4.6 Clapeyron's equation and application to vaporization

For the vaporization (liquid $\rightarrow$ gas) dp/dT is always positive, since ΔV is positive in any case. For the integration of Eq. (4.5) we will use three approximations:

- Approximation 1: Neglecting $V(liquid)$ we get $\Delta V = V(vapor)$.
- Approximation 2: The vapor is a perfect gas.
- Approximation 3: The T-dependence of C_p will be neglected.
- (Approximation 4): Instead of Approximation 3 sometimes Trouton's rule (cf. Eq. (3.19)) is used: $\Delta S_{vap,m} = \Delta H_{vap,m}/T = 85$ J/(mol K) is used.

$$\begin{aligned} \frac{dp}{dT} &= \frac{\Delta H_{vap,m}}{T\,\Delta V_{vap,m}} \quad \text{with} \quad \Delta V_{vap,m} \approx V_{vap,m} \approx \frac{RT}{p} \\ \Rightarrow \frac{d\ln p}{dT} &= \frac{\Delta H_{vap,m}}{RT^2} \quad \Rightarrow \quad p_2 = p_1 \exp\left[-\frac{\Delta H_{vap,m}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right] \end{aligned} \tag{4.8}$$

The last line is the Clausius-Clapeyron equation and holds for $\Delta H_{vap,m}$ to be constant.
If we instead assume Kirchoff's law, i.e. $\Delta H_{vap,m} = \Delta H^0_{vap,m} + \Delta C_p\left(T - T^0\right)$ we find

$$\begin{aligned} \frac{d\ln p}{dT} &= \frac{\Delta H^0_{vap,m} + \Delta C_p\left(T - T^0\right)}{RT^2} \\ \Rightarrow \ln p &= \left(\frac{-\Delta H^0_{vap,m} + \Delta C_p T^0}{R}\right)\frac{1}{T} + \frac{\Delta C_p}{R}\ln T + const. = \frac{A}{T} + B\ln T + C \end{aligned} \tag{4.9}$$

For many materials extended tables for the parameters A, B, and C are available.