4.5 Clapeyron's equation and application to melting

We now discuss the condition for phase equilibrium of two phases (α, β) of a pure substance. From the proof of Gibbs phase rule we learned that p, T, and $\mu = \mu^\alpha = \mu^\beta$ are the same for all phases in equilibrium. With the fundamental equation of $\mu = G_m$ (cf. Eq. (3.84) and related discussion) we get

$$-S_{\alpha,m}\,dT + V_{\alpha,m}\,dp = -S_{\beta,m}\,dT + V_{\beta,m}\,dp \quad \Rightarrow \quad \frac{dp}{dT} = \frac{\Delta S_m}{\Delta V_m} = \frac{\Delta H_m}{T\,\Delta V_m} \tag{4.4}$$

For the last equality we just used $0 = \mu^\alpha - \mu^\beta = \Delta G_m = \Delta H_m - T\Delta S_m$.
So as a fundamental rule we find that the slope of lines in the $p-T$ diagram (dp/dT) correlate with the stability of a phase, i.e. larger slope means lower stability. This can easily be understood: if the slope dp/dT is steep one can more easily (lower ΔT) switch from one phase to another one. The absolute slope values depend on the nature of the structural change.
Focusing now on the solid/liquid transition we find:

$$\frac{dp}{dT} = \frac{\Delta S_m}{\Delta V_m} = \frac{\Delta H_{melt,m}}{T\,\Delta V_{melt,m}} \tag{4.5}$$

here $\Delta V_{melt,m}$ could be positive (the usual) or negative (e.g. for water: its $\Delta V_{melt,m}$ for the MELTING process is negative (because water expands during crystallization)).
Assuming $\Delta H_{melt,m}$ and $\Delta S_{melt,m}$ to be independent from T and p we can integrate Eq. (4.5)

$$\int_{p_1}^{p_2} dp = \frac{\Delta H_{melt,m}}{\Delta V_{melt,m}} \int_{T_1}^{T_2} \frac{dT}{T} \tag{4.6}$$

Here T_1 and T_2 are the melting temperatures at p_1 and p_2. We get

$$\Delta p = \frac{\Delta H_{melt,m}}{\Delta V_{melt,m}} \ln\frac{T_2}{T_1} \approx \frac{\Delta H_{melt,m}}{\Delta V_{melt,m}} \frac{T_2 - T_1}{T_1} \quad \Rightarrow \quad p_2 = p_1 + \frac{\Delta H_{melt,m}}{T_1\,\Delta V_{melt,m}}\,(T_2 - T_1) \tag{4.7}$$

Here we used $\ln(1 + x) \approx x$ for small x. Soon we will use this result to discuss $p - T$ diagrams.