Atmospheric Thermodynamics - Tutorial 2

Robert Ruta

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1 Latent Heats

In order for a substance to undergo a phase change from one state of matter to another, it must be heated. The substance will only fully complete the phase change if it absorbs the right amount of heat energy, and this amount of energy is called the latent heat, and is expressed mathematically in the form of

$$L = \int_{q_1}^{q_2} dq = \int_{u_1}^{u_2} du + \int_{v_1}^{v_2} pdv = (u_2 - u_1) + p(v_2 - v_1), \tag{1}$$

where q_1 is the heat energy absorbed up until the beginning of the phase change, and q_2 is the total heat absorbed up until the end of the phase change. Latent heat is dependent on temperature, and so one may wonder about the outcome of taking the derivative of equation (1) with respect to temperature T. Considering the case of vaporisation, we have the fact that $v_2 >> v_1$, and so the v_1 term can be ignored. With this simplification, taking the derivative of equation (1) yields:

$$\frac{dL_v}{dT} = \frac{du_2}{dT} - \frac{du_1}{dT} + \frac{pv_2}{dT} = c_{\mathrm{v}v} - c_l + R_v, \tag{2}$$

where $c_{v\mathrm{v}}$ is the specific heat capacity of vapour at constant volume, c_l the specific heat capacity of water, and R_v is the individual gas constant of water vapour. Given that $R_v = c_{\mathrm{p}} - c_{\mathrm{v}}$, integrating equation (2) yields the latent heat of vaporisation as a 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 figures 1.

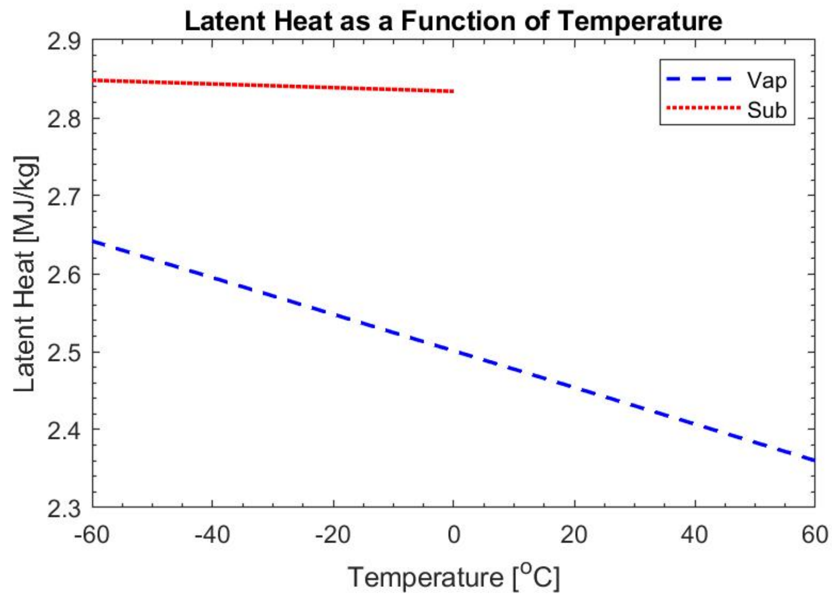

Figure 1. Relationships between latent heats and temperature.

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

$$\epsilon_i = \frac{L - L_i}{L_i}, \tag{5}$$

where L is a true value and L_i is a measured value.

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

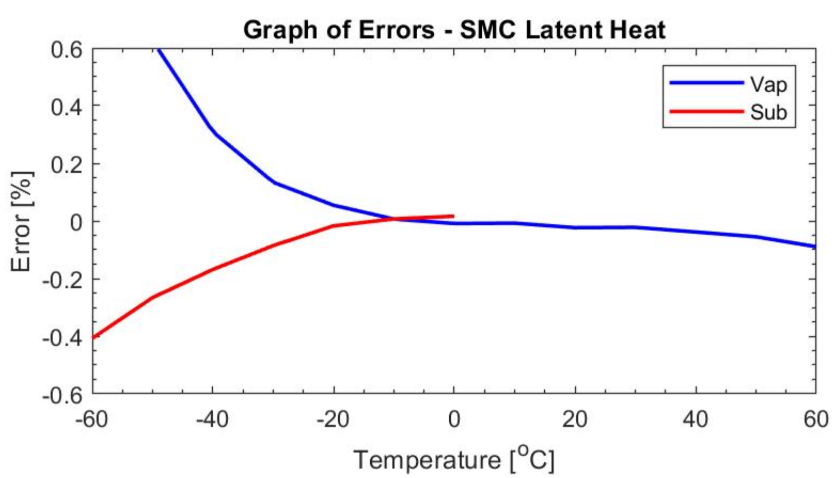

Figure 2. Plot of errors associated with data from Smithsonian Meteorological Tables.

As can be seen, the model is most accurate in the neighbourhood of $-10\,°\mathrm{C}$. Both curves cross over at $[-10\,°\mathrm{C}, 0\,\%]$. 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. One can analyse the suitability of this approximation through the error metric provided in equation (5). Generating the ϵ_i values leads to the error plots seen in figure 3.

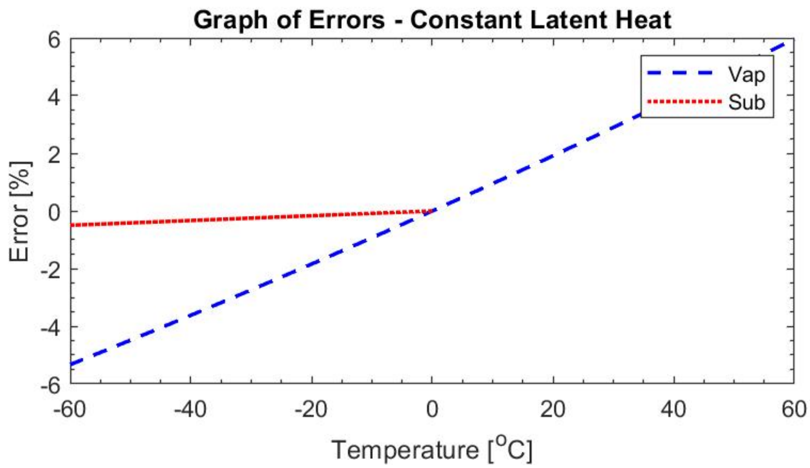

Figure 3. Plot of errors associated with constant latent heat.

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.