E_2. Ergänzungen zu Kapitel 2

E_2.1 Die Grundgleichung und die Zustandsgleichungen

Grundgleichung der Thermodynamik

$$dS = \frac{1}{T} dE + \frac{P}{T} dV$$

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

somit

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

da dS ein totales Differential ist, gelten die Integrabilitätsbedingungen, also

$$\frac{\partial^2 S}{\partial V \partial T} = \frac{\partial}{\partial V}\left[\frac{1}{T}\left(\frac{\partial E}{\partial T}\right)_V\right]_T = \frac{\partial}{\partial T}\left[\frac{1}{T}\left(\frac{\partial E}{\partial V}\right)_T + \frac{P}{T}\right]_V = \frac{\partial^2 S}{\partial T \partial V}$$

Differentiation ergibt

$$\frac{1}{T}\left(\frac{\partial^2 E}{\partial V \partial T}\right) = -\frac{1}{T^2}\left(\frac{\partial E}{\partial V}\right)_T + \frac{1}{T}\left(\frac{\partial^2 E}{\partial T \partial V}\right) - \frac{1}{T^2}P + \frac{1}{T}\left(\frac{\partial P}{\partial T}\right)_V$$

somit

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

wobei (A) aus der

kalorischen Zustandsgleichung – $E = E(V, T)$

und (B) aus der

thermischen Zustandsgleichung – $P = P(V, T)$

folgen

E.2 Berechnung von $C_P - C_V$

Die Wärmekapazitäten sind gegeben durch

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = -T\left(\frac{\partial^2 F}{\partial T^2}\right)_V = -T\frac{\partial}{\partial T}\left(\frac{\partial F}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V$$

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_P = -T\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_P$$

somit

$$\begin{aligned} C_P &= T\left(\frac{\partial S}{\partial T}\right)_P = T\frac{\partial}{\partial T}\left[S(T, V(P,T))\right] = \\ &= T\left[\left(\frac{\partial S}{\partial T}\right)_V + \left(\frac{\partial S}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P\right] \end{aligned}$$

daher

$$\begin{aligned} C_P - C_V &= \left[T\left(\frac{\partial S}{\partial T}\right)_V + T\left(\frac{\partial S}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P\right] - T\left(\frac{\partial S}{\partial T}\right)_V = \\ &= T\left(\frac{\partial S}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P \end{aligned}$$

unter Verwendung der Integrabilitätsbedingung von F,

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

folgt

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

somit

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

der Faktor $(\partial P/\partial T)_V$ läßt sich nun weiter umformen:

Ausgangspunkt ist die allgemein gültige Relation

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

in der sich die 'response'-Funktionen $\alpha_P = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$ und $\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$ identifizieren lassen:

$$\underbrace{\left(\frac{\partial V}{\partial T}\right)_P}_{V\alpha_P}\left(\frac{\partial T}{\partial P}\right)_V\underbrace{\left(\frac{\partial P}{\partial V}\right)_T}_{-1/(V\kappa_T)} = -1$$

somit

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{\alpha_P}{\kappa_T}$$

insgesamt also

$$C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V\underbrace{\left(\frac{\partial V}{\partial T}\right)_P}_{V\alpha_P} = T\frac{\alpha_P}{\kappa_T}V\alpha_P = TV\frac{\alpha_P^2}{\kappa_T} > 0$$