

3.29 Residual functions of enthalpy and Gibbs potential

To calculate the residual function of the enthalpy $H^{res}(T, p)$ we now start with

$$H(T, 0) - H^{ideal}(T, 0) = 0 \quad \left(\frac{\partial H}{\partial p} \right)_T = V - T \left(\frac{\partial V}{\partial T} \right)_p \quad \left(\frac{\partial H^{ideal}}{\partial p} \right)_T = V^{ideal} - T \frac{nR}{p} = 0 \quad (3.71)$$

and get

$$\begin{aligned} H^{res}(T, p) &= H(T, p) - H^{ideal}(T, p) \\ &= H(T, 0) - H^{ideal}(T, 0) + \int_0^p \left(\left(\frac{\partial H}{\partial p} \right)_T - \left(\frac{\partial H^{ideal}}{\partial p} \right)_T \right) dp \\ \Rightarrow H^{res}(T, p) &= \int_0^p \left(V - T \left(\frac{\partial V}{\partial T} \right)_p \right) dp \end{aligned} \quad (3.72)$$

Combining Eq. (3.70) and Eq. (3.72) we find according to the definition of the Gibbs potential

$$\begin{aligned} G^{res}(T, p) &= H^{res}(T, p) - T S^{res}(T, p) \\ &= \int_0^p \left(V - T \left(\frac{\partial V}{\partial T} \right)_p \right) dp - T \left[\int_0^p \left(- \left(\frac{\partial V}{\partial T} \right)_p + \frac{nR}{p} \right) dp \right] \\ &= \int_0^p \left(V - \frac{nRT}{p} \right) dp \end{aligned} \quad (3.73)$$