Some consequences of the second law of thermodynamics.

For a reversible process $E(V,T)$

$$E(V,T) \Rightarrow dE = \frac{\partial E}{\partial V}\Big|_T dV + \frac{\partial E}{\partial T}\Big|_V dT$$

$$dQ = \cancel{TdT}\ TdS$$

$$dS = \frac{1}{T}dQ = \frac{1}{T}\left[\left(\frac{\partial E}{\partial V}\right)_T + P\right]dV + \frac{1}{T}\left(\frac{\partial E}{\partial T}\right)_V dT$$

$$dS = \frac{1}{T}\left[\left(\frac{\partial E}{\partial V}\right)_T + P\right]dV + \frac{C_V}{T}dT$$

$$\frac{\partial S}{\partial T}\Big|_V = \frac{C_V}{T}, \quad \frac{\partial S}{\partial V}\Big|_T = \frac{1}{T}\left[\left(\frac{\partial E}{\partial V}\right)_T + P\right]$$

$$\frac{\partial}{\partial V}\left(\frac{C_V}{T}\right) = \frac{\partial}{\partial T}\left[\frac{1}{T}\left(\frac{\partial E}{\partial V}\right)_T + P\right]$$

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

Now from first law $\quad dE = dQ - PdV$

$$TdS = C_V dT + T\frac{\partial P}{\partial T}\Big|_V dV$$

$$TdS = C_p dT - T\frac{\partial V}{\partial T}\Big|_P dP$$

Let us define some coefficients

$$\alpha \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \quad \text{Coefficients of thermal expansion}$$

$$K_T \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \rightarrow \text{isothermal compressibility}$$

$$K_S \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S \rightarrow \text{Adiabatic compressibility}$$

$F(T, V, P) = 0$

$$\frac{\partial P}{\partial T}\Big|_V \frac{\partial T}{\partial V}\Big|_P \frac{\partial V}{\partial P}\Big|_T = -1$$

$$\frac{\partial P}{\partial T}\Big|_V = \frac{-1}{\left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T} = \frac{(\partial V/\partial T)_P}{-(\partial V/\partial P)_T}$$

or $$\boxed{\frac{\partial P}{\partial T}\Big|_V = \frac{\alpha}{K_T}} \quad \text{—— (1)}$$

Thus Tds equations are written as

$$\boxed{\begin{aligned} Tds &= C_v dT + \frac{\alpha T}{K_T} dV \\ Tds &= C_p dT - \alpha T v dP \end{aligned}} \quad \text{—— (2)}$$

Expressions for $C_p - C_v$

From above eqs.

$$C_V dT + T\frac{\partial P}{\partial T}\Big|_V dT = C_p dT - T\frac{\partial V}{\partial T}\Big|_P dP$$

$$T(P,V) \rightarrow dT = \frac{\partial T}{\partial P}\Big|_V dP + \frac{\partial T}{\partial V}\Big|_P dV$$

$$(C_p - C_v) dT = T\frac{dP}{\partial T}\Big|_V dV + T\frac{\partial V}{\partial T}\Big|_P dP$$

or $$(C_p - C_v)\left[\frac{\partial T}{\partial P}\Big|_V dP + \frac{\partial T}{\partial V}\Big|_P dV\right] = T\frac{\partial P}{\partial T}\Big|_V dV + T\frac{\partial V}{\partial T}\Big|_P dP$$

$$\left[(C_p - C_v)\frac{\partial T}{\partial P}\Big|_V - T\frac{\partial V}{\partial T}\Big|_P\right] dP - \left[(C_p - C_v)\frac{\partial T}{\partial V}\Big|_P - T\frac{\partial P}{\partial T}\Big|_V\right] dV = 0$$

$$\Rightarrow (C_p - C_v)\frac{\partial T}{\partial V}\Big|_P = T\frac{\partial P}{\partial T}\Big|_V$$

$$\Rightarrow \quad C_p - C_V = \frac{\partial V}{\partial T}\Big|_P \cdot \left(T \frac{\alpha}{K_T}\right) = \frac{TV\alpha^2}{K_T}$$

$$\boxed{C_p - C_v = \frac{TV\alpha^2}{K_T}} \quad \text{--- } (3)$$

$$\Rightarrow C_p \geq C_v \quad \text{if } K_T \geq 0$$

Next, $\frac{C_p}{C_v} = \gamma$

From Tds eqs

$$C_v = -T \frac{\partial P}{\partial T}\Big|_V \frac{\partial V}{\partial T}\Big|_s$$

$$C_p = T \frac{\partial V}{\partial T}\Big|_P \frac{\partial P}{\partial T}\Big|_s$$

$$\frac{C_p}{C_v} = \frac{-\frac{\partial V}{\partial T}\Big|_P \frac{\partial P}{\partial T}\Big|_s}{\frac{\partial P}{\partial T}\Big|_V \frac{\partial V}{\partial T}\Big|_s} = \left(-\frac{\partial V}{\partial T}\Big|_P \frac{\partial T}{\partial P}\Big|_V\right) \times \left(\frac{\partial P}{\partial T}\Big|_s \frac{\partial T}{\partial V}\Big|_s\right)$$

$$= \frac{\partial V}{\partial P}\Big|_T \frac{\partial P}{\partial V}\Big|_s$$

$$\boxed{\frac{C_p}{C_v} = \frac{K_T}{K_s}} \quad \text{--- } (4)$$

From (3) & (4)

$$C_p = \frac{TV\alpha^2}{K_T - K_s}$$

$$C_v = \left(\frac{TV\alpha^2}{K_T - K_s}\right) \cdot \frac{K_s}{K_T}$$