

$$dA = Tds - PdV - Tds - sdT$$

$$dA = -PdV - sdT$$

$$du = Tds - PdV$$

$$dH = Tds + v dP$$

$$C_v = \left(\frac{\partial u}{\partial T}\right)_v = T \left(\frac{\partial s}{\partial T}\right)_v - P \left(\frac{\partial v}{\partial T}\right)_v = T \left(\frac{\partial s}{\partial T}\right)_v = C_v$$

$$C_p = \left(\frac{\partial h}{\partial T}\right)_p = T \left(\frac{\partial s}{\partial T}\right)_p + v \left(\frac{\partial P}{\partial T}\right)_p = T \left(\frac{\partial s}{\partial T}\right)_p = C_p$$

we're gonna plus in for this

$$C_p - C_v = T \left(\frac{\partial s}{\partial T}\right)_p - T \left(\frac{\partial s}{\partial T}\right)_v$$

$$\alpha = \frac{1}{V_m} \left(\frac{\partial V_m}{\partial T}\right)_p$$

$$K = -\frac{1}{V_m} \left(\frac{\partial V_m}{\partial P}\right)_T$$

we know:

$$ds = \left(\frac{\partial s}{\partial T}\right)_v dT + \left(\frac{\partial s}{\partial v}\right)_T dv$$

$$\left(\frac{\partial s}{\partial T}\right)_p = \left(\frac{\partial s}{\partial T}\right)_v \left(\frac{\partial T}{\partial T}\right)_p + \left(\frac{\partial s}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_p$$

$$= \left(\frac{\partial s}{\partial T}\right)_v + \left(\frac{\partial s}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_p$$

$$C_p - C_v = T \left(\frac{\partial s}{\partial T}\right)_v + T \left(\frac{\partial s}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_p - T \left(\frac{\partial s}{\partial T}\right)_v$$

$$C_p - C_v = T \left(\frac{\partial s}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_p$$

from dA:

$$\left(\frac{\partial P}{\partial T}\right)_v = \left(\frac{\partial s}{\partial v}\right)_T$$

$$C_p - C_v = T \left(\frac{\partial P}{\partial T}\right)_v \left(\frac{\partial v}{\partial T}\right)_p$$

$$= T \left(\frac{\partial P}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_p \left(\frac{\partial v}{\partial T}\right)_p$$

$$C_p - C_v = -T \frac{v^2}{v} \left(\frac{\partial v}{\partial P}\right)_T \left[\frac{1}{v^2} \left(\frac{\partial v}{\partial T}\right)_p^2\right]$$

$$C_p - C_v = -\frac{TV\alpha^2}{K}$$