CH353 – Physical Chemistry I
Spring 2012 Unique 52135
Free energy summary

Helmholtz free energy: $A \equiv U - TS$
Gibbs free energy: $G \equiv H - TS$

Natural variables:

$$dU = TdS - PdV$$
$$dH = TdS + VdP$$
$$dA = -SdT - PdV$$
$$dG = -SdT + VdP$$

Maxwell relations:

$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P \text{ (from } dG\text{)} \qquad \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \text{ (from } dH\text{)}$$

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \text{ (from } dU\text{)} \qquad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \text{ (from } dA\text{)}$$

We will see how these expressions are very useful in expressing any thermodynamic property in terms of something that is easy (or at least easier) to measure.