

# Coefficient of Volume Expansion

$$\beta = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_{P,N} \quad \text{of increase / } ^\circ\text{C}$$

$$\Rightarrow \beta V = \left( \frac{\partial V}{\partial T} \right)_{P,N} \stackrel{\text{Maxwell relation}}{=} - \left( \frac{\partial S}{\partial P} \right)_{T,N}$$

natural variables, matches G

$$\begin{aligned} dU &= TdS - PdV + \mu dN \\ dH &= TdS + VdP + \mu dN \\ dF &= -SdT - PdV + \mu dN \\ dG &= -SdT + VdP + \mu dN \end{aligned}$$

$$\beta = -\frac{1}{V} \left( \frac{\partial S}{\partial P} \right)_{T,N} \quad \text{isothermal change in entropy with pressure}$$

$T, N$  constant

$$dS = -\beta V dP$$

as  $P$  increases at constant  $T$ ,  
heat flows out ( $dS < 0$ )

$$Q = -\beta V T dP$$

$Q = T dS$

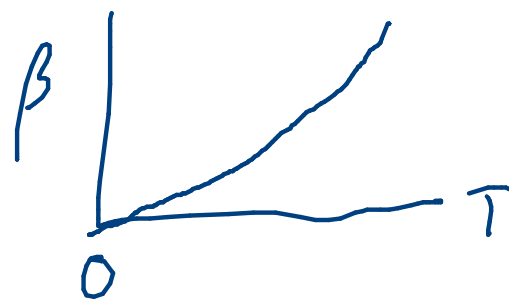
At  $T=0$ ,  $S=0$  and doesn't change

$$dS=0 = -\beta V dP \text{ at } T=0$$

either  $\beta = 0$   
solid

or

$V=0$  at  $T=0$   
ideal gas  
 $PV = NKT$   
not realistic  
(singularity)



coefficient of volume expansion goes to zero as  $T \rightarrow 0$ .

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

$$\begin{aligned} dU &= TdS - PdV + \mu dN \\ dH &= TdS + VdP + \mu dN \\ dF &= -SdT - PdV + \mu dN \\ dG &= -SdT + VdP + \mu dN \end{aligned}$$

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

$$\underbrace{\left(\frac{\partial V}{\partial T}\right)_{P,N}}_{dG} = - \left(\frac{\partial S}{\partial P}\right)_{T,N}$$

Another neat trick

$$\left(\frac{\partial a}{\partial b}\right)_c \left(\frac{\partial b}{\partial c}\right)_a \left(\frac{\partial c}{\partial a}\right)_b = -1$$

$$\stackrel{\text{const}}{N} \quad \left(\frac{\partial T}{\partial P}\right)_V \left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P = -1$$

$$\left(\frac{\partial V}{\partial P}\right)_T = -K \bar{V} \quad \left(\frac{\partial V}{\partial T}\right)_P = \beta \bar{V}$$

isothermal compressibility      coefficient of volume expansion

$$\left(\frac{\partial T}{\partial P}\right)_V \left(-\frac{1}{K \bar{V}}\right) (\beta \bar{V}) = -1$$

$$\left(\frac{\partial T}{\partial P}\right)_V = \frac{K}{\beta}$$