Beziehung zwischen C_p und C_V

$$\begin{aligned}
dQ &= TdS = dU + pdV = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT + pdV \\
C_p &= \left(\frac{dQ}{\partial T}\right)_p = \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p + \left(\frac{\partial U}{\partial T}\right)_V \left(\frac{\partial T}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p \\
C_p &= \left(\frac{\partial U}{\partial T}\right)_V + \left[p + \left(\frac{\partial U}{\partial V}\right)_T\right] \left(\frac{\partial V}{\partial T}\right)_p \\
C_p - C_v &= \left[p + \left(\frac{\partial U}{\partial V}\right)_T\right] \left(\frac{\partial V}{\partial T}\right)_p
\end{aligned}$$

nun ist nach der Beziehung zwischen thermischer und kalorischer Zustandsgleichung

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

$$\boxed{C_p - C_V = T\left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_p}$$

weiterhin ist

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

Nach Maxwell gilt

$$\left(\frac{\partial p}{\partial S}\right)_V = -\left(\frac{\partial T}{\partial V}\right)_S$$

außerdem

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

$\Rightarrow$

$$\left(\frac{\partial p}{\partial T}\right)_V = -\frac{\frac{\partial^2 U}{\partial S \partial V}}{\left(\frac{\partial^2 U}{\partial S^2}\right)_V}$$

mit

$$\begin{aligned}
dp &= \left(\frac{\partial p}{\partial S}\right)_V dS + \left(\frac{\partial p}{\partial V}\right)_S dV \\
dT &= \left(\frac{\partial T}{\partial S}\right)_V dS + \left(\frac{\partial T}{\partial V}\right)_S dV
\end{aligned}$$

und Eliminierung von dS

$$\begin{aligned}
dp &= \left(\frac{\partial p}{\partial S}\right)_V \frac{dT - \left(\frac{\partial T}{\partial V}\right)_S dV}{\left(\frac{\partial T}{\partial S}\right)_V} + \left(\frac{\partial p}{\partial V}\right)_S dV \\
dp &= \frac{\left(\frac{\partial p}{\partial S}\right)_V}{\left(\frac{\partial T}{\partial S}\right)_V} dT + \left[\left(\frac{\partial p}{\partial V}\right)_S - \frac{\left(\frac{\partial p}{\partial S}\right)_V \left(\frac{\partial T}{\partial V}\right)_S}{\left(\frac{\partial T}{\partial S}\right)_V}\right] dV
\end{aligned}$$

daraus

$$(*) \qquad \left(\frac{\partial V}{\partial T}\right)_p = \frac{\left(\frac{\partial p}{\partial S}\right)_V}{\left(\frac{\partial p}{\partial S}\right)_V \left(\frac{\partial T}{\partial V}\right)_S - \left(\frac{\partial p}{\partial V}\right)_S \left(\frac{\partial T}{\partial S}\right)_V}$$

aus $p = -\left(\frac{\partial U}{\partial V}\right)_S$ folgt

$$\left(\frac{\partial p}{\partial S}\right)_V = -\frac{\partial^2 U}{\partial S \partial V}, \qquad \left(\frac{\partial p}{\partial V}\right)_S = -\left(\frac{\partial^2 U}{\partial V^2}\right)_S$$

und aus $T = \left(\frac{\partial U}{\partial S}\right)_V$ folgt

$$\left(\frac{\partial T}{\partial V}\right)_S = \frac{\partial^2 U}{\partial V \partial S}, \qquad \left(\frac{\partial T}{\partial S}\right)_V = \left(\frac{\partial^2 U}{\partial S^2}\right)_V$$

einsetzen in $(*)$

$$\left(\frac{\partial V}{\partial T}\right)_p = \frac{-\frac{\partial^2 U}{\partial S \partial V}}{-\frac{\partial^2 U}{\partial S \partial V}\frac{\partial^2 U}{\partial V \partial S} + \left(\frac{\partial^2 U}{\partial V^2}\right)_S \left(\frac{\partial^2 U}{\partial S^2}\right)_V}$$

und schließlich mit $T = \left(\frac{\partial U}{\partial S}\right)_V$

$$\begin{aligned} C_p &= C_V + T\left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_p \\ &= \frac{\left(\frac{\partial U}{\partial S}\right)_V}{\left(\frac{\partial^2 U}{\partial S^2}\right)_V} - \left(\frac{\partial U}{\partial S}\right)_V \frac{\frac{\partial^2 U}{\partial S \partial V}}{\left(\frac{\partial^2 U}{\partial S^2}\right)_V} \frac{\frac{\partial^2 U}{\partial S \partial V}}{\left(\frac{\partial^2 U}{\partial S \partial V}\right)^2 - \left(\frac{\partial^2 U}{\partial V^2}\right)_S \left(\frac{\partial^2 U}{\partial S^2}\right)_V} \\ &= C_V\left[1 - \frac{\left(\frac{\partial^2 U}{\partial S \partial V}\right)^2}{\left(\frac{\partial^2 U}{\partial S \partial V}\right)^2 - \left(\frac{\partial^2 U}{\partial V^2}\right)_S \left(\frac{\partial^2 U}{\partial S^2}\right)_V}\right] \end{aligned}$$

$$C_p = C_V \frac{\left(\frac{\partial^2 U}{\partial V^2}\right)_S \left(\frac{\partial^2 U}{\partial S^2}\right)_V}{\left(\frac{\partial^2 U}{\partial V^2}\right)_S \left(\frac{\partial^2 U}{\partial S^2}\right)_V - \left(\frac{\partial^2 U}{\partial S \partial V}\right)^2}$$

einsetzen von C_V

$$\boxed{C_p = \frac{\left(\frac{\partial U}{\partial S}\right)_V \left(\frac{\partial^2 U}{\partial V^2}\right)_S}{\left(\frac{\partial^2 U}{\partial V^2}\right)_S \left(\frac{\partial^2 U}{\partial S^2}\right)_V - \left(\frac{\partial^2 U}{\partial S \partial V}\right)^2}}$$

Offensichtlich ist der Weg über $H = H(p, S)$ wesentlich einfacher!