12.5: Summary, the Maxwell Relations, and the Gibbs-Helmholtz Relations

$$dU = TdS - PdV + \sum XdY \tag{12.5.1}$$

$$dH = TdS + VdP + \sum XdY \tag{12.5.2}$$

$$dA = -SdT - PdV + \sum XdY \tag{12.5.3}$$

$$dG = -SdT + VdP + \sum XdY \tag{12.5.4}$$

If the only reversible work done on or by a system is PdV work of expansion or compression, we have the more familiar forms

$$dU = TdS - PdV \tag{12.5.5}$$

$$dH = TdS + VdP \tag{12.5.6}$$

$$dA = -SdT - PdV \tag{12.5.7}$$

$$dG = -SdT + VdP \tag{12.5.8}$$

All four thermodynamic functions are functions of state (and hence their differentials are exact differentials) and therefore

$$\left(\frac{\partial U}{\partial S}\right)_V = T \quad \left(\frac{\partial U}{\partial V}\right)_S = -P \tag{12.5.9}$$

$$\left(\frac{\partial H}{\partial S}\right)_P = T \quad \left(\frac{\partial H}{\partial P}\right)_S = V \tag{12.5.10}$$

$$\left(\frac{\partial A}{\partial T}\right)_V = -S \quad \left(\frac{\partial A}{\partial V}\right)_T = -P \tag{12.5.11}$$

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \qquad \left(\frac{\partial G}{\partial P}\right)_T = V \tag{12.5.12}$$

Further, by equating the mixed second derivatives, we obtain the four Maxwell Thermodynamic Relations:

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \tag{12.5.13}$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \tag{12.5.14}$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \tag{12.5.15}$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \tag{12.5.16}$$

The Gibbs-Helmholtz Relations are trivially found from $A = U - TS$ and together with equations 12.6.11a and 12.6.12a. $G = H - TS$ They are

$$U = A - T\left(\frac{\partial A}{\partial T}\right)_V \tag{12.5.17}$$

$$H = G - T\left(\frac{\partial G}{\partial T}\right)_P \tag{12.5.18}$$