{s0}$  = saturation pressure of water vapor = 4.58 mmHg @  $T_0$ ;

$h_{fg} = M_{\text{vapor}} C_{\text{vapor}} = 18.016 \text{ (g / mol)} * 2.4045 * 10^3 \text{ (joules / g)} = 43319 \text{ joules/mol}$ ;

$R = 8.3143 \text{ joules / mol / }^{\circ}\text{K}$

$h_{fg} / R = 5210$  °K.

<b>Table 1</b> <b>Saturation Pressure</b> <b>of Water Vapor</b> <b>- Experimental Data -</b>	
°C	ps (mmHg)
0	4.58
5	6.51
10	8.94
15	12.67
20	17.50
40	55.10
60	149.00
<b>80</b>	<b>355.00</b>
<b>At the Everest peak</b> <b>(8850 m, 241 mmHG)</b> <b>water boils at ~70°C</b>	
<b>100</b>	<b>760.00</b>
<b>At sea level</b> <b>water boils at 100°C</b>	
<b>120</b>	<b>1 490.00</b>
<b>Inside a pressure cooker</b> <b>water boils at 120°C</b>	
140	2 710.00
160	4 630.00
180	7 510.00
200	11 650.00
220	17 390.00

Nowadays, this equation, known as the "Clausius-Clapeyron Equation", is derived from the first (conservation of energy) and the second (entropy never decreases) principles of Thermodynamics (See Annex D, as well as R. P. Feynman, "Lectures on Physics", Vol. 1, item 45-3, Addison-Wesley Pub., 1963).

The equation states that:

- (1) At a given temperature, the amount of water vapor in a certain volume, can not increase forever, or
- (2) There is a physical limit to the amount of water the volume can hold, or
- (3) The density of water vapor always has a maximum (or "saturation") value (Table 2).

This is welcomed limit, since without it all the water on Earth would be found in the atmosphere, thus making life would be impossible on land, due to the lack of liquid water and oxygen. This limit also governs the formation of clouds, rain and snow.

For example, inside a volume of 1.0 liter volume, at 20°C, the maximum amount of water vapor that could exist is 17.23 mg (172.3 drops of liquid water). This corresponds to a pressure of 17.5 mmHg, according to Ideal Gas Law (see annex A):

$$p_s = \frac{mRT}{VM} = \frac{0.01723\text{g} \cdot 0.08207(\text{liter} \cdot \text{atm}/\text{mol}/^\circ\text{K})(273.15 + 20)^\circ\text{K}}{(1 \text{ liter})18(\text{g}/\text{mol})} \cdot 760(\text{mmHg}/\text{atm}) = 17.5 \text{ mmHg}$$

This is the "saturation pressure of water vapor at 20°C", or  $p_s(20^\circ\text{C})$ , as found on Table 1. It corresponds to the maximum amount of water vapor a volume of 1.0 liter can hold at 20°C, or to a maximum density of 17.23 g/m<sup>3</sup>. It is important to emphasize that the volume of 1 liter may be void or occupied by other gases or vapors: This does not change the saturation pressure of water vapor. Nature adjusts the pressure of the other gases so that the total pressure is maintained at a given value, e.g., the atmospheric pressure, if water vapor is in the air.

**Note:** This "natural adjust" of pressures is valid for any temperature, although the numerical value of the saturation pressure is not always given by that equation, which is only valid for temperatures within the range 0-50°C (more later).

If the air pressure is less than  $p_s$ , liquid water begins to boil, if sufficient heat is added to it. Note that at sea level the air pressure is 1 atmosphere = 760 mmHg = 101.325 kPascal = 14.7 psi (pounds per square inch), which is the same saturation pressure shown on the table for 100°C (212°F), the well known boiling point of liquid water at sea level.

Of course, if one plans to make a cup of tea by heating a kettle with water on the top of a very high mountain, the tea will never be very hot. In this case, a pressure cooker must be used instead: As pressure inside the cooker increases, so increases the saturation pressure and, with it, the boiling point of water increases. For instance, if pressure inside the cooker is around 2 atmospheres (1520 mmHg), water will boil around 120°C (Table 1).

Now let's suppose that the amount of water vapor in the air, at 20°C, is less than 17.23 mg per liter, say, 9.86 mg/liter (98.6 drops per liter). Using again the Ideal Gas Law, the vapor pressure in this case is 10 mmHg or only 57.2% ( $100 \times 9.86 / 17.23$ ) of the saturation mass of water vapor. The same figure is obtained dividing  $p_s$  by  $p$ :  $100 (10 / 17.5) = 57.2\%$ . This is the "Relative Humidity of the Air", measured by the psychrometer.

Going back to the saturation-pressure equation, when comparing the experimental values of  $p_s$  (Table 1) with the predicted values of the Clausius-Clapeyron equation, the fit is poor for temperatures outside the range 0-50°C, indicating that this equation does not best represent the real data, meaning that the underlying theory is not quite adequate.

To improve the fit between the measured and the predicted values, several empirical formulas (empirical = no theoretical foundation) have been proposed, such as: Goff-Gratch (1946), WMO (2000), Hyland and Wexler (1983), Buck (1981), Sonntag (1994), Magnus Teten (1967) and Bolton (1980). (See "Discussion of saturation vapor pressure formulations" by Dr. Holger Völmer at <http://cires.colorado.edu/~voemel/home.html>).

Although the Goff-Gratch equation is considered the "standard", the most used is the Teten formula, due to its simplicity (consuming less computer time) and small fitting error:

Note also its similarity with the Clausius-Clapeyron equation.

$$p_s(t^\circ\text{C}) = (0.61078 * 7.501) e^{\left(\frac{17.2694t}{238.3+t}\right)} \text{ mmHg}$$

$$1 \text{ kPascal} = 7.501 \text{ mmHg}$$

This expression is used in this paper. It must be noted that the Teten formula and Ideal Gas Law should also be used only for temperatures within the range 0-50°C, since outside this range the calculated values using these expressions do not fit anymore the experimental values. (Compare tables 1 and 2)

Table 2 shows the maximum density of water vapor at a given temperature, calculated using the Teten formula and the Ideal Gas Law:

$$\frac{m}{V} = \left( \frac{M}{RT} \right) p_s(t)$$

where

$m/V$  = density of water vapor, grams / ( cubic meters )

$M$  = 18 grams/mol of water

$R = p_0 V_0 / T_0 = 760 \text{ mmHg} (22.415/1000) (\text{m}^3/\text{mol}) / (273.15 \text{ }^\circ\text{C}) =$   
 $= 0.0623665 \text{ mmHg} \times \text{m}^3 / \text{ }^\circ\text{C} / \text{mol}$

t	ps	m/V
°C	mmHg	g/m3
0	4.6	4.8
5	6.5	6.8
10	9.2	9.4
15	12.7	12.8
20	17.4	17.2
25	23.6	22.9
30	31.6	30.1
35	41.8	39.2
40	54.8	50.5
45	71.2	64.6
50	91.6	81.8

