

Determination of Relative Humidity in Subzero Temperatures

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Abstract: Relative Humidity of a gas, at any given temperature, is defined as the percentage ratio of the amount of water vapor present in the gas to the maximum amount of water vapor possible at that same temperature. At temperatures above freezing, water can exist in only one of two thermodynamically stable states. It can exist in the gaseous form, known as water vapor, or it can condense into a liquid, often referred to as dew. And as might be expected at subzero temperatures, water can exist as either a gas, again known as water vapor, or it can condense in the form of a solid, often referred to as either frost or ice. But contrary to intuition, water at subzero temperature can also exist in a third thermodynamic state, liquid. The subzero liquid state is an achievable metastable state with an energy level between that of the gas and solid. Subzero water in this metastable state is said to be super-cooled. It is most often referred to as super-cooled water, super-cooled dew, or super-cooled liquid, all of which mean the same thing. Water in the super-cooled state is a liquid, but is at a subzero (below freezing) temperature. In the temperature range 0 to -40°C , the super-cooling phenomenon is quite prevalent. At these subzero temperatures, where the possibility of super-cooling exists, Relative Humidity may be computed in either of two distinct methods, termed *Standard* and *WMO*.

Standard RH: Mathematically, the formula for calculation of Relative Humidity is expressed as

$$\%RH = e / e_s * 100 \tag{1}$$

where e is the water vapor content of the gas (water vapor pressure)
 e_s is the maximum possible water vapor content of the gas at that same temperature (saturation vapor pressure)

As expressed in the above formula, only two things must be known (namely e and e_s) in order to determine the Relative Humidity.

The saturation vapor pressure, e_s , which is an expression of the maximum possible water vapor content at the gas temperature, is a well-known quantity. Saturation vapor pressure is determined by measuring the gas temperature, then computing the corresponding saturation vapor pressure using documented saturation vapor pressure formulas¹. These formulas express vapor pressure as a function of temperature. Note that there is a formula for saturation vapor pressure over water for temperatures above freezing, and one over ice for subzero temperatures.

The actual water vapor content (or water vapor pressure) is often determined through measurement. One popular measurement method is chilled mirror hygrometry. Through measurement of either the frost point or dew point from the chilled mirror hygrometer, the actual vapor pressure is determined from the same saturation vapor pressure formulas¹ as above. When doing so, the formula for saturation vapor pressure over water is used for dew point temperatures, while frost points require the saturation vapor pressure over ice. Not that regardless which measurement is obtained from the chilled mirror (dew or frost point), the corresponding vapor pressure will be the same.

Now for Standard RH, the denominator of equation 1 (the maximum possible water vapor content) is computed over water for temperatures above freezing, and over ice for all below freezing temperatures. In a two-temperature humidity generator, where the saturator is condensing/subliming to/from ice, this is the proper representation of the maximum possible water vapor content.

Likewise, the numerator (the actual water vapor content) is computed over water when the mirror measures a dew point, and over ice for all frost point measurements. In this way, Standard RH values are achievable up to 100% both for warmer, and subzero temperatures. Standard RH assumes that the maximum water vapor content possible is through saturation over ice for subzero temperatures.

WMO RH: WMO RH computations, and the following discussion, apply *only* to temperatures below freezing. In the atmosphere, it is possible to have condensation of vapor into the liquid (rather than ice) state at temperatures below freezing through the phenomenon known as super-cooling. In fact, most chilled mirrors exhibit this super-cooled state at temperatures between 0 and about -20°C . Whether the measurement indicates it is super-cooled or not, is completely independent of any methods used to saturate or otherwise impart water vapor into the gas, or any methods used to remove water vapor from the gas. Super-cooled condensation on a mirror (a dew point measurement) is a perfectly allowable metastable state, just as condensation on the mirror to ice (a frost point measurement) would be a perfectly allowable stable state. However, the super-cooled dew will occur at a temperature below that of the ice, and results in the same measure of water vapor content.

Since the super-cooling phenomenon does occur in clouds and the upper atmosphere, it was decided nearly a half century ago by the World Meteorological Organization (WMO) that RH be calculated by computing the denominator (or maximum possible water vapor content) over *water* rather than ice regardless of the temperature. This results in a higher value of maximum possible water vapor content at any given temperature, than does the corresponding computation over ice at the same temperature. It appears that the basis behind the decision was to prevent the occasional possibility of RH values in excess of 100% when the atmosphere was in a super-cooled state. In this state, an atmosphere saturated with respect to super-cooled water is considered over saturated with respect to ice. An RH of 100% calculated with the WMO method would actually be $>100\%$ if

computed as Standard RH. It is also important to note that with both methods, the *actual* water vapor content is equal and identical. It is only the *maximum possible* vapor content that is different which is dependent upon whether the atmosphere is in a super-cooled metastable state or not.

Standard vs. WMO Computations: The Standard and WMO methods of RH computation will produce different numeric results, given the same actual water vapor content (e), and the same temperature. The following tables illustrate the differences at various temperatures, first at 100% RH_{WMO}, and then again at 100% RH_{Standard}:

t°C	RH _{WMO}	RH _{Standard}
0	100%	100%
-10	100%	110.3%
-20	100%	121.7%
-30	100%	134.3%
-40	100%	148.3%

t°C	RH _{WMO}	RH _{Standard}
0	100%	100%
-10	90.7%	100%
-20	82.2%	100%
-30	74.5%	100%
-40	67.4%	100%

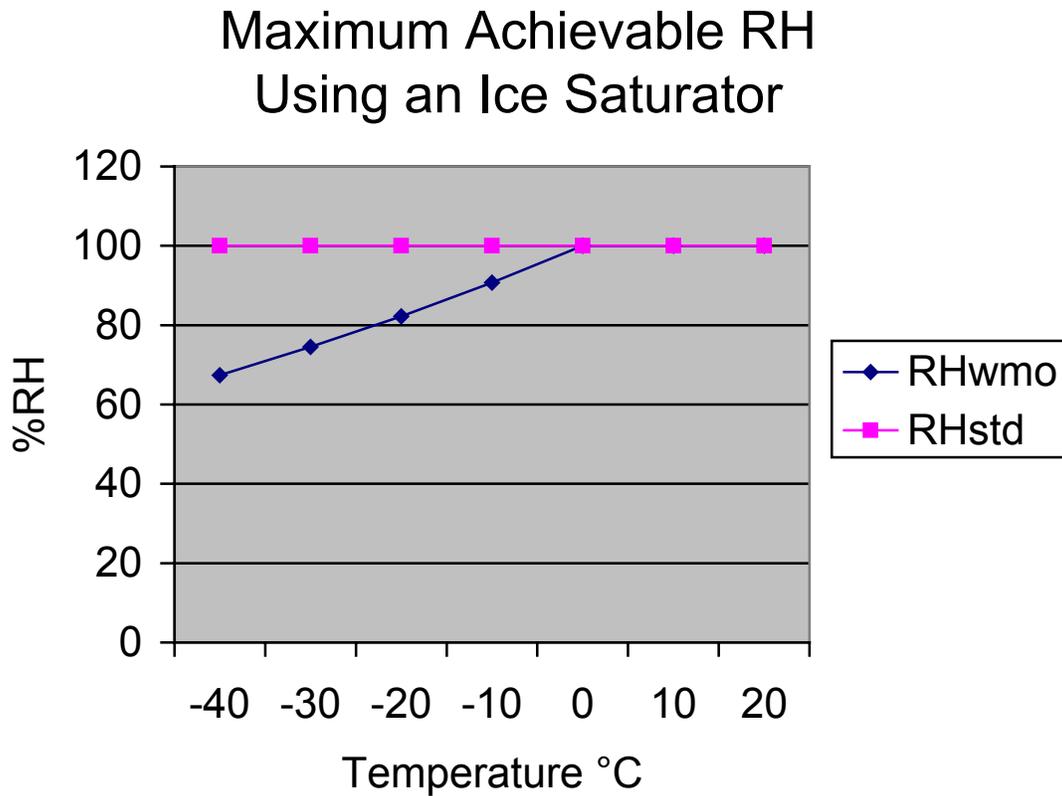
Again, the only difference between the WMO and Standard methods is whether the denominator of the RH equation is calculated with respect to water or with respect to ice. In the Standard method, it is assumed that water vapor in excess of the maximum possible will condense out in the form of ice. With the WMO method, it is assumed that the water vapor can be over saturated with respect to ice, and any water vapor in excess of the maximum possible with respect to super-cooled water will condense out in the form of super-cooled dew.

Note also that in the case of 100% RH_{WMO}, there is a significant amount of over saturation with respect to ice. If ice does begin to form somewhere, the effect will be for a significant amount of icing to occur in that area as the gas attempts to reduce its actual water vapor content to 100% RH_{Standard}.

Take the case in the above table of -40°C with 100% RH_{WMO}. Since the RH_{Standard} is 148%, if icing does begin to occur somewhere, the excess 48% will be attempting to condense into additional ice buildup in order to drive the actual water vapor content down toward 67% RH_{WMO} or 100% RH_{Standard}.

Humidity Generation: When generating RH from an ice filled saturator, or from one which condenses to ice, the maximum possible water vapor content obtainable is with respect to ice at the saturation temperature, provided the gas undergoes no further cooling after leaving the saturator. Also, in a gas stream saturated to 100%RH with this method, condensation should not occur on any object who's temperature is even slightly warmer than the saturation temperature (also equivalent to the measured frost point temperature when the gas is saturated to 100%RH).

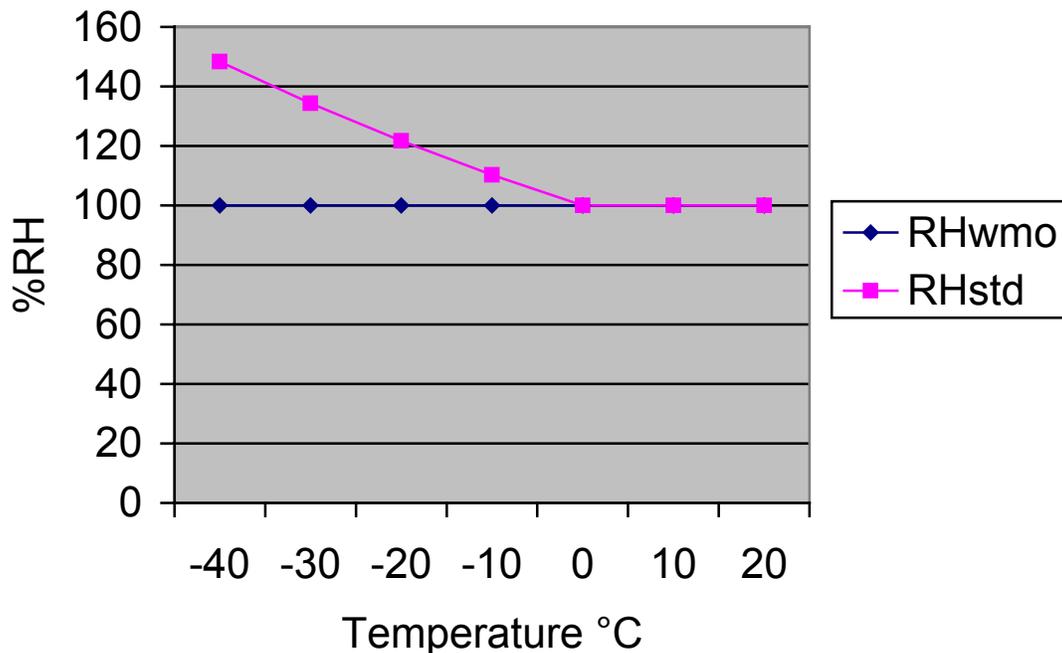
The following graph illustrates the maximum obtainable RH assuming that the humidity is generated using two-temperature techniques in an ice saturator, and that there is no further cooling of the gas.



If the humidity can be generated in such a way as to provide full saturation with respect to super-cooled water (over saturation with respect to ice) without causing ice or frost formation, then the following graph illustrates the maximum achievable RH. Note that any formation of ice will attempt to limit the maximum to the equivalent of 100% $RH_{Standard}$.

$RH_{Standard}$.

Maximum Achievable RH Under Super-Cooled Conditions



Note that in each of the graphs above, $RH_{Standard}$ and RH_{WMO} , at a given temperature, represent the exact same water vapor content in the gas. The only reason the RH values differ from each other in value is that the denominator of the equation (the maximum possible water vapor content) is different.

Reference:

1. Hardy, Bob, *ITS-90 Formulations for Vapor Pressure, Frostpoint Temperature, Dewpoint Temperature, and Enhancement Factors in the Range -100 to +100 C*, Papers and Abstracts from the Third International Symposium on Humidity & Moisture, London, England, April 1998, Volume 1, 214-222.