Relations between derivatives of thermodynamic functions

Heat capacities

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V$$

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

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$ – thermal expansion coefficient

$$\beta = \frac{1}{P}\left(\frac{\partial P}{\partial T}\right)_V$$ – thermal pressure coefficient

$$\delta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$ – isothermal compressibility

Find a relation between them

$\exists\ X = X(Y, Z)$

$$\left(\frac{\partial X}{\partial Y}\right)_Z\left(\frac{\partial Y}{\partial Z}\right)_X\left(\frac{\partial Z}{\partial X}\right)_Y = -1$$

$$\frac{\alpha}{\delta} = -\frac{\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial P}\right)_T} = \left(\frac{\partial P}{\partial T}\right)_V = P\beta \rightarrow \alpha = P\beta\delta$$

Adiabatic compressibility

$$\gamma_S = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S$$

Isothermal compressibility

$$\gamma_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

$$\left(\frac{\partial V}{\partial P}\right)_S = -\frac{\left(\frac{\partial S}{\partial P}\right)_V}{\left(\frac{\partial S}{\partial V}\right)_T} \;;\; \left(\frac{\partial V}{\partial P}\right)_T = -\frac{\left(\frac{\partial T}{\partial P}\right)_V}{\left(\frac{\partial T}{\partial V}\right)_P}$$

$$\frac{\gamma_S}{\gamma_T} = \frac{\left(\frac{\partial V}{\partial P}\right)_S}{\left(\frac{\partial V}{\partial P}\right)_T} = \frac{\left(\frac{\partial S}{\partial P}\right)_V \left(\frac{\partial T}{\partial V}\right)_P}{\left(\frac{\partial T}{\partial P}\right)_V \left(\frac{\partial S}{\partial V}\right)_P} = \frac{\left(\frac{\partial S}{\partial T}\right)_V}{\left(\frac{\partial S}{\partial T}\right)_P} = \frac{C_V}{C_P}$$

Let's assume we know some function as a function of two parameters, $t = t(x, y)$.
And we want to re-express it as a function of another two parameters, $t = t(y, z)$
Then we say $t = t(x(y,z), y)$

$$\left(\frac{\partial t}{\partial y}\right)_z = \left(\frac{\partial t}{\partial y}\right)_x + \left(\frac{\partial t}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z$$

Apply this to S, T and V

$$\left(\frac{\partial S}{}\right) = \left(\frac{\partial S}{\partial T}\right) + \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

$$\left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial S}{\partial T}\right)_V + \underbrace{\left(\frac{\partial S}{\partial V}\right)_T}_{= \left(\frac{\partial P}{\partial T}\right)_V} \left(\frac{\partial V}{\partial T}\right)_P$$

Multiplying this by T gives

$$C_P = C_V + T \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P = C_V - T \frac{\left(\frac{\partial V}{\partial T}\right)_P^2}{\left(\frac{\partial V}{\partial P}\right)_T}$$

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

$$\boxed{C_P = C_V - T \frac{\left(\frac{\partial V}{\partial T}\right)_P^2}{\left(\frac{\partial V}{\partial P}\right)_T}}$$

$$C_P = C_V + \frac{\alpha^2}{\delta} T V$$

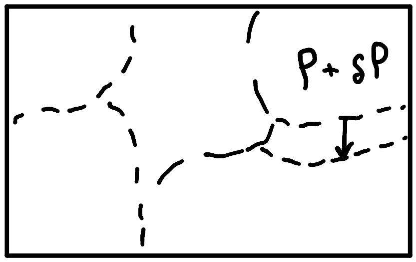
Thermal compressibility

Stability requires $\left(\frac{\partial V}{\partial P}\right)_T < 0$

Otherwise, we would separate our system into parts, and they will collapse onto each other.

Therefore, $C_P \geq C_V$

$C_P = C_V$ only when $\left(\frac{\partial V}{\partial T}\right)_P = 0$



(water at 4°C)

Another stability condition: $\frac{\partial^2 E}{\partial S^2} \geq 0$
(at V= const)

Since $T = \frac{\partial E}{\partial S}$, $\left(\frac{\partial T}{\partial S}\right)_V \geq 0$

$\rightarrow \frac{T}{C_V} \geq 0$

So, $\boxed{C_P \geq C_V \geq 0}$