

$$\underline{9.1.} \quad d\underline{U} = \bar{T} dS + \sigma dA$$

$$a) \quad H = \underline{U} - \sigma A$$

$$dH = d\underline{U} - d(\sigma A) = \bar{T} dS - A d\sigma$$

$$b) \quad F = \underline{U} - \bar{T} S$$

$$dF = d\underline{U} - d(\bar{T} S) = -S d\bar{T} + \sigma dA$$

$$c) \quad G = F - \sigma A$$

$$dG = dF - d(\sigma A) = -S d\bar{T} - A d\sigma$$

$$\underline{9.2} \quad \left(\frac{\partial \sigma}{\partial S}\right)_A = \left(\frac{\partial \bar{T}}{\partial A}\right)_S \quad (\text{from } d\underline{U})$$

$$\left(\frac{\partial A}{\partial S}\right)_\sigma = -\left(\frac{\partial \bar{T}}{\partial \sigma}\right)_S \quad (\text{from } dH)$$

$$\left(\frac{\partial S}{\partial A}\right)_\bar{T} = -\left(\frac{\partial \sigma}{\partial \bar{T}}\right)_A \quad (\text{from } dF)$$

$$\left(\frac{\partial S}{\partial \sigma}\right)_\bar{T} = \left(\frac{\partial A}{\partial \bar{T}}\right)_\sigma \quad (\text{from } dG)$$

9.3 a)

$$d\underline{u} = \bar{T} dS - p dV$$

$$dS = \frac{1}{\bar{T}} d\underline{u} + \frac{p}{\bar{T}} dV$$

use
$$d\underline{u} = \left(\frac{\partial \underline{u}}{\partial \bar{T}} \right)_V d\bar{T} + \left(\frac{\partial \underline{u}}{\partial V} \right)_{\bar{T}} dV$$

$$dS = \frac{1}{\bar{T}} \left(\frac{\partial \underline{u}}{\partial \bar{T}} \right)_V d\bar{T} + \left[\frac{p}{\bar{T}} + \frac{1}{\bar{T}} \left(\frac{\partial \underline{u}}{\partial V} \right)_{\bar{T}} \right] dV$$

• mixed 2nd derivatives of S must be equal

$$\frac{1}{\bar{T}} \frac{\partial}{\partial V} \left[\left(\frac{\partial \underline{u}}{\partial \bar{T}} \right)_V \right]_{\bar{T}} = \frac{\partial}{\partial \bar{T}} \left[\frac{p}{\bar{T}} + \frac{1}{\bar{T}} \left(\frac{\partial \underline{u}}{\partial V} \right)_{\bar{T}} \right]_V$$

$$\frac{1}{\bar{T}} \cancel{\frac{\partial^2 \underline{u}}{\partial V \partial \bar{T}}} = -\frac{1}{\bar{T}^2} \left[p + \left(\frac{\partial \underline{u}}{\partial V} \right)_{\bar{T}} \right] + \frac{1}{\bar{T}} \left[\cancel{\frac{\partial^2 \underline{u}}{\partial \bar{T} \partial V}} + \left(\frac{\partial p}{\partial \bar{T}} \right)_V \right]$$

$$\left(\frac{\partial \underline{u}}{\partial V} \right)_{\bar{T}} = -p + \bar{T} \left(\frac{\partial p}{\partial \bar{T}} \right)_V$$

b)
$$pV = Nk_B \bar{T} \quad p = \frac{Nk_B \bar{T}}{V}$$

$$\left(\frac{\partial \underline{u}}{\partial V} \right)_{\bar{T}} = -p + \bar{T} \frac{Nk_B}{V} = -p + p = 0$$