Problem Set 5
(Due, Monday October 8)

1. The Gibbs differentials imply that

\[ S = -\frac{\partial G}{\partial T}_p = -\frac{\partial A}{\partial T}_V \] . This is a remarkable result. Prove it from the defining relation

\[ G(T, p) = A(T, V(T, p)) + pV(T, p). \]

2. You have containers of pure H\(_2\) and He at 298 K and 1 atm pressure. Calculate \( \Delta G_{mixing} \) relative to the unmixed gases of

a. a mixture of 10 mol of H\(_2\) and 10 mol of He
b. a mixture of 10 mol of H\(_2\) and 20 mol of He
c. For what composition (proportion of the two gases) does \( \Delta G_{mixing} \) have its minimum value? Explain physically and show it with calculus.

3. Show that

\[ pV \frac{\partial C}{\partial T} \frac{\partial T}{\partial p} = -\frac{\partial V}{\partial T} \] . (These are all easily measurable properties for a gas and are useful for e.g. Joule-Thompson calculations). HINT – It will prove useful to consider \( G(T, p) = -S \) and what this produces for \( \frac{\partial G}{\partial p} \).

4. Based on the result of 3, show that the Joule-Thompson coefficient for an ideal gas is zero.

5. \( C_p - C_v = \left[ p + \left( \frac{\partial U}{\partial V} \right)_T \right] \left( \frac{\partial V}{\partial T} \right)_p \) isn’t the most convenient form for solids and liquids.

Show that an equivalent expression is: 

\[ C_p - C_v = -T \left( \frac{\partial p}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_p \]

First obtain

\[ \left( \frac{\partial U}{\partial V} \right)_T = T \left( \frac{\partial P}{\partial T} \right)_V - P \] by starting with the Gibbs expression for \( dA \) (Levine 4.35) and differentiating it with respect to \( V \) for fixed \( T \). Then use a Maxwell relation and an appropriate definition of the pressure.

Use this result in (1) and then keep going to get the desired result.