2.14 Calculation of μ for different models

For virial coefficients as well as for the vdW-equation we will prove some quite fundamental results related to the Joule-Thomson coefficient μ. The following equation already needs results from the second law of thermodynamics, i.e. the entropy S is used as well as a Maxwell relation between mixed partial derivatives. So you may take this section as a motivation for discussing the second law, because obviously not all problems can be solved just by conservation of energy.

$$\begin{aligned} \mu &= \left(\frac{\partial T}{\partial p}\right)_H = -\frac{\left(\frac{\partial H}{\partial p}\right)_T}{\left(\frac{\partial H}{\partial T}\right)_p} \stackrel{1}{=} \frac{T\left(\frac{\partial V}{\partial T}\right)_p - V}{C_p} \stackrel{2}{=} \frac{V}{C_p}(\alpha T - 1) \\ 1 &: \quad -\left(\frac{\partial H}{\partial p}\right)_T = \left(\frac{\partial}{\partial p}\right)_T (-T\,dS - V\,dp) = -T\left(\frac{\partial S}{\partial p}\right)_T - V = T\left(\frac{\partial V}{\partial T}\right)_p - V \\ 2 &: \quad \alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \qquad \alpha\text{: expansion coefficient.} \end{aligned} \tag{2.42}$$

The expansion coefficient we discussed before in Eq. (2.6). Applying the above equation to different thermal equations of state we find

- Ideal gas

$$\mu_{ideal} = \frac{T\left(\frac{\partial V}{\partial T}\right)_p - V}{C_p} = \frac{1}{C_p}\left(\frac{n\,R\,T}{p} - V\right) = 0 \tag{2.43}$$

- Virial approach according to the Berlin form (cf. Eq. (1.10)): $V = R\,T/p + B$

$$\mu_{virial}(T) = \frac{T\left(\frac{\partial V}{\partial T}\right)_p - V}{C_p} = \frac{T\left(\frac{R}{p} + \left(\frac{\partial B}{\partial T}\right)_p\right) - \left(\frac{R\,T}{p} + B\right)}{C_p} = \frac{T\left(\frac{\partial B}{\partial T}\right)_p - B}{C_p} \tag{2.44}$$

  At the Boyle temperature T_B the virial coefficient B is zero (the gas behaves much like a perfect gas), thus $\mu(T \to T_B) = 0$.

- vdW approach with $B = b - a/(RT)$ (cf. Eq. (1.25))

$$\mu_{vdW} = \frac{T\left(\frac{\partial B}{\partial T}\right)_p - B}{C_p} = \frac{\frac{2\,a}{RT} - b}{C_p} \quad \Rightarrow \quad T_i = \frac{2\,a}{R\,b} \tag{2.45}$$

  with T_i: inversion temperature where μ changes sign.

The Joule-Thomson effect is highly relevant for cooling. Fig. 2.10 shows the Linde process for production of liquid air: The gas must be beneath its inversion temperature (examples for upper inversion temperatures: He: 35 K, H_2: 224 K, N_2: 866 K). The gas cooled by expansion cools compressed gas, further expansion could lead to liquid.

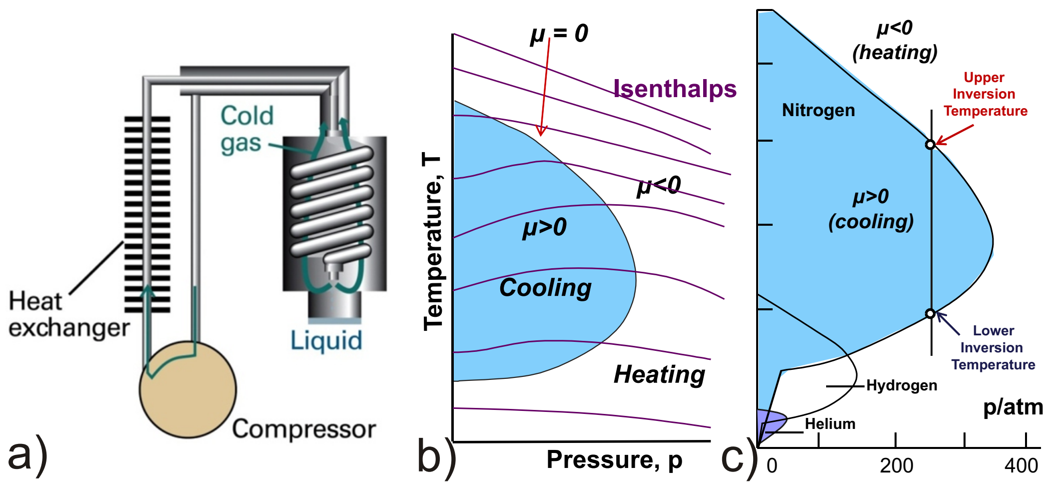

Figure 2.10: a) scheme of Linde process; b) pT diagram showing the regimes separated by $\mu = 0$; c) cooling regime for several gases.