

Coefficient of Volume Expansion

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

$$\text{or } \beta V = \left(\frac{\partial V}{\partial T} \right)_{P,N} \stackrel{\text{Maxwell relation } \frac{\partial^2 G}{\partial P \partial T}}{=} - \left(\frac{\partial S}{\partial P} \right)_{T,N}$$

natural variables, matches G

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

$$\beta = -\frac{1}{V} \left(\frac{\partial S}{\partial P} \right)_{T,N}$$

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

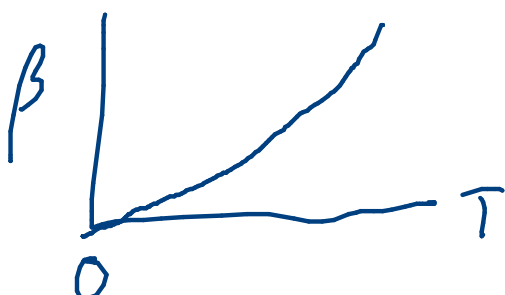
or

$$V=0 \text{ at } T=0$$

ideal gas

$$PV = NKT$$

not realistic
(singularity)



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

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

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

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

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

Another neat trick

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

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

$$\begin{aligned} \left(\frac{\partial V}{\partial P}\right)_T &= -\frac{1}{K} V \\ \left(\frac{\partial V}{\partial T}\right)_P &= \beta V \end{aligned}$$

isothermal compressibility

coefficient of volume expansion

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

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