

HW #1

Show that the entropy maximum principle
 \Rightarrow the energy minimum principle

given $\left(\frac{\partial S}{\partial X}\right)_E = 0$, $\left(\frac{\partial^2 S}{\partial X^2}\right)_E < 0$

show $\left(\frac{\partial E}{\partial X}\right)_S = 0$, $\left(\frac{\partial^2 E}{\partial X^2}\right)_S > 0$

$$\left(\frac{\partial E}{\partial X}\right)_S = - \frac{\left(\frac{\partial S}{\partial X}\right)_E}{\left(\frac{\partial S}{\partial E}\right)_X} = -T \left(\frac{\partial S}{\partial X}\right)_E$$

so $\left(\frac{\partial S}{\partial X}\right)_E = 0 \Rightarrow \left(\frac{\partial E}{\partial X}\right)_S = 0$

Let $\left(\frac{\partial E}{\partial X}\right)_S = y$

$$dy = \left(\frac{\partial y}{\partial X}\right)_E dx + \left(\frac{\partial y}{\partial E}\right)_X dE$$

$$\left(\frac{\partial y}{\partial X}\right)_S = \left(\frac{\partial y}{\partial X}\right)_E + \left(\frac{\partial y}{\partial E}\right)_X \left(\frac{\partial E}{\partial X}\right)_S$$

$$\Rightarrow \left(\frac{\partial^2 E}{\partial X^2}\right)_S = - \frac{\partial}{\partial X} \left[T \left(\frac{\partial S}{\partial X}\right)_E \right] = -T \left(\frac{\partial^2 S}{\partial X^2}\right)_E$$

$$\Rightarrow \left(\frac{\partial^2 E}{\partial X^2}\right)_S > 0$$

consider $dg = \frac{\partial g}{\partial x} dx + \frac{\partial g}{\partial y} dy$

is not a state function
 integration of dg depends on path

Note: $\frac{dg}{T}$ is a state function

$$\frac{\partial g}{\partial x} = \frac{\partial g}{\partial y} \frac{\partial y}{\partial x} \quad \frac{\partial g}{\partial x} = \frac{\partial g}{\partial y} \frac{\partial y}{\partial x}$$

dg not an exact differential
 $\frac{dg}{T}$ is exact

2. Find the Maxwell relations corresponding to H and G

$$dH = TdS + VdP + \sum u_i dn_i$$

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



I have suppressed the subscript indicating that the n_i are fixed.

$$dG = -SdT + VdP + \sum u_i dn_i$$

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

#3 Using the Maxwell relations show that

$$\left(\frac{\partial H}{\partial V}\right)_{T,n} = \frac{T\alpha - 1}{\chi_T}$$

$$\left(\frac{\partial H}{\partial V}\right)_{T,n} = T\left(\frac{\partial S}{\partial V}\right)_{T,n} + V\left(\frac{\partial P}{\partial V}\right)_{T,n}$$

$$= T\left(\frac{\partial S}{\partial P}\right)_{T,n}\left(\frac{\partial P}{\partial V}\right)_{T,n} + V\left(\frac{\partial P}{\partial V}\right)_{T,n}$$

$$= -T\left(\frac{\partial V}{\partial T}\right)_{P,n}\left(\frac{\partial P}{\partial V}\right)_{T,n} + V\left(\frac{\partial P}{\partial V}\right)_{T,n}$$

$$= \left(\frac{\partial P}{\partial V}\right)_{T,n} \left[-T\left(\frac{\partial V}{\partial T}\right)_{P,n} + V \right]$$

$$= \frac{\left[-T\left(\frac{\partial V}{\partial T}\right)_{P,n} + V \right]}{\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,n}} = \frac{\left[-\frac{T}{V}\left(\frac{\partial V}{\partial T}\right)_{P,n} + 1 \right]}{\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,n}}$$

$$= \frac{-T\alpha + 1}{-\chi_T} = \frac{T\alpha - 1}{\chi_T}$$

α = coefficient of thermal expansion

χ_T = isothermal compressibility