

3.27 Maxwell relations, example for vdW gas

We now apply Maxwell relations to the equation of a vdW gas to find some astonishing parameter dependencies:

- Dependency of the entropy on the volume for a vdW gas:

$$\begin{aligned} \left(\frac{\partial S}{\partial V}\right)_T &= \left(\frac{\partial p}{\partial T}\right)_V \Rightarrow \Delta S = \int_{V_1}^{V_2} \left(\frac{\partial p}{\partial T}\right)_V dV \\ \Delta S &= \int_{V_1}^{V_2} \left[\left(\frac{\partial}{\partial T}\right)_V \left(\frac{nRT}{V-nb} - \frac{an^2}{V^2} \right) \right] dV = nR \ln \frac{V_2-nb}{V_1-nb} \end{aligned} \quad (3.65)$$

So (astonishingly) ΔS does not depend on a .

- Internal pressure π_T of a vdW gas.

We start with the total differential of $U(S, V)$:

$$\begin{aligned} \pi_T &= \left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{\partial U}{\partial S}\right)_V \left(\frac{\partial S}{\partial V}\right)_T + \left(\frac{\partial U}{\partial V}\right)_S = T \left(\frac{\partial S}{\partial V}\right)_T - p = T \left(\frac{\partial p}{\partial T}\right)_V - p \\ p &= \frac{nRT}{V-nb} - \frac{an^2}{V^2} \Rightarrow \left(\frac{\partial p}{\partial T}\right)_V = \frac{nR}{V-nb} \\ \pi_T &= \left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial p}{\partial T}\right)_V - p = \frac{nRT}{V-nb} - \left(\frac{nRT}{V-nb} - \frac{an^2}{V^2} \right) = \frac{an^2}{V^2} \end{aligned} \quad (3.66)$$

So (astonishingly) the internal pressure π_T does not depend on b .