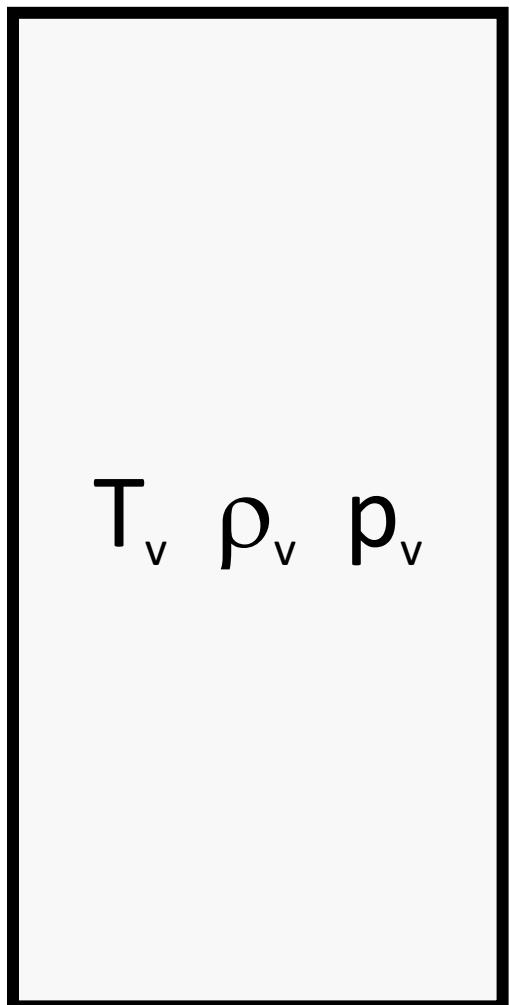


Unit 6

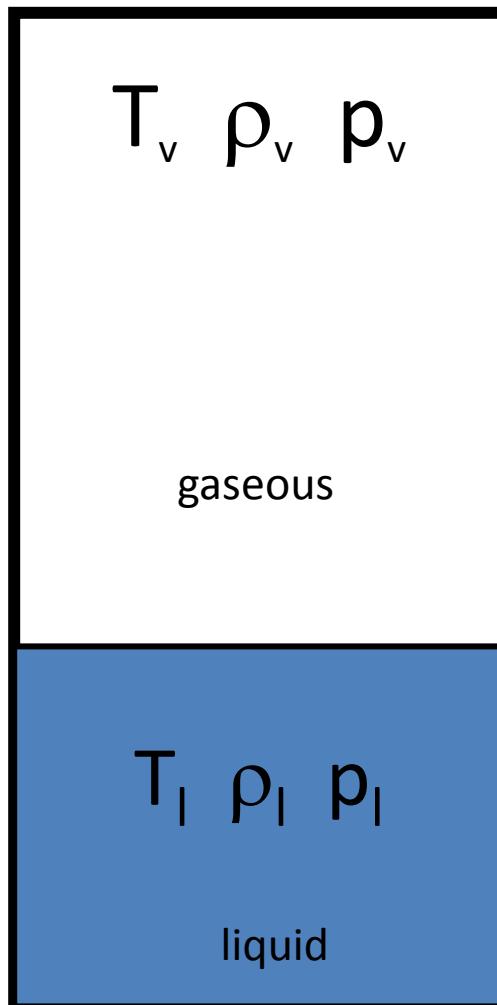
Phase transitions

Nicole Mölders

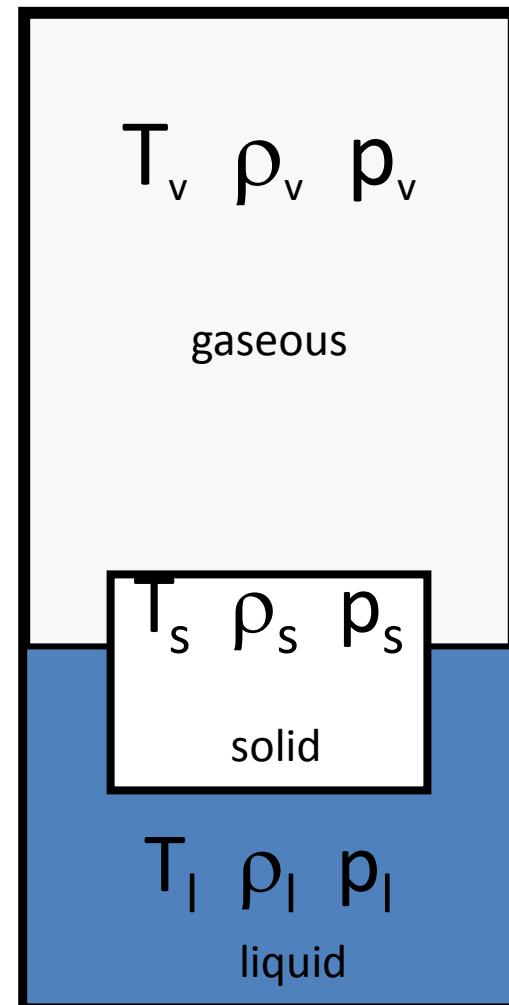
Heterogeneous system



Homogeneous

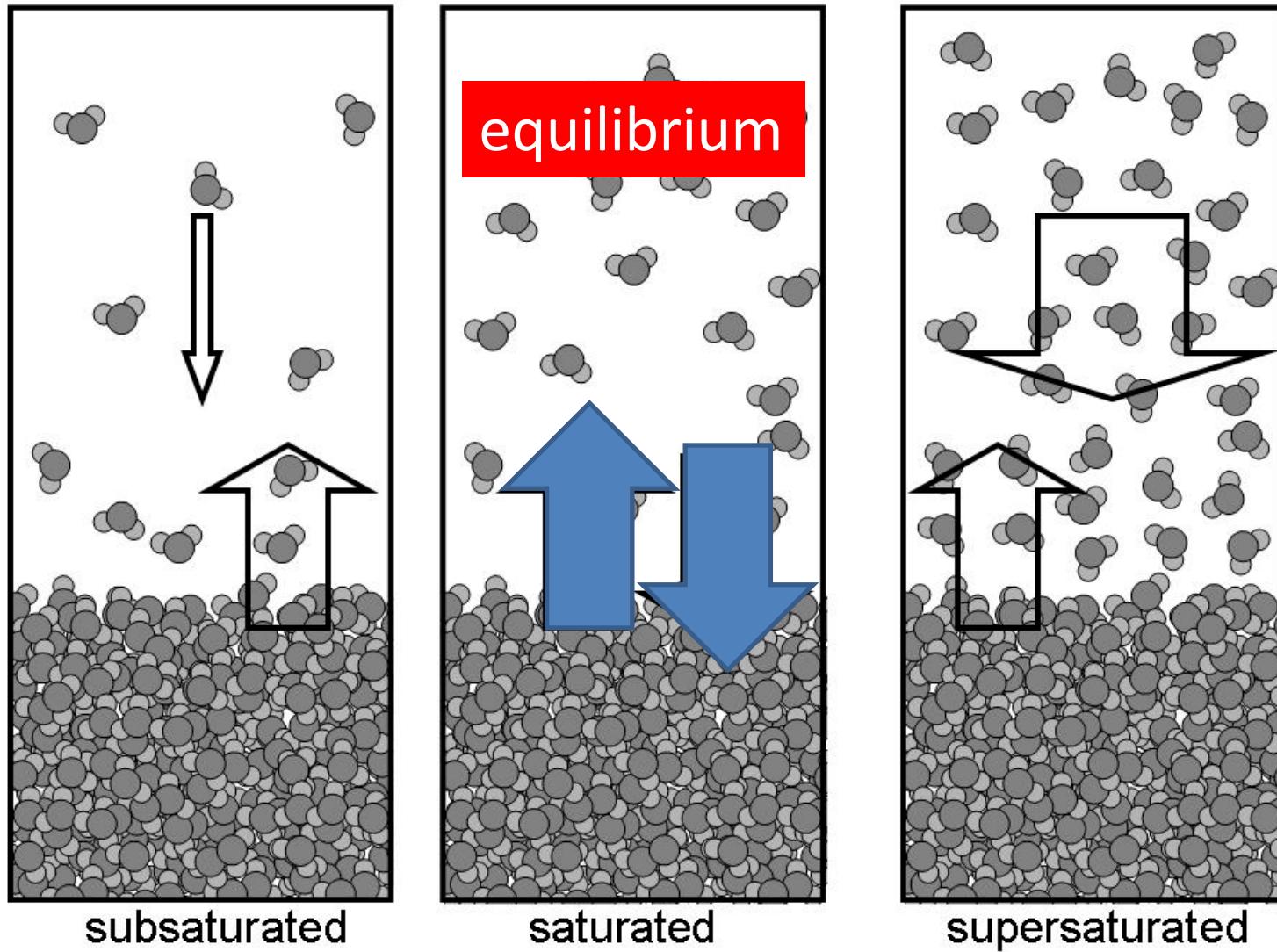


Heterogeneous



Heterogeneous

Phase transitions

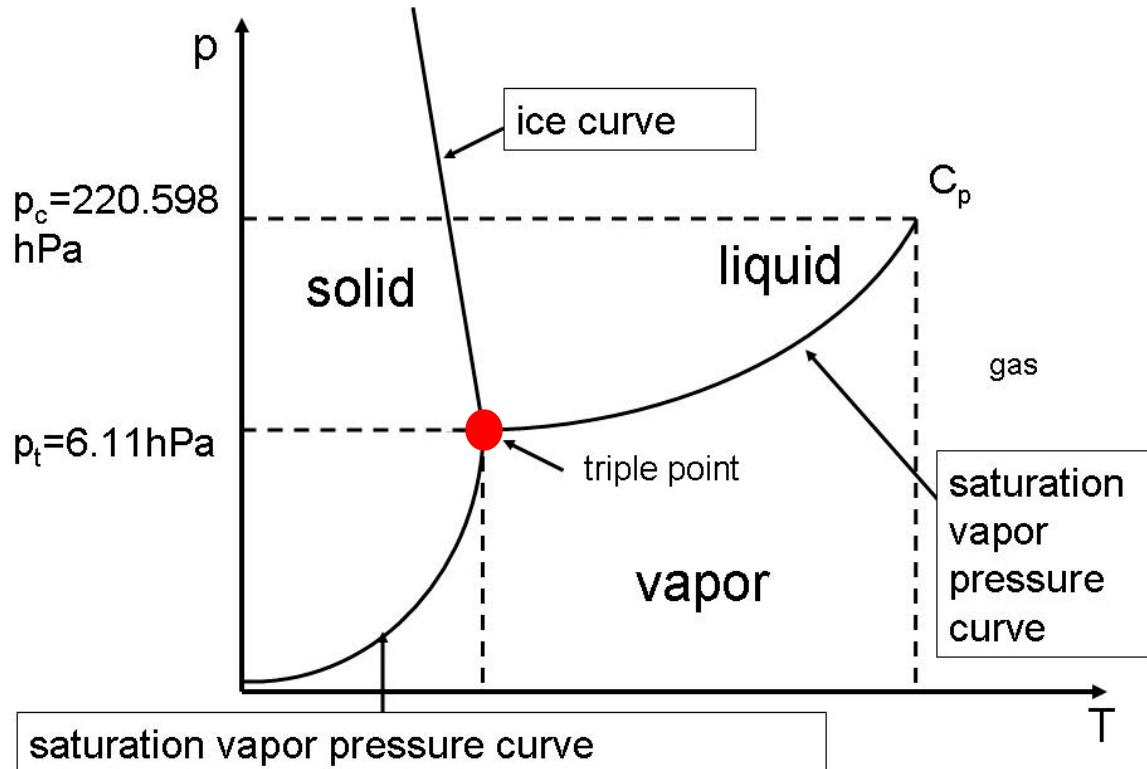


Thermodynamic properties of water

$$\Rightarrow \mu = \mu(p, T) = \mu'(p', T')$$

$$\Rightarrow p = f(T) \text{ or } T = f(p)$$

⇒ In one-component system with 2 phases, 1 independent variable exists!



Latent heat

$$L_v = H_v - H_w = U_v - U_w + p_{wv}(V_v - V_w)$$

$$L_f = H_w - H_i = U_w - U_i + p_{wi}(V_w - V_i)$$

$$L_s = H_v - H_i = U_v - U_i + p_{vi}(V_v - V_i)$$

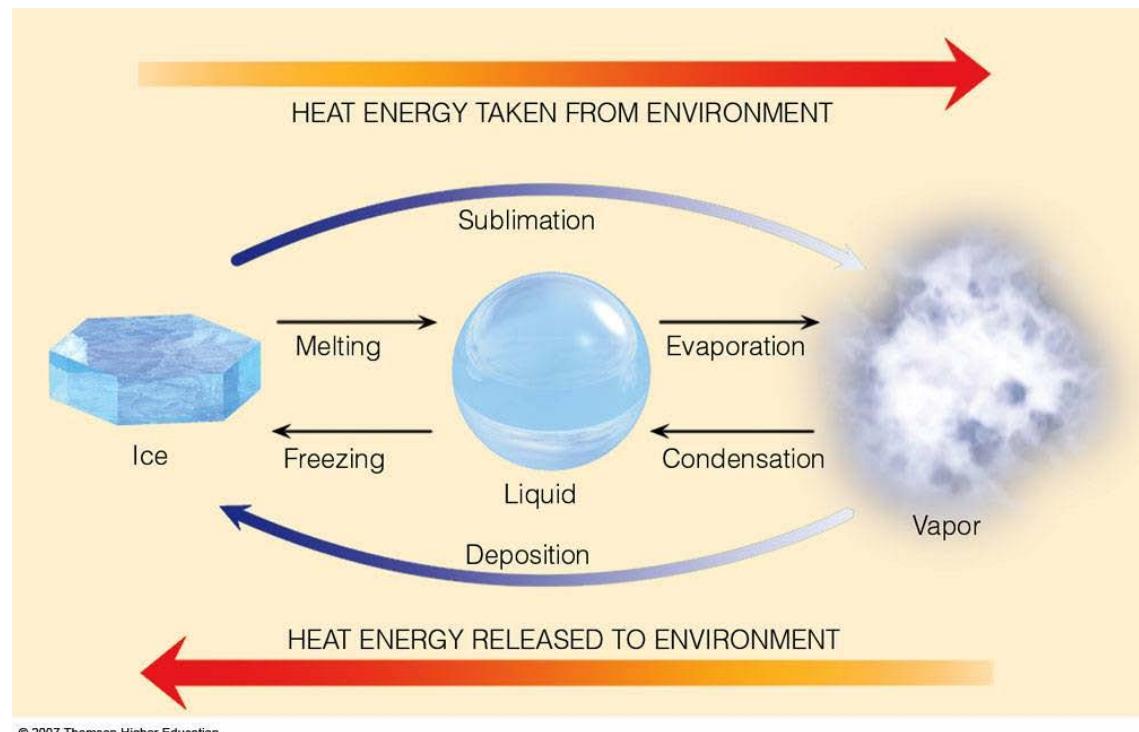
$$dU = L - pdV = L - R_v T$$

$dV = V_v - V_{wi} \sim V_v$ for vaporization & sublimation

$dV \sim 0$ for fusion

$$dU = L$$

$$dU = L - mR_v T$$



Clausius-Clapeyron-equation

$$V = m_w \alpha_w + m_v \alpha_v$$

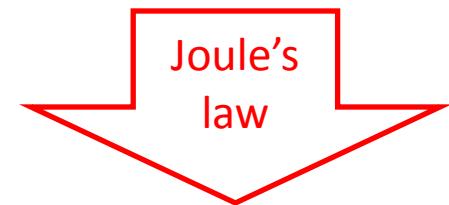
$$U = m_w u_w + m_v u_v$$

$$V + dV = (\bar{m}_w - dm) \alpha_w + (m_v + dm) \alpha_v \text{ or } dV = (\alpha_v - \alpha_w) dm$$

$$dU = (u_v - u_w) dm.$$

$$u_v - u_w + e_{sw}(\alpha_v - \alpha_w) = l_v$$

$$\frac{dU}{dV} = \frac{l_v}{\alpha_v - \alpha_w} - e_{sw}$$



$$TdS = dU + pdV$$

$$T \frac{\partial p}{\partial T} \mid_V = \frac{\partial U}{\partial V} \mid_T + p.$$

$$\frac{\partial U}{\partial V} \mid_T = 0$$

$$\frac{\partial U}{\partial V} \mid_T = T \frac{\partial p}{\partial T} \mid_V - p$$

$$\frac{\partial U}{\partial V} \mid_T = \frac{dU}{dV} \text{ or } \frac{\partial e_{sw}}{\partial T} \mid_V = \frac{de_{sw}}{dT}$$

$$\boxed{\frac{de_{sw}}{dT} = \frac{l_v}{T \Delta v}}$$

Analytical solution of the Clausius-Clapeyron-equation

$$l_v = \text{const. } v_w \ll v_v \rightarrow \Delta v \sim v_v \quad \frac{de_{sw}}{dT} = \frac{l_v}{T} \frac{e_{sw}}{R_v T}$$

$$\frac{de_{sw}}{e_{sw}} = \frac{l_v}{R_v} \frac{dT}{T^2}$$

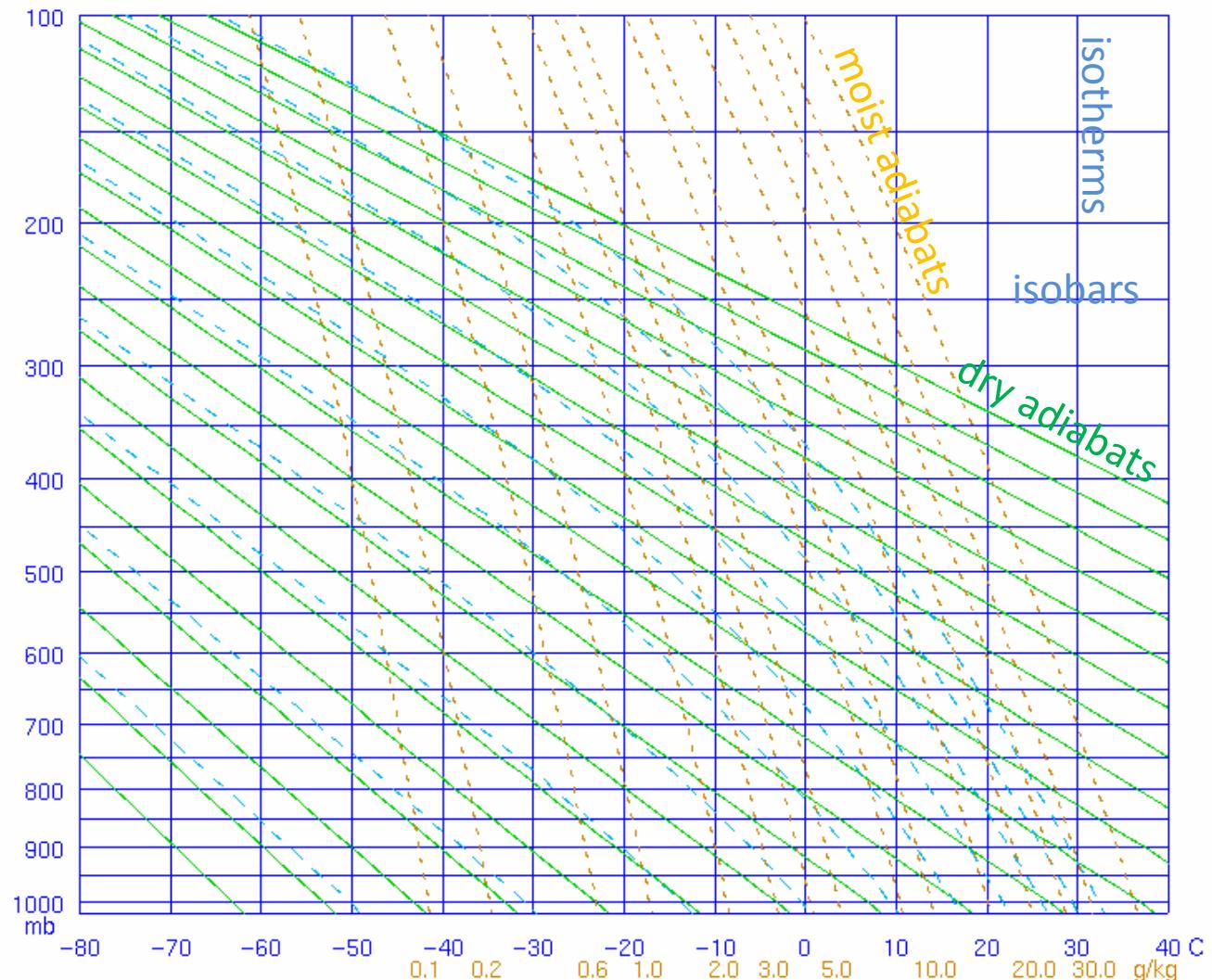
$$\ln \frac{e_{sw}}{e_{sw,o}} = -\frac{l_v}{R_v} \left(\frac{1}{T} - \frac{1}{T_o} \right) = \frac{l_v}{R_v T_o} \left(\frac{T_o - T}{T} \right)$$

$$e_{sw} = e_{sw,o} \exp \left(\frac{l_v}{R_v T_o} \frac{T_o - T}{T} \right)$$

With $l_v = 2.5 \times 10^6 \text{ J/kg}$, $R_v = 461.5 \text{ J/(kg K)}$, $e_{sw,o} = 6.1078 \text{ hPa}$, $T_o = 273.15 \text{ K}$

$$\Rightarrow l_v / (R_v T_o) = 19.81$$

Stüve diagram



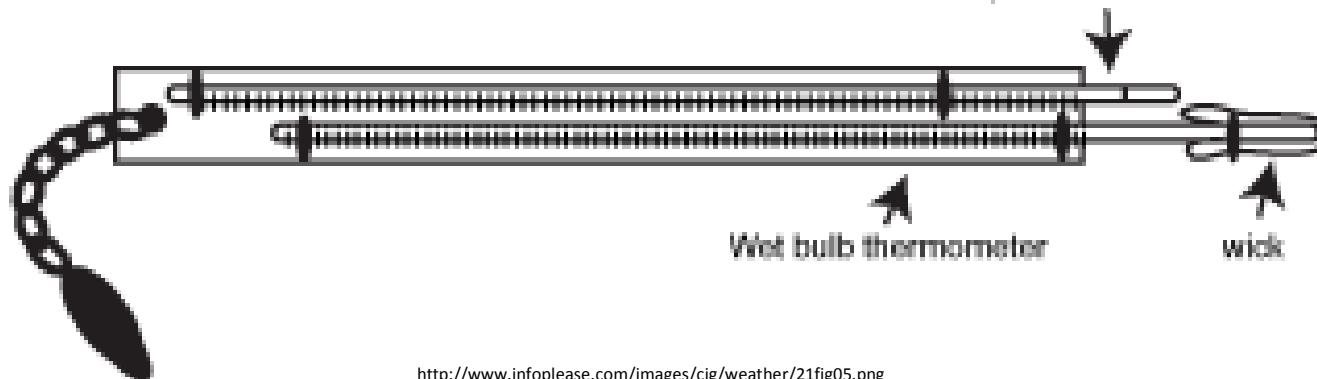
Relative humidity is a relative measure for the degree of saturation

$$rh = \frac{e}{e_s} = \frac{q}{q_s} = \frac{r}{r_s}$$

Hair hygrometer measures relative humidity



Sling psychrometer for measuring humidity by use of Temperature and dewpoint temperature

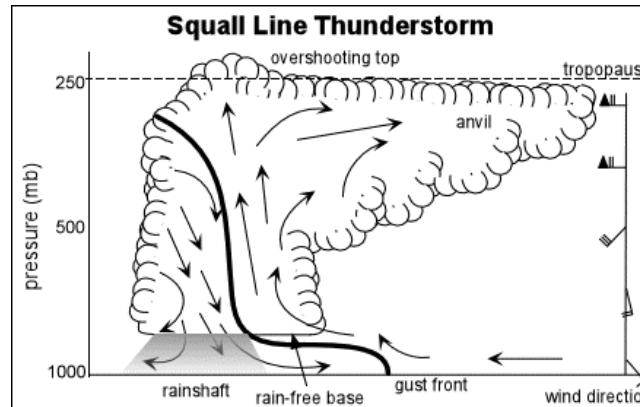


<http://en.wikipedia.org/wiki/Hygrometer#mediaviewer/File:Haar-Hygrometer.jpg>

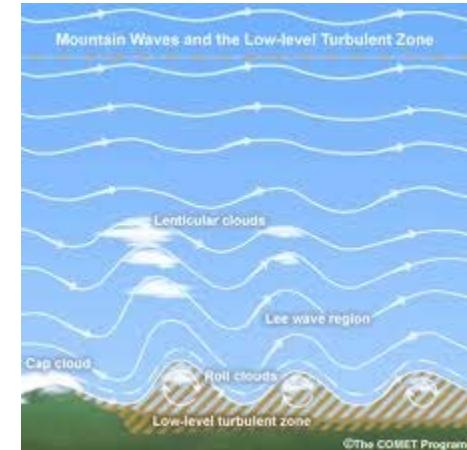
Dew-point temperature gradient

$$\frac{dp}{dz} = -\frac{p}{R_d T} g$$

$$\boxed{\frac{1}{e_s} \frac{de_s}{dT} = \frac{L_v}{R_v T^2}}$$

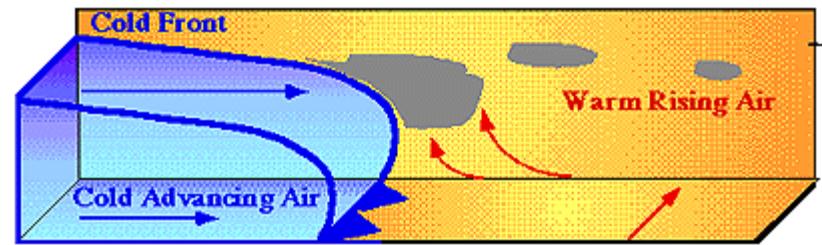


<http://ww2010.atmos.uiuc.edu/guides/mtr/svr/modl/line/gifs/squal3.gif>



$$\frac{de_s}{dz} = \frac{de_s}{dT} \frac{dT}{dz}$$

$$\frac{1}{e_s} \frac{de_s}{dz} = \frac{L_v}{R_v T^2} \Gamma_d$$



<http://ww2010.atmos.uiuc.edu/guides/mtr/af/frnts/gifs/home.gif>

$$\frac{1}{e} \frac{de}{dz} = \frac{1}{p} \frac{dp}{dz}$$

$$\boxed{\frac{dT_d}{dz} = \frac{de}{dz} \left(\frac{de}{dT_d} \right)^{-1} = \frac{1}{e} \frac{de}{dz} \left(\frac{1}{e_s(T_d)} \frac{de_s(T_d)}{dT_d} \right)^{-1} = \frac{0.172K}{100m}}$$

Vertical mixing requires to know your extensive and intensive quantities for correct calculations

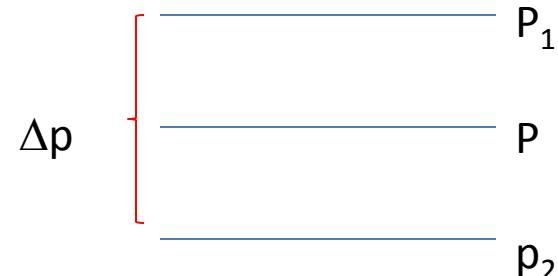
$$T \approx \frac{m_1 T'_1 + m_2 T'_2}{m}$$

$$q \approx \frac{m_1 q'_1 + m_2 q'_2}{m}$$

$$\Theta \approx \frac{m_1 \Theta'_1 + m_2 \Theta'_2}{m}$$

$$\bar{x} = \frac{\int_0^m x dm}{m}$$

$$\bar{x} = \frac{\int_0^z x dz}{\int_0^z \rho dz} = -\frac{\int_{p_1}^{p_2} x dp}{p_1 - p_2}$$



h <http://www.susanstevenson.com/Journal/2013/November/90210PushingCarOffCurbP.jpg>