## Application Note - Effect of System Pressure on the Water Vapor Content of Humidified Gases

Why does the water consumption rate of the fuel cell test stand humidifiers decrease with increasing pressure? Does the relative humidity of the gas change with pressure, all else being equal?

To answer the first question, we will re-phrase it in a way that may be more intuitive to understand. What we are really asking is: Why does the amount of water vapor ( $w v$ ) per unit of mass, or standard volume of dry gas $(g)$, decrease with an increase in pressure?
(In this context, a dry gas refers to a reactant gas such as hydrogen or air, or a purge gas such as nitrogen. Text books on psychrometrics, which is the science of moist gas or water vapor-gas mixtures, may refer to the dry gas component as dry air because of the discipline's application to building heating and cooling where air is the primary dry gas.)

Re-phrasing the question immediately reveals that if the water consumption rate decreases with increasing pressure, then the amount of water per mass of dry gas must decrease with increasing pressure.

We can understand this in terms of compression of saturated gas because this is the principle by which heat exchangers that are based on a phase-change function. This includes refrigerators and heat pumps.

Consider the case for the heat cycle of a heat pump. If a gas saturated with vapor phase component $X$ is compressed, some of the vapor will condense to the liquid phase of component $X$. The heat released during the gas-to-liquid phase change - the heat of condensation - is what is used to heat the air. Thus, the compressed gas, that is the gas under higher pressure, contains less of the vapor phase of component $X$ than the same gas at lower pressure.

Consider a volume saturated in water vapor. Therefore, the partial pressure of water vapor ( $p_{w v}$ ) is the saturated water vapor pressure ( $p_{\text {wvs }}$ ),

$$
\begin{equation*}
p_{w v, 1}=p_{w v s}(T) \tag{1}
\end{equation*}
$$

The saturated water vapor pressure is solely a function of temperature.
If we now instantly double the pressure of the system (at constant temperature) by reducing the volume to half of the initial value, than the partial pressure of water vapor (and partial pressure of dry gas) doubles,

$$
\begin{equation*}
p_{w v, 2}=2 p_{w v, 1}=2 p_{w v s}(T) \tag{2}
\end{equation*}
$$

By definition, because $p_{w v, 2}>p_{w v s}(T)$, the volume is supersaturated with respect to water vapor and water will condense such that the actual water vapor pressure again equals the saturated water vapor pressure, $p_{w v, f i n a l}=p_{\text {wvs }}(T)$. This example illustrates that a water vapor-saturated gas
at higher pressure must have lower water vapor content than a gas saturated in water vapor at a lower pressure.

## Mathematical Approach:

Dalton's Law states that the total pressure exerted by a gaseous mixture is equal to the sum of the partial pressure of each individual component in a gas mixture. The law relates to the Ideal Gas Laws and assumes that the gases do not react with each other. Mathematically, the total pressure ( $p_{\text {total }}$ ) of a mixture of gases can be defined as the sum of the partial pressure ( $p_{i}$ ) of each component,

$$
\begin{equation*}
p_{\text {total }}=\sum_{i} p_{i} \tag{3}
\end{equation*}
$$

and,

$$
\begin{equation*}
p_{i}=p_{\text {total }} \frac{n_{i}}{n_{\text {total }}} \tag{4}
\end{equation*}
$$

where $n_{i}$ is the number of moles of the $i^{\text {th }}$ component and $n_{\text {total }}$ is the total number of moles.
Dalton's Law also states that each gas behaves as if it alone occupied the volume ( $V$ ),

$$
\begin{equation*}
V=V_{1}=V_{2}=\ldots=V_{i} \tag{5}
\end{equation*}
$$

For a two-component mixture of dry gas (g) and water vapor ( $w v$ ), Eq. (3) becomes,

$$
\begin{equation*}
p_{\text {total }}=p_{g}+p_{w v} \tag{6}
\end{equation*}
$$

and Eq. (5),

$$
\begin{equation*}
V_{\text {total }}=V_{g}=V_{w v}=V \tag{7}
\end{equation*}
$$

The humidity ratio ( $W, \mathrm{~kg}_{\mathrm{wv}} / \mathrm{kgg}_{\mathrm{g}}$ ), is defined as ratio of the mass of water vapor ( $m_{w v}$ ) to the mass of dry gas $\left(m_{g}\right)$,

$$
\begin{equation*}
W=\frac{m_{v w}}{m_{g}}=\frac{n_{v w} M_{w v}}{n_{g} M_{g}} \tag{8}
\end{equation*}
$$

where $n$ is the number of moles and $M$ is the molecular weight ( $\mathrm{g} / \mathrm{mole}$ ).
Using the Ideal Gas Law,

$$
\begin{equation*}
n=\frac{p V}{R T} \tag{9}
\end{equation*}
$$

and substituting for $n$ in to Eq. (8),

$$
\begin{equation*}
W=\frac{p_{w v} M_{w v}}{p_{g} M_{g}} \tag{10}
\end{equation*}
$$

Substituting for the dry gas partial pressure, Eq (6),

$$
\begin{equation*}
W=\frac{p_{w v}}{\left(p_{\text {total }}-p_{w v}\right)} \frac{M_{w v}}{M_{g}} \tag{11}
\end{equation*}
$$

Substituting Eq. (8) and solving for the mass of water vapor,

$$
\begin{equation*}
m_{w v}=\frac{p_{w v}}{\left(p_{\text {total }}-p_{w v}\right)} \frac{M_{w v}}{M_{g}} m_{g} \tag{12}
\end{equation*}
$$

Equation 12 reveals that increasing the total pressure of the system decreases the mass of water vapor in the gas.

For example, referring to Figure 1, consider 1 L of humidified gas at 1 atmosphere pressure composed of $25 \%$ water vapor and $75 \%$ nitrogen (i.e., the dry gas). Based on Dalton's Law, both gases occupy the 1 L volume. The partial pressure exerted by the water vapor is 0.25 atm and the nitrogen partial pressure is 0.75 atm.


Figure 1. The total pressure $\boldsymbol{p}_{\text {total }}$ of a mixture of two gases occupying volume $\boldsymbol{V}$ can be considered as the sum of the partial pressures of the two gases each contained in that same space.

When considering the water content or partial pressure of a gas exiting a sparger or bubbler-type humidifier in a fuel cell test system, we are assuming that the gas mixture is saturated in water vapor. Therefore, the water vapor pressure $p_{w v}$ equals the pressure of water vapor at saturation $p_{\text {wvs }}$, which is a function only of temperature ( T ),

$$
\begin{equation*}
p_{w v}=p_{w v s}(T) \tag{13}
\end{equation*}
$$

Assuming the humidified gas is saturated in water vapor then Eq. (12) becomes,

$$
\begin{equation*}
m_{w v}=\frac{p_{w v s}(T)}{\left[p_{\text {total }}-p_{w v s}(T)\right]} \frac{M_{w v}}{M_{g}} m_{g} \tag{14}
\end{equation*}
$$

Note that as the total pressure $p_{\text {total }}$ increases the denominator of the first term gets larger and the mass of water vapor per unit of dry gas decreases. Eq. (14) also indicates that the mass of water is proportional to the dry gas mass. This makes sense because the rate of water consumption increases linearly with increasing mass flow rate of reactant gas.

The plots in Figure 2 show the effect of total system pressure on the water consumption rate.
Note that if the gas were not saturated in water vapor, then the water content of the gas would not decrease as a result of the increase in pressure up until the actual water vapor pressure exceeded the saturated water vapor pressure.

## Does the relative humidity change with total pressure?

All else being equal, No. Relative humidity $(R H)$ is the ratio of the actual water vapor pressure to the saturated water vapor pressure and is independent of the total pressure of the system,

$$
\begin{equation*}
R H(\%) \equiv \frac{p_{w v}}{p_{w v s}(T)} \times 100 \% \tag{15}
\end{equation*}
$$

Increasing the total pressure of the system decreases the quantity - mass or molar content - of water vapor per quantity of dry gas but does not change the partial pressure of water vapor. Thus, the relative humidity is unchanged.


Figure 2. Water consumption rate as a function of dew point (or humidifier temperature) at various total pressures shown in linear (top) and semi-log (bottom) scale. Basis: 1 standard liter per min (SLM) of dry gas (standard state defined as $0{ }^{\circ} \mathrm{C}, 1$ atmosphere). BP = back pressure = absolute pressure - atmospheric pressure.

