Atmospheric Thermodynamics - Tutorial 2

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1 Latent Heats

As a substance changes phase, it absorbs or releases energy in the form of heat until the transition to the new state of matter is complete. The amount of energy that the substance exchanges in the process of a complete phase change is called the latent heat. The latent heat is expressed mathematically in the form:

$$L = \int_{q_1}^{q_2} dq = \int_{h_1}^{h_2} dh + \int_{p_1}^{p_2} vdp = (h_2 - h_1) + 0, \tag{1}$$

where the $1, 2$ subscripts represent the start and end points of a complete phase change and $h = c_{\mathrm{p}}T$ is the enthalpy. The pressure integral yields 0 since $p_1 = p_2$.

Since latent heat is dependent on temperature, one may wonder about the outcome of taking the derivative of equation (1) with respect to temperature T. Considering the case of vaporisation,

$$\frac{dL_v}{dT} = \frac{dh_2}{dT} - \frac{dh_1}{dT} = c_l - c_{\mathrm{p}v}, \tag{2}$$

where $c_{\mathrm{p}v}$ is the specific heat capacity of vapour at constant pressure and c_l the specific heat capacity of water. Integrating equation (2) yields the latent heat of vaporisation as a linear function of T:

$$L_{lv}(T) = L_{lv0} - (c_l - c_{\mathrm{p}v})(T - T_0). \tag{3}$$

Carrying over the same logic to the case of sublimation, where the substance is initially and solid and changes into a gas, the latent heat of sublimation takes the form:

$$L_{iv}(T) = L_{iv0} - (c_i - c_{\mathrm{p}v})(T - T_0). \tag{4}$$

The constants relevant to the above equations have the values: $c_l = 4.218\,\frac{\mathrm{kJ}}{\mathrm{kgK}}$, $c_i = 2.106\,\frac{\mathrm{kJ}}{\mathrm{kgK}}$, $c_{\mathrm{p}v} = 1.870\,\frac{\mathrm{kJ}}{\mathrm{kgK}}$, $L_{lv0} = 2501\,\frac{\mathrm{kJ}}{\mathrm{kg}}$, and $L_{iv0} = 2834\,\frac{\mathrm{kJ}}{\mathrm{kg}}$. These values are taken from the Smithsonian Meteorological Tables at $T = 0\,^{\circ}\mathrm{C}$.

Plotting equations (3) and (4) generates the linear plots seen in Fig. 1.

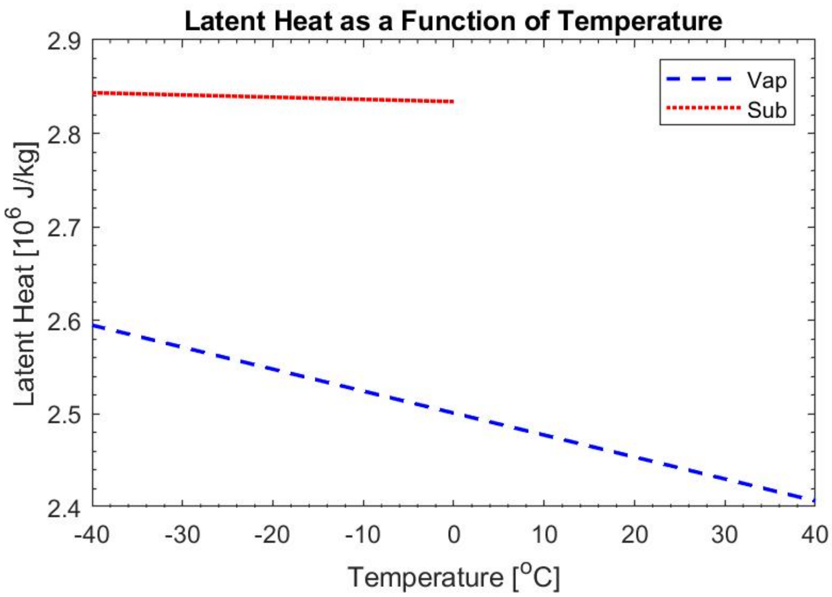

Figure 1. Relationships between latent heats and temperature.

To check the validity of this model, an error metric is designed and is described by the equation:

$$\epsilon_i = \frac{L(T_i) - L_{kv}(T_i)}{L_{kv}(T_i)}, \tag{5}$$

where $L(T_i)$ is a measured latent heat value at a temperature (T_i) and $L_{kv}(T_i)$ is a the corresponding latent heat generated by the linear model.

Taking data from the Smithsonian Miscellaneous Collections of meteorological data and treating it as the $L(T_i)$ in equation (5) generates the error plot seen in figure 2.

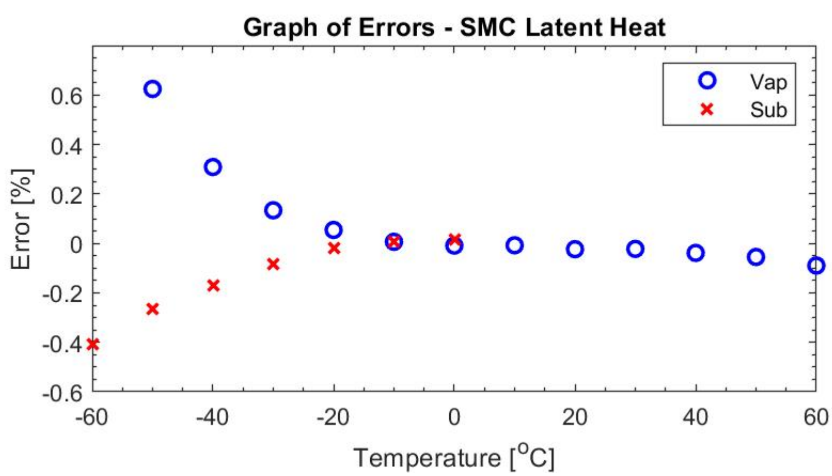

Figure 2. Plot of errors associated with data from Smithsonian Meteorological Tables.

As can be seen, the model is most accurate in the neighbourhood of $-10\,^{\circ}\mathrm{C}$. Both curves cross over at $[-10\,^{\circ}\mathrm{C}, 0\,\%]$. The curves diverge in the vertical direction for values of T away from the crossover point, especially in the negative direction. Nevertheless, the errors are very small, and the linear model of latent heat and temperature dependence works very well within the range of $(-60, 60)\,^{\circ}\mathrm{C}$, with error magnitudes not exceeding $0.6\,\%$. The sublimation error curve is notably less extreme, which is to say the linear model is better suited for the case of sublimation.

Latent heat is commonly treated as if it is a constant despite its evident variation with temperature. With the goal of judging the suitability of this approximation, the error metric provided in equation (5) is reused with the $L(T_i)$ term being held constant. Generating the ϵ_i values leads to the error plots seen in Figure 3.

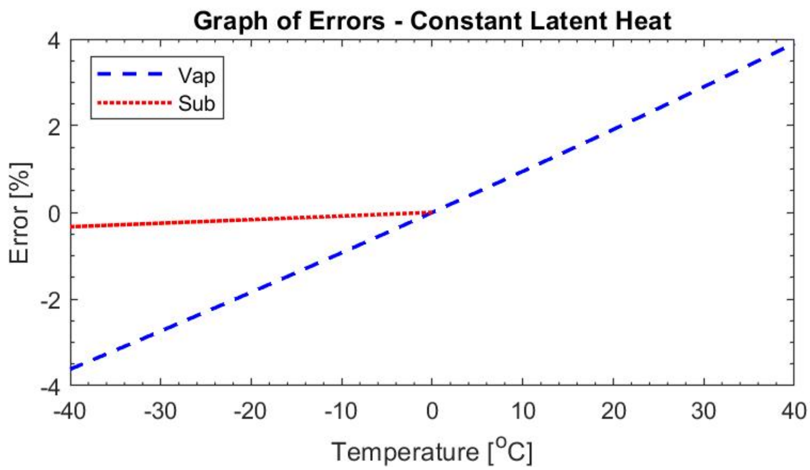

Figure 3. Plot of errors associated with constant latent heats $L_l v0$ and $L_i v0$.

As is expected given the temperature at which the constants are associated with, the error magnitudes minimise in the neighbourhood of $0\,^{\circ}\mathrm{C}$, where both lines intersect. The constant latent heat assumption becomes more erroneous at a constant rate for temperatures greater or smaller than $0\,^{\circ}\mathrm{C}$. If an error tolerance of $3\,\%$ is assumed, the latent heat of vaporisation model is suitable within the range of about $(-30, 30)\,^{\circ}\mathrm{C}$, whereas the sublimation model is suitable across the whole tested range of its temperature values, $(-60, 0)\,^{\circ}\mathrm{C}$, being on the order of 10 times less erroneous than vaporisation model.