# Vapor pressure

- Consider a container with some substance in a solid or liquid phase but with a volume which is bigger than the volume of that solid or liquid. The remaining part of the container will not be a pure vacuum but will contain a gas. The pressure of this gas depends on the temperature.
- The **vapor pressure**, $P_v(T)$, is defined as the pressure exerted by a vapor in thermodynamic equilibrium with its condensed phases (solid or liquid) at a given temperature in a closed system.
- This equilibrium can be thought of as an equilibrium between evaporation and condensation at the surface of the liquid. The rate of condensation should depend on the number of times the molecules hit the surface and is therefore directly related to the pressure.

# Vapor pressure in the presence of air

Let us now discuss this for the case of $H_2O$. The gas phase is called steam.

- Start with the same container as before, but now add some air to the gaseous side. This will give an increase in the total pressure but the **partial pressure** excerted by the water molecule will remain the same.
- This is in agreement with the "equilibrium between evaporation and condensation" discussed above. The presence of air shouldn't affect that equilibrium.
- The humidity of the air is often given as a relative humidity, which is

$$\text{relative humidity} = \frac{P_{\mathrm{H_2O}}}{P_v(T)}.$$

where $P_{\mathrm{H_2O}}$ is the partial pressure due to $H_2O$.

# Saturated steam

Table 4.1

Properties of water + steam (saturated steam)

| $T$ °C | $P$ bar | $H_{\text{water}}$ kJ | $H_{\text{steam}}$ kJ | $S_{\text{water}}$ kJ/K | $S_{\text{steam}}$ kJ/K |
|---|---|---|---|---|---|
| 0 | 0.006 | 0 | 2501 | 0 | 9.156 |
| 10 | 0.012 | 42 | 2520 | 0.151 | 8.901 |
| **20** | **0.023** | **84** | **2538** | **0.297** | **8.667** |
| 30 | 0.042 | 126 | 2556 | 0.437 | 8.453 |
| 50 | 0.123 | 209 | 2592 | 0.704 | 8.076 |
| 100 | 1.013 | 419 | 2676 | 1.307 | 7.355 |

# The dew point

We are familiar with the formation of dew as the outdoor temperature drops.

- Assuming that the content of water vapor remains the same the partial pressure also remains the same. When the temperature drops $P_v(T)$ decreases and the relative humidity will eventually reach 100%.
- As the temperature is reduced even further some of the water vapor then has to condense to liquid water.

Numerical example:

- Starting with 35% humidity at 20°C the partial pressure is

$$P_{\mathrm{H_2O}} = 0.35 \times 0.023 \approx 0.008 \ \mathrm{bar}.$$

- According to the table this is the vapor pressure at $\approx 3$°C, which means that dew will start forming below that temperature.

# Boiling temperature and/or pressure

- Another important consequence is that boiling takes place at the temperature, $T$, for which $P_v(T) = P$, where $P$ is the ambient pressure.
- This is then the reason why water boils at a lower temperature at higher altitude.

But how can that be reconciled with our earlier reasoning?

- We have just realized that the presence or absence of air doesn't affect the equilibrium between evaporation and condensation. How can then the boiling temperature depend on the air pressure?
- The answer seems to be that the bubbles of steam that form during boiling do have the same pressure and the relevant equilibrium is then the between these bubbles and the liquid water.