Beispielaufgabe: Kalorische und thermische Zustandsgleichung

Wir beweisen eine einfache Relation zwischen kalorischer Zustandsgleichung $U = U(T, V)$ und thermischer Zustandsgleichung $p = p(T, V)$:

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

U in Basis (T, V): $\quad dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \quad (1)$

1. & 2. Hauptsatz: $\quad dU = T\,dS - p\,dV,$

wobei $\quad dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$

$$\Longrightarrow \quad dU = T\left(\frac{\partial S}{\partial T}\right)_V dT + \left[T\left(\frac{\partial S}{\partial V}\right)_T - p\right] dV \quad (2)$$

Koeffizientenvergleich von (1) & (2):

$$\left(\frac{\partial U}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V \quad \longrightarrow \quad \frac{\partial}{\partial V}\left(\frac{\partial U}{\partial T}\right) = T\,\frac{\partial}{\partial V}\left(\frac{\partial S}{\partial T}\right)$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - p \quad \longrightarrow \quad \frac{\partial}{\partial T}\left(\frac{\partial U}{\partial V}\right) = \frac{\partial S}{\partial V} + T\,\frac{\partial}{\partial T}\left(\frac{\partial S}{\partial V}\right) - \frac{\partial p}{\partial T}$$

$$\Longrightarrow \quad \frac{\partial S}{\partial V} = \frac{\partial p}{\partial T} \quad \longrightarrow \quad \frac{\partial p}{\partial T} = \frac{1}{T}\left(\frac{\partial U}{\partial V} + p\right)$$

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

Bsp.: ideales Gas, $pV = nRT$

$$\frac{\partial p}{\partial T} = \frac{nR}{V} \longrightarrow \left(\frac{\partial U}{\partial V}\right)_T = T\,\frac{nR}{V} - p = 0$$

Bsp.: Photonengas

Annahme: $U(T,V) = V f(T)$, $p(T,V) = \frac{1}{3} f(T)$

$$\longrightarrow \frac{\partial U}{\partial V} = f(T), \qquad \frac{\partial p}{\partial T} = \frac{1}{3}\frac{\partial f}{\partial T}$$

$$\longrightarrow f(T) = \frac{T}{3}\frac{\partial f}{\partial T} - \frac{1}{3} f(T), \qquad \text{wobei: } \frac{\partial f}{\partial T} = \frac{df}{dT}$$

$$4 f(T) = T\frac{df}{dT} \longrightarrow 4\,\frac{dT}{T} = \frac{df}{f} \longrightarrow \ln f = 4 \ln T + C$$

$$\Longrightarrow \underline{\underline{f(T) = b T^4}}, \qquad b \equiv e^C = \text{const}$$