Work in groups on these problems. You should try to answer the questions without referring to your textbook. If you get stuck, try asking another group for help.

How does the Gibbs energy depend on its natural variables?

We can use the Gibbs Helmholtz equation to think about the temperature dependence. The Gibbs Helmholtz equation is

$$\left(\frac{\partial (G/T)}{\partial T}\right)_P = -\frac{H}{T^2}$$

We can also cast this equation in terms of the change in Gibbs energy and enthalpy,

$$\left(\frac{\partial (\Delta G/T)}{\partial T}\right)_P = -\frac{\Delta H}{T^2}$$

This means we can look up values for the Gibbs energy and enthalpy and figure out if a process is spontaneous or not.

If you have a glass of water at 5°C, what does your intuition tell you about whether the water will spontaneously (and immediately) form ice crystals in it?

How could you use the Gibbs Helmholtz equation to confirm your intuition? First, let's make approximations about the equation.

If you want to approximate a derivative, for example \(\frac{df}{dx}\), where \(f\) is a function of \(x\) as shown in the graph below, how would you find it? (don't overthink this - it is meant to be as easy as it looks).

![Graph](image)

How would you find the derivative \(\frac{dg}{dx}\) for the function shown on the next graph? Here it depends on where you want to find \(\frac{dg}{dx}\). Without knowing the form of the function \(g(x)\), how could you find \(\frac{dg}{dx}\) at \(x=0\)? At \(x=5\)?
Now go back to our original question, that is, how can you use the Gibbs Helmholtz equation to prove your intuition about whether ice crystals will form spontaneously in water at 5°C? We can approximate the Gibbs Helmholtz equation

\[
\left( \frac{\partial \Delta G}{\partial T} \right)_P = -\frac{\Delta H}{T^2}
\]

as

\[
\frac{(\Delta_{fusion}(T_{final})/(T_{final})-(\Delta G_m(T_{initial})/T_{initial})}{T_{final}-T_{initial}}=rac{\Delta H_{fusion}(T_{initial})}{T^2_{initial}}
\]

Now the key is finding \(\Delta G_{fusion}\) and \(\Delta H_{Fusion}\) (which you can look up in a table like the NIST Chemistry webbook or the CRC handbook of Chemistry and Physics (or even most likely in a google search).

What value do you use for \(T_{initial}\)? What value do you use for \(T_{final}\)? What value are you seeking to solve this problem?

Now consider the other natural variable for \(G\), that is pressure. How does \(G\) vary with pressure? We know from the Maxwell relations that \(\frac{\partial G}{\partial P}\)\(\frac{\partial P}{\partial T}\)\(=V\). From this expression, we can find

\[
\int_{G_{initial}}^{G_{final}} dG = \int_{P_{initial}}^{P_{final}} V dP
\]

How does volume vary with pressure? If you dramatically increase the pressure on a liquid, how much does its volume change? We can simplify the expression by realizing that the volume stays pretty much constant. This means that for a liquid

\[
\Delta G = \int_{G_{initial}}^{G_{Final}} dG = \int_{P_{initial}}^{P_{final}} V dP = V(P_{final}-P_{initial})
\]

How is this different for a gas? How would you solve this problem for a gas?

Now, calculate the change in Gibbs energy upon compression from 1.0 to 2.0 bar at 298K for

a. Liquid water (treated as incompressible)

b. Water vapor treated as an ideal gas.

Note: the molar volume of liquid water at 1.0 bar and 298K is 18.0 mL/mol.