Relazione generale tra c_p e c_v per un sistema idrostatico

(pag. 28)

Ricordiamo: $$c_V = \frac{1}{n}\left(\frac{\delta Q}{dT}\right)_V = \frac{1}{n}\left(\frac{\partial U}{\partial T}\right)_V$$

$$c_p = \frac{1}{n}\left(\frac{\delta Q}{dT}\right)_p$$

Ora: $$(\delta Q)_p = dU + p\,dV \underset{U=U(T,V)}{=} \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV + p\,dV$$

$$= \left(\frac{\partial U}{\partial T}\right)_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right] dV$$

$$\downarrow * \qquad \downarrow V = V(T,p)$$

$$= \left(\frac{\partial U}{\partial T}\right)_V + \left[T\left(\frac{\partial p}{\partial T}\right)_V\right]\left[\left(\frac{\partial V}{\partial T}\right)_p dT + \underbrace{\left(\frac{\partial V}{\partial p}\right)_T dp}_{=0}\right]$$

$=0$ perché p costante $dp = 0$

$$\downarrow **$$

$$= \left(\frac{\partial U}{\partial T}\right)_V - \left[T\left(\frac{\partial p}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_p\right]\left(\frac{\partial V}{\partial T}\right)_p dT$$

Quindi $$c_p = \frac{1}{n}\left(\frac{\delta Q}{dT}\right)_p = \frac{1}{n}\left[\underbrace{\left(\frac{\partial U}{\partial T}\right)_V}_{c_V} - T\left(\frac{\partial p}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_p^2\right]$$

$$\boxed{c_p - c_V = -\frac{T}{n}\underbrace{\left(\frac{\partial p}{\partial V}\right)_T}_{<0}\underbrace{\left(\frac{\partial V}{\partial T}\right)_p^2}_{>0}} \quad \Rightarrow \quad c_p > c_V$$

NOTE:
- $c_p \geq c_V$
- $T \to 0 \Rightarrow c_p \to c_V$
- $c_p = c_V$ quando $\left(\frac{\partial V}{\partial T}\right)_p = 0$ (ad esempio per l'acqua a 4 °C)
- nei solidi e nei liquidi è difficile misurare c_V
  $\Rightarrow$ misuro c_p ed uso questa formula per trovare c_V

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* vedi 1.4.2 a p.5 oppure 3.8.5 a pag. 2

** Relazione ciclica:

$$\left(\frac{\partial x}{\partial y}\right)_z\left(\frac{\partial y}{\partial z}\right)_x\left(\frac{\partial z}{\partial x}\right)_y = -1 \quad \Rightarrow \quad \left(\frac{\partial p}{\partial T}\right)_V = -\left(\frac{\partial V}{\partial T}\right)_p\left(\frac{\partial p}{\partial V}\right)_T$$