3.28 Maxwell relations, calculation of residual functions

The residual function $\Gamma^{res}(T,p)$ of a caloric state function $\Gamma(T,p)$ is defined as the difference between the real and the ideal state function

$$\Gamma(T,p) = \Gamma^{real}(T,p) = \Gamma^{res}(T,p) + \Gamma^{ideal}(T,p) \tag{3.67}$$

The calculation of the residual function and other thermodynamic properties starts from the volume-explicit thermal equation of state $V(T,p,n)$ of a real fluid. As an example we calculate the residual entropy. Taking into account that for zero pressure all gases/fluids behave ideally and using a Maxwell relation we start with

$$S(T,0) - S^{ideal}(T,0) = 0 \qquad \left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p \qquad \left(\frac{\partial S^{ideal}}{\partial p}\right)_T = -\left(\frac{\partial V^{ideal}}{\partial T}\right)_p = -\frac{n\,R}{p} \tag{3.68}$$

Using

$$S(T,p) = S(T,0) + \int_0^p \left(\frac{\partial S}{\partial p}\right)_T dp \tag{3.69}$$

we find for the residual entropy

$$\begin{aligned} S^{res}(T,p) =&\ S(T,p) - S^{ideal}(T,p) \\ =&\ S(T,0) - S^{ideal}(T,0) + \int_0^p \left(\left(\frac{\partial S}{\partial p}\right)_T - \left(\frac{\partial S^{ideal}}{\partial p}\right)_T\right) dp \\ \Rightarrow S^{res}(T,p) =&\ \int_0^p \left(-\left(\frac{\partial V}{\partial T}\right)_p + \frac{n\,R}{p}\right) dp \end{aligned} \tag{3.70}$$

So no explicit measurements of entropies are necessary to calculate the residual entropy. The experimentally much more easily accessible $V(T,p,n)$ relation allows for the complete calculation.