

a)  $F = U - TS$

$dF = dU - Tds - SdT$

$= Tds - PdV - Tds - SdT$

$= -SdT - PdV$

$\stackrel{\text{constant } V}{=} -SdT \Rightarrow \left(\frac{\partial F}{\partial T}\right)_V = -S, \text{ or}$

$F = U + T\left(\frac{\partial F}{\partial T}\right)_V$

b)  $c_v = \left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial U}{\partial S}\right)_V \left(\frac{\partial S}{\partial T}\right)_V$   
 $= T \left(\frac{\partial S}{\partial T}\right)_V$

and  $dF = -SdT - PdV \Rightarrow \left(\frac{\partial F}{\partial T}\right)_V = -S$

$\Downarrow$   
 $\left(\frac{\partial S}{\partial T}\right)_V = -\left(\frac{\partial}{\partial T}\left(\frac{\partial F}{\partial T}\right)_V\right)_V$

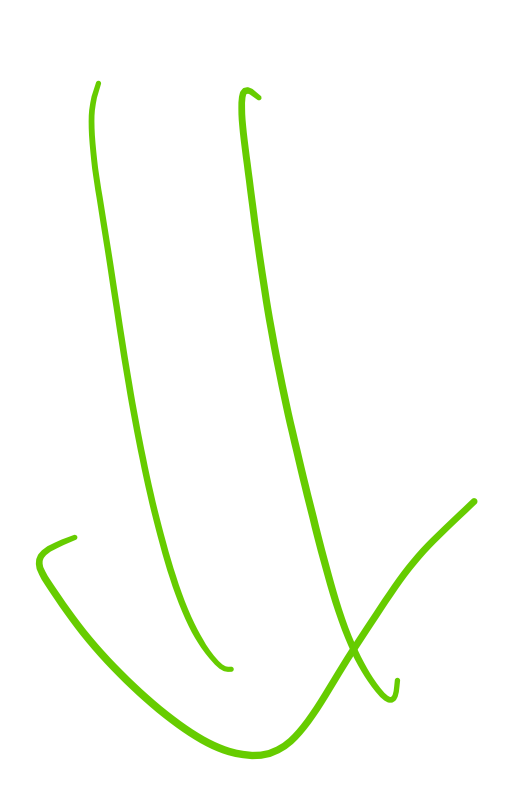
$\Downarrow$   
 $c_v = -T \left(\frac{\partial}{\partial T}\left(\frac{\partial F}{\partial T}\right)_V\right)_V$   
 $= -T \left(\frac{\partial^2 F}{\partial T^2}\right)_V$

c)  $H = U + PV$

$G = U - TS + VP$

$= H - TS \rightarrow H = G + TS$

$dG = dU - SdT - Tds + VdP + PdV$   
 $= Tds - PdV - SdT - Tds + VdP + PdV$   
 $= VdP - SdT$



$\left(\frac{dG}{dT}\right)_P = -S$

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

d)

$c_p = \left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial H}{\partial S}\right)_P \left(\frac{\partial S}{\partial T}\right)_P$

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

$= -T \left(\frac{\partial^2 G}{\partial T^2}\right)_P$