VOLUMETRIC CHANGES AT VAPORIZATION AND AT CONDENSATION

Avogadro's Law, in essence, states that at any specific combination of temperature and pressure the number of molecules in a specified volume of gas or mixture of non-reacting gases is the same. For a kilogram-mole of gas or gases, that number is known as Avogadro's number. Its value is:

$$\boldsymbol{N_A = 6.0221414 \text{ x } 10^{23}} \textbf{ molecules per mole}$$

When divided by the molar volume at any specific combination of temperature and pressure, we get the number density in number of molecules per unit volume:

$$\bar{n} = \frac{N_A}{V_{mol}} \qquad \text{VOL01}$$

The number density is directly proportional to the ambient pressure and inversely proportional to the ambient temperature. The relationship is:

$$\bar{n} = \frac{\bar{p}}{\mathrm{k_B}\bar{T}} \qquad \text{VOL02}$$

At 25°C and a pressure of a thousand hectopascals, the number density is some $2.42930 \text{ x } 10^{25}$ molecules per cubic meter. Under those conditions, this will be the number of dry air molecules per cubic meter and it will also be the number of humid air molecules per cubic meter.

Adding water vapor to the atmosphere is not like adding water to a sponge. The water vapor molecules do not take up unused space between the air molecules. Instead, adding water vapor to the atmosphere is more like adding a collection of

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blue marbles to a box of multicolored ones. The augmented collection takes up more room than before. Each water molecule takes up just as much “room” as each air molecule.

Part of the problem lies in the use of the term “saturation” in discussions of humidity. It implies that there is no more space available. Actually, of course, the air and vapor molecules take up only a small fraction of one percent of the available “room”. Moreover, supersaturation is extremely common in the upper troposphere, and is not at all an unstable condition.

Thus, the addition of any amount of water vapor to the free atmosphere under isobaric and isothermal conditions must increase the volume of the atmosphere. The increase in volume is given by:

$$\Delta \boldsymbol{V} = \frac{\underset{\sim}{\bar{\boldsymbol{n}}}}{\bar{\boldsymbol{n}}} = \frac{\underset{\sim}{\bar{\boldsymbol{n}}}\mathbf{k}_{\mathbf{B}}\bar{\boldsymbol{T}}}{\bar{\boldsymbol{p}}} \tag{VOL03}$$

Here, $\Delta \boldsymbol{V}$ is the increase in volume of atmosphere as liquid water becomes water vapor, $\underset{\sim}{\bar{\boldsymbol{n}}}$ is the mean number of molecules per unit volume of liquid water, $\bar{\boldsymbol{n}}$ is the mean number of molecules per unit volume of atmosphere, and the other terms retain their previous meanings.

This increase in volume is substantial, and ranges from just over a thousand-fold two-thousand meters deep in a mine shaft to over eighteen-thousand fold at an elevation of twenty thousand meters. Since humid air is lighter than dry air, this vaporization accounts for much of the ‘lift” experienced by evaporating air.

Lighter, humid air does not automatically rise, of course, anymore than warm air does. Nothing moves upward against the force of gravity unless pushed up by a stronger force. What happens is that denser air moves in along the base of the less dense air, forcing it up. When the upward force stops, the air mass stops rising.

Balloonists know that warm air does not rise automatically. They have been known to drop sandbags into hot parking lots to “break loose” the warm air gathered there in the early morning hours, so as to ride the resulting thermals.

Table VOL01

Volumetric Changes with Vaporization at Selected Elevations

Elevation	Pressure	Temperature	Number Density Air	Increase
z	**p**	**T**	**$\bar{n}$**	**ΔV**
meters	bars	°K	m^{-3}	-
0	1.01325	288.15	2.5469×10^{25}	1,313
500	0.9546	284.9	2.4269×10^{25}	1,377
1000	0.8988	281.7	2.3110×10^{25}	1,447
1500	0.8456	278.4	2.1999×10^{25}	1,520
2000	0.7950	275.2	2.0924×10^{25}	1,598
2500	0.7469	271.9	1.9896×10^{25}	1,680
3000	0.7012	268.7	1.8901×10^{25}	1,769
3500	0.6578	265.4	1.7952×10^{25}	1,862
4000	0.6166	262.2	1.7033×10^{25}	1,963
4500	0.5775	258.9	1.6156×10^{25}	2,069
5000	0.5405	255.7	1.5310×10^{25}	2,183
5500	0.5054	252.4	1.4503×10^{25}	2,305
6000	0.4722	249.2	1.3724×10^{25}	2,436
6500	0.4408	245.9	1.2984×10^{25}	2,575
7000	0.4111	242.7	1.2269×10^{25}	2,725
7500	0.3830	239.5	1.1583×10^{25}	2,886
8000	0.3565	236.2	1.0932×10^{25}	3,058
8500	0.3315	233.0	1.0305×10^{25}	3,244

Temperatures and pressures at specified elevations are based on the International Standard Atmosphere. Number densities for air are calculated from these pressures and temperatures. The number density for liquid water is assumed to be constant at 3.3420×10^{28} molecules per cubic meter. Liquid water has been found in the free atmosphere at temperatures as low as 231°K. Water vapor exists at all known atmospheric temperatures. For the vaporization of ice, an approximation may be obtained by multiplying the ΔV value by 0.916.

Condensation has just the opposite effect of vaporization. Condensation diminishes the volume of the atmosphere in the same proportion as vaporization increases it.

Table VOL01 can thus be used to ascertain how large a volume of humid air must be removed from the atmosphere to produce a given volume of condensate.

The implications of this inflow and outflow for the generation of gross air movement (winds) are obvious. This subject is covered in more detail in the section that deals with moving air.