

## 6. Saturation Vapor Pressure

Imagine a closed container partly filled with water. Let's assume that the container is maintained at some constant temperature. Obviously, water in the container will evaporate filling the space above. As you know, unlike molecules in ideal gases such as air, molecules in liquids are much closer to each other. In fact, they are so close that they are held in close proximity of each other by the attractive electrostatic forces due to asymmetries of positive (nuclei of atoms) and negative (electrons) charges. Water molecule, for example, consists of two tiny atoms of hydrogen (simple proton as a nucleus) and much heavier (16 times) atom of oxygen. Of course, the total number of electrons in the molecule of water equals the number of positively charged protons in nuclei, so the molecule, as the whole, does not have net electric charge. However, because of much more positively charged nucleus of oxygen than nucleus of hydrogen, electrons like to spend more time around the oxygen nucleus rather than hydrogen nuclei as the former is more, so to speak, attractive; hence, the water molecule behaves more like a negatively charged oxygen particle with attached positively charged hydrogen particles. In liquid water, the negative "sides" of molecules are attracted to positive sides, forming a jiggling net of connected molecules. The thermal jiggling prevents molecules from forming a solid crystal or ice; however, when temperature is low enough, the thermal jiggling can't keep the molecules apart, so they lock into fixed positions forming a crystal of ice.

Let's return to our container. At the interface between water and air, or the water surface, some molecules are randomly, through collisions, acquire just enough of kinetic energy to overcome the electrostatic attraction of other molecules and are kicked-out from the liquid into the gas above. This process is called *evaporation*. Thus, there is a constant flux of molecules leaving the liquid and mixing with the air. This process increases the pressure of water vapor in the air (remember, the pressure is proportional to number of molecules per unit volume). At the same time, some molecules of vapor collide with the surface and can be incorporated back into the liquid. This process is called *condensation*. It tends to decrease the vapor pressure.

Thus, in addition to the flux out of the liquid, there is a continuous flux of molecules going back to the liquid. When the rate of evaporation exceeds the rate of condensation, the vapor pressure over the liquid increases until the equilibrium is reached, that is, the flux of molecules escaping the liquid balances the flux of molecules going back to the liquid. Such equilibrium between evaporation and condensation is called *saturation*, and the partial vapor pressure at equilibrium is called *saturation vapor pressure*. Note that the equilibrium is an exact balance of two large fluxes of water constantly moving molecules in and out the liquid, and, hence, it is an example of a so-called *dynamic equilibrium*.

It is clear that the equilibrium pressure should increase with temperature as the number of molecules being able to escape the liquid should increase with increasing temperature, because at higher temperature the molecules would have higher kinetic

energy, and, hence, higher chance to have velocities large enough to overcome the electrostatic forces that keep them at the surface. And vice versa.

Let us now derive the mathematical expression that relates the rate of change of saturation vapor pressure to change in temperature. The usual derivations found in many textbooks involve an introduction of the so-called Gibbs free energy. However, we will not complicate the matter here, and directly apply the First Law of Thermodynamics in the form (4.5).

The evaporation process can be equivalent to taking a tiny volume of liquid, bringing it out of the liquid, and then, slowly, expanding both isothermally (at constant temperature) and isobarically (at constant pressure) to the density of saturated vapor around. Why slowly? Because, one does not want to disturb a delicate thermodynamic equilibrium. Why isothermally and isobarically? Because in thermodynamic equilibrium, all parts of the system should be at the same temperature and partial pressure for each component.

According to (4.5), transition from liquid to vapor at temperature  $T$  and vapor pressure  $p_V$  can be written as (replacing differentials with finite differences because the transition from liquid to vapor by itself means big finite change in entropy and specific volume)

$$T(S_V - S_L) = p_V(v_V - v_L)$$

where  $S_L$  and  $S_V$  are entropies,  $v_L$  and  $v_V$  are specific (per the same mass) volumes of liquid and vapor, respectively. Let us now perturb the temperature of the system, just so-so slightly, that is by infinitesimally small amount  $dT$ . The system will obtain a new equilibrium with slightly different saturation vapor pressure. Mathematically, the change in the system is written using differentials and the chain rule applied to the above equation:

$$dT(S_L - S_V) + Td(S_L - S_V) = dp_V(v_L - v_V) + p_V d(v_L - v_V) \quad (6.1)$$

As the system is still very close to the equilibrium

$$Td(S_V - S_L) = p_V d(v_V - v_L)$$

Hence, the equation (6.1) can be simplified as

$$dT(S_L - S_V) = dp_V(v_L - v_V)$$

or, rearranging, we obtain the equation for the rate of change of saturation partial vapor pressure with temperature, which was first derived by Clapeyron in 19th century:

$$\frac{dp_v}{dT} = \frac{S_L - S_V}{v_L - v_V} \quad (6.2)$$

Let's now derive an equation, which is suitable for use in atmospheric science. First, we will recall (4.4) that the entropy change in any reversible physical process (evaporation and condensation are perfectly reversible) is related to the applied or released heat. The heat needed to evaporate a parcel of liquid water at constant temperature and pressure is called the *latent heat of evaporation*. Note that the ratio in the r.h.s. of (6.2) does not depend on the amount of water (why?). For the unit of mass, the entropy change is given by

$$S_V - S_L = \frac{L}{T}$$

where  $L=2.5 \times 10^6$  J/kg at  $0^\circ\text{C}$  is a specific heat of evaporation of water. If we recall that a unit mass of liquid water is several orders (thousands of times) of magnitude denser than the water vapor at atmospheric conditions, then it is clear that the specific volume of vapor is much larger than the specific volume of water; therefore, their difference in (6.2) can be replaced with the specific volume of vapor alone. By convention, in meteorology, the partial vapor pressure is often denoted by  $e$  to make a clear distinction from air pressure. The saturation pressure is then denoted as  $e_s$ . Thus, Clapeyron equation (6.1) can be rewritten as

$$\frac{de_s}{dT} = \frac{L}{Tv_V}$$

At atmospheric condition, the water vapor is diluted enough to be described well by the ideal-gas law

$$e_s v_V = R_V T$$

where  $R_V=460$  J/kg/K is the gas constant for water vapor. Using the ideal-gas law, the Clapeyron equation can be written as

$$\frac{de_s}{dT} = \frac{Le_s}{R_V T^2}$$

This is the Clausius-Clapeyron equation. If we assume that  $L$  is approximately constant for typical atmospheric conditions (true to about 10%), then we can integrate the equation above. First, let's rearrange it as

$$\frac{de_s}{e_s} = \frac{L}{R_V} \frac{dT}{T^2}$$

Integrate from some base temperature  $T_0$  to temperature  $T$  :

$$\int_{e_s(T_0)}^{e_s(T)} \frac{de_s}{e_s} = \frac{L}{R_V} \int_{T_0}^T \frac{dT}{T^2}$$

one can easily get the following form of the Clausius-Clapeyron equation that relates the saturation water vapor pressure over liquid water to temperature:

$$e_s(T) = e_s(T_0) \exp \left[ \frac{L}{R_V} \left( \frac{1}{T_0} - \frac{1}{T} \right) \right] \quad (6.3)$$

If we take the freezing temperature of 273.16 K as the base temperature  $T_0$ , then  $e_s(T_0) = 611$  Pa.

A similar derivation can be done for the equilibrium or saturation vapor pressure over ice. Ice can evaporate, and, also, it can grow by ‘condensation’ of vapor on its surface. The corresponding processes, though, in the case of ice, are not called evaporation and condensation, but instead *sublimation* and *deposition*, respectively. The dependence of the saturation vapor pressure over ice  $e_{si}$  on temperature has the form similar to (6.3), but with the specific heat of condensation  $L$  replaced with the *specific heat of sublimation*  $L_s = 2.85 \times 10^6$  J/kg:

$$e_{si}(T) = e_{si}(T_0) \exp \left[ \frac{L_s}{R_V} \left( \frac{1}{T_0} - \frac{1}{T} \right) \right] \quad (6.4)$$

where  $e_{si}(T_0) = e_s(T_0) = 611$  Pa. Notice that the saturation pressure over ice and water are the same at the ice melting point temperature of 273.16 K or 0.16 °C. This temperature when all three phases of water, vapor, liquid and ice, are at equilibrium with each other is called the *triple point*.

The difference between  $L_s$  and  $L$  is the specific heat of fusion or freezing or melting  $L_s - L = L_f = 0.35 \times 10^6$  J/kg. This makes sense, as in order to evaporate ice, in principle, we could melt ice, which, obviously takes energy, and then, evaporate water. In reality, water can evaporate directly from the ice surface without first melting it, but thermodynamically, the amount of energy needed to do so should be equal to the sum of the heat of melting and the heat of evaporation. When some part of water in the mixture of water and ice freezes as the result of cooling, the heat of fusion is released, which keeps the water-ice mixture at constant temperature (0.16°C in the atmosphere) until all water freezes solid.

It is easy to see that the ratio of  $e_s$  to  $e_{si}$

$$\frac{e_{si}}{e_s} = \exp\left[\frac{L_f}{R_v}\left(\frac{T_0 - T}{TT_0}\right)\right] \quad (6.5)$$

is always greater than 1 for  $T < T_0$  when the ice can exist, that is saturation vapor pressure over ice is always smaller than saturation vapor pressure over water.

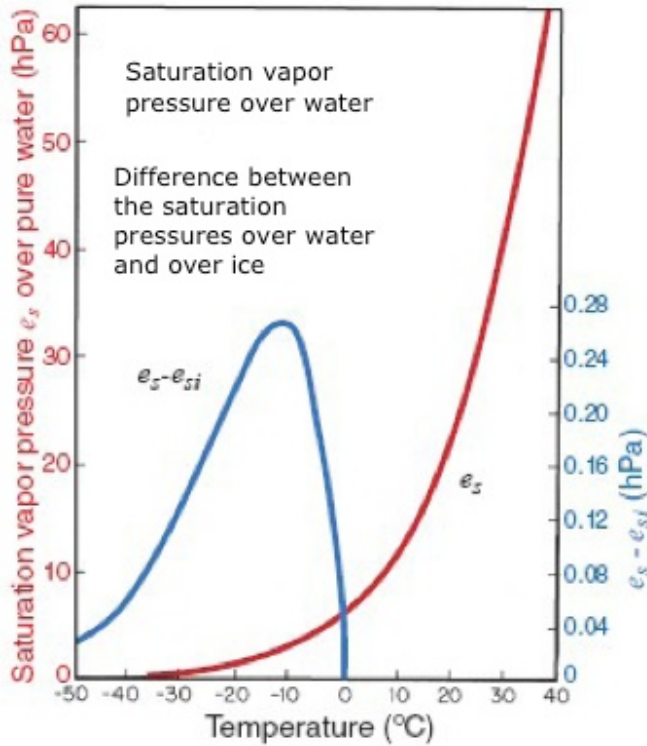


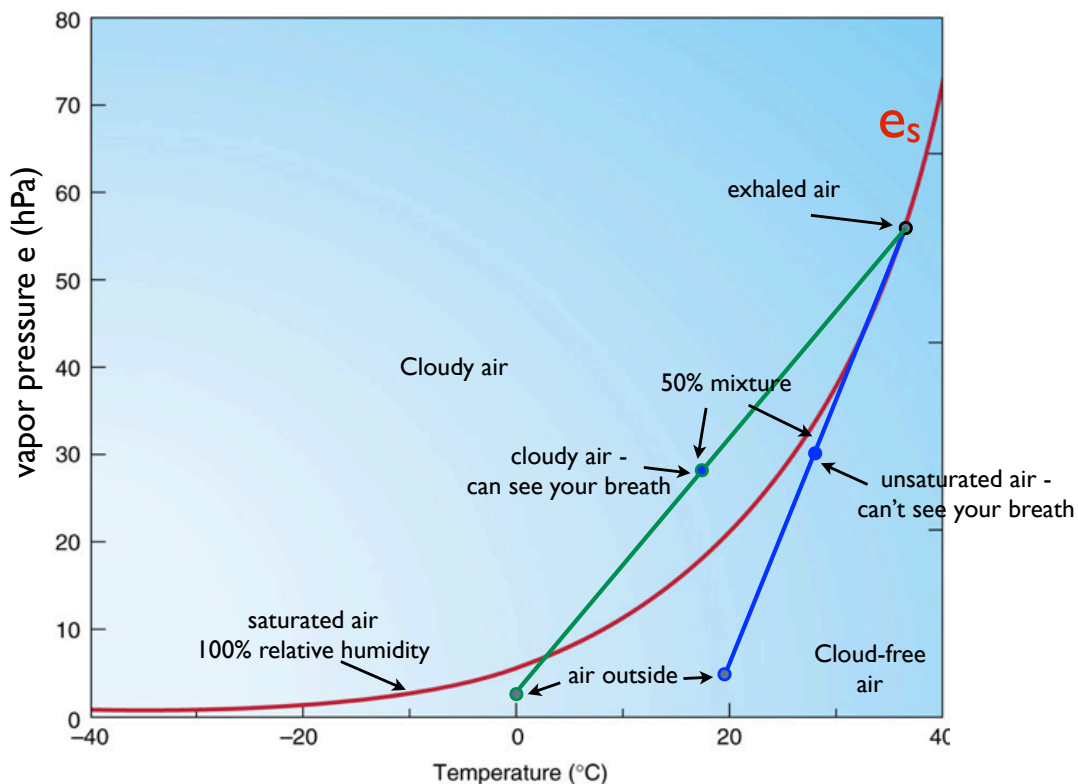
Figure above shows the saturation of water vapor over liquid as the function of temperature as well as the excess of saturation vapor pressure over vapor pressure over ice. Note how quickly the saturation pressure (red curve) changes even for relatively small change of temperature, with the rate of change (steepness of the curve) increasing considerably as air becomes warmer. The expression (6.3\_ can be rewritten as

$$e_s(T) = e_s(T_0) \exp\left[\frac{L}{R_v}\left(\frac{T - T_0}{T_0 T}\right)\right] \approx e^{\alpha(T - T_0)}$$

where  $\alpha$  is approximately constant. That is the dependence on temperature is exponential. Compare, for example, the difference in saturation vapor pressure between 0°C and 10°C, and between 20°C and 30°C. The excess of saturation over water over saturation over ice reaches maximum at about -12°C . This difference plays an important role in growth of the ice and snow in so-called mixed-phase clouds,

where both ice crystals and water droplets co-exist, as will be discussed in more details when the cold-cloud processes are reviewed.

The apparent ‘curvature’ of the near-exponential function  $e_s(T)$  provides a way for a cloud to form simply by mixing air parcels with different temperatures and vapor contents. A familiar example of such an isobaric (without cooling due to adiabatic ascent) cloud formation is the phenomenon of *visible breath*, which is illustrated by the figure below. The air that we exhale has the temperature close to the body temperature of  $36.6^\circ\text{C}$ , and, because it comes from moist lungs, it is nearly saturated with respect to liquid water. When exhaled, the breath air is mixed with the outside air. The straight blue and green lines are the so called mixing lines, so that the characteristics of the mixture of the breath and outside air will be somewhere along those lines, depending on the mixture proportions. Let’s assume that the exhaled air mixes at 50/50 proportion, that is, the mixture has 50% of breath air and 50% of outside air.



As the vapor pressure is proportional to vapor density and, hence, mass, the vapor pressure of the mixture will be about half-way between the vapor pressures of the breath and the outside air. The heat content of air is also proportional to its mass, and, hence, the temperature of the mixture will also be the half-way between the body temperatures and the outside temperature. Let’s assume that the outside air is unsaturated, that is its vapor pressure is below the red curve. Depending on the temperature and humidity of the outside air, the vapor pressure of the mixture can be above or below the red curve, because of the curvature of  $e_s(T)$ . When the outside air is relatively cool and dry (green line), the vapor pressure of the mixture will be above

the red curve, that is above the saturation, and the excess of vapor will condense into a visible ‘cloud’. When the outside air is relatively warm (blue line), the mixture will always be below the red curve, that is unsaturated, so no visible condensation will occur.

Similar phenomenon occurs sometimes above cold water surfaces, when a warm and humid air is advected above it. Turbulence mixes that warm and humid air with the relatively cold air formed close to the surface, creating the mixture that has the vapor pressure above the saturation, so that the condensation occurs in the form of fog. Similar effect occurs when cold air is advected over warm water. Thus, one can form cloudy air simply by mixing two cloudless air-masses, one warm and humid and another cold and, hence, relatively dry. Again, this phenomenon is only possible because of the curvature or nonlinearity of the  $e_s(T)$  function.