This comment illustrates pages 35-37 of my Chapter 22 lecture notes, which is also in video lecture Ch22_8.mp4. We are considering the phase transition $H_2O(\ell) \rightleftharpoons H_2O(g)$ where the vapor pressure of the water vapor is 1 bar.

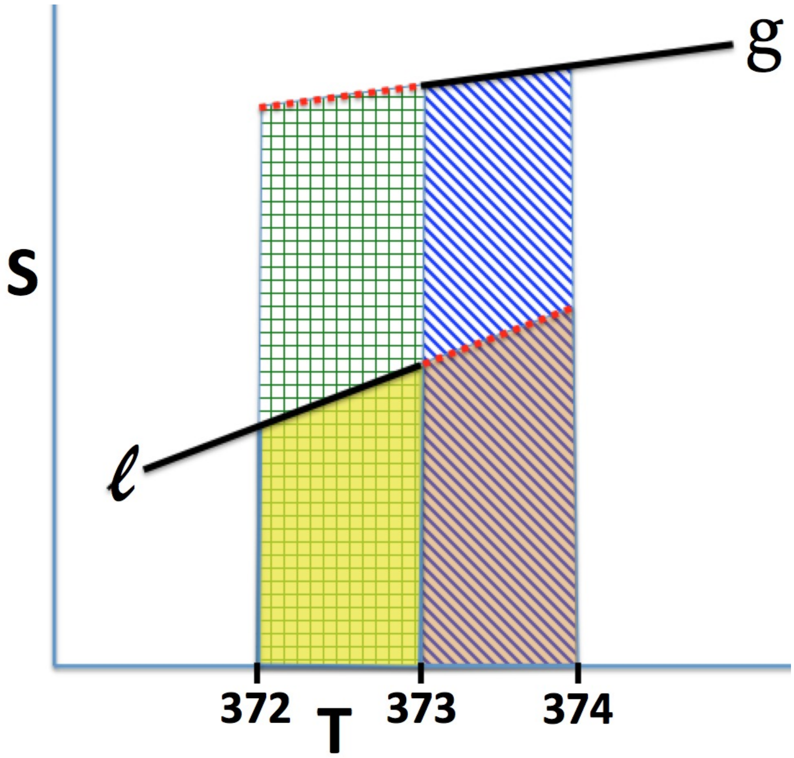

FIG. 1: Entropy vs. temperature for water. The entropy of the liquid is shown in black line for its thermodynamically stable range, and in dotted red line for its unstable (superheated) range. The entropy of the vapor is shown in black line for its thermodynamically stable range, and in dotted red line for its unstable (supercooled) range. The four shaded regions (squares, stripes, solid yellow, and solid orange) correspond to the area of the various integrals discussed in the text.

At 373 K, $\Delta G = 0$ because the system is at equilibrium (373 K is the boiling point of water at 1 atm). At 372 K, the system is not at equilibrium because the equilibrium vapor pressure is less than 1 atm. At 374 K, the system is not at equilibrium because the equilibrium vapor pressure is more than 1 atm. I would like to estimate ΔG at these non-equilbrium temperatures. We can use the basic result

$$\frac{\partial G}{\partial T}_P = -S \tag{1}$$

along with the thermodynamic cycles shown in Fig. 2. Also, we need ΔS at 373 K, which is

$$\Delta S = \frac{\Delta H^\circ_\text{vap}}{373\,\text{K}} = 109.0\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1} \tag{2}$$

This value for ΔS at 373 K represents the height difference between the two solid black lines at 373 K in Fig. 1.

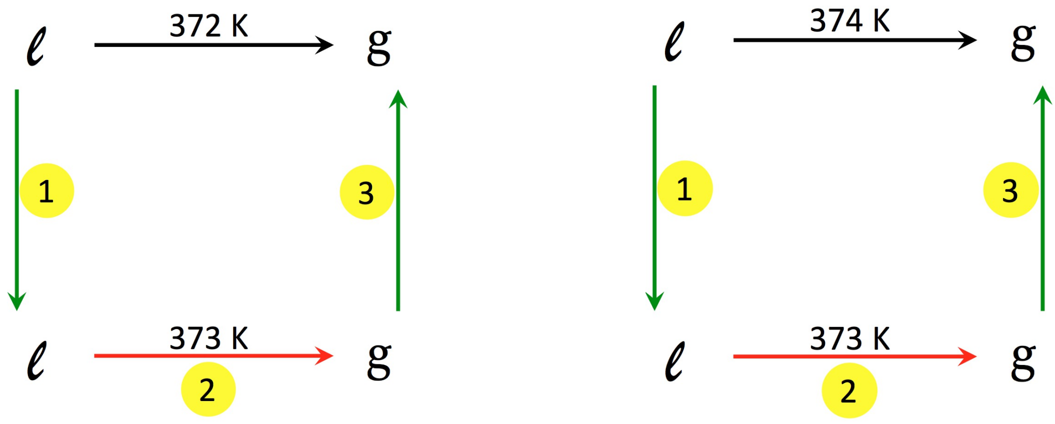

FIG. 2: Thermodynamic cycle for 372 K and 374 K.

Using Fig. 2, at 372 K we have $\Delta G = \Delta G_1 + \Delta G_2 + \Delta G_3$. We already know that $\Delta G_2 = 0$. ΔG_1 is the negative of the solid yellow area in Fig. 1, and ΔG_3 is the squared area in Fig. 1. To get the correct sign, you must consider both the negative sign in Eqn. (1) and whether the path involves the temperature increasing or decreasing. This means we get a positive ΔG for 372 K. What value do we get? Roughly the height $\times$ the width of the green squared box with the white background, which is $1\,\text{K} \times 109.0\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1} = +109\,\text{J}\,\text{mol}^{-1}$.

Using Fig. 2, at 374 K we have $\Delta G = \Delta G_1 + \Delta G_2 + \Delta G_3$. We already know that $\Delta G_2 = 0$. ΔG_1 is the solid orange area in Fig. 1, and ΔG_3 is the negative of the striped area in Fig. 1. To get the correct sign, you must consider both the negative sign in Eqn. (1) and whether the path involves the temperature increasing or decreasing. This means we get a negative ΔG for 374 K. What value do we get? Roughly the negative of the height $\times$ the width of the blue striped box with the white background, which is $-1\,\text{K} \times 109.0\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1} = -109\,\text{J}\,\text{mol}^{-1}$.