Chemistry 223A
Homework assignment # 5
Reading: Callen Chapters 8 and 9

Thermodynamic stability and first order phase transitions. Each problem is still worth ten points.

1. **Stability and fundamental relations: Callen 8.2-1**

2. **Isothermal versus isentropic compressibility**
   In class we proved that $C_p \geq C_V \geq 0$ and that $\kappa_T \geq 0$. Now show that isentropic compressibility is smaller than the isothermal compressibility but still positive: $\kappa_T \geq \kappa_S$.

3. **The triplet point: Callen 9.3-5.**

4. **Two-phase systems: 9.3-6.**

5. **Phase coexistence with the van der Waals fluid: Callen 9.4-8 and 9.4-10.**

6. **The Clausius-Clapeyron equation**
   Consider an alternate derivation from the one we discussed in class using a Carnot engine with one mole of water. At the source $(P, T)$ the latent heat $L$ is supplied converting the liquid into vapor (i.e. steam). There is a volume increase $V$ associated with this process. The pressure is adiabatically decreased to $P - dP$. At the sink $(P - dP, T - dT)$ steam is condensed back into liquid, i.e. water.

   a) Show that the work output of the engine is $W = VdP + O(dP^2)$. Hence
show that the Clausius Clapeyron equation is
\[ \frac{dP}{dT} \bigg|_{\text{liquid/vapor coexistence}} = \frac{L}{TV}. \]

b) Explain the flaw in the following argument: “The heat \( Q_H \) supplied at the source to the convert one mole of water to steam is \( L(T) \). At the sink \( L(T - dT) \) is supplied to condense one mole of steam to water. The difference is \( dT \frac{dL}{dT} \) must equal the work \( W = pdV \), equal to \( L \frac{dT}{T} \) from the above equation. Hence \( \frac{dL}{dT} = \frac{L}{T} \), implying that \( L \) is proportional to \( T \)!" 

c) Assume that \( L \) is approximately temperature independent, and the volume change is dominated by the volume of the steam treated as an ideal gas, that is \( V = \frac{Nk_B T}{P} \). Integrate your result from part (a) to get \( P(T) \).

d) A hurricane works rather like the heat engine described above. Water evaporates at the warm ocean’s surface, the vapor rises up into the cooler atmosphere at higher altitudes and condenses back to water. The Coriolis force converts the upward motion of the air into the characteristic spiral motion of a hurricane. Typical values of the temperatures are 80°F and -120°F for the warm ocean and upper atmosphere respectively. The warm ocean water is roughly 200 feet thick and the hurricane needs about 90 million tons of water vapor per hour to maintain itself. Estimate the maximum possible efficiency and power output of this typical hurricane! The latent heat of vaporization of water is about \( 2.3 \times 10^6 \text{J/kg} \).