4.7 Clapeyron's equation and application to sublimation

Sublimation and vaporization have much in common, mainly $\Delta H_{sub,m}$ ($= \Delta H_{melt,m} + \Delta H_{vap,m}$) is larger than $\Delta H_{vap,m}$.
So according to

$$\frac{dp}{dT} = \frac{\Delta S_m}{\Delta V_m} = \frac{\Delta H_{sub,m}}{T\,\Delta V_{sub,m}} \tag{4.10}$$

the sublimation line in the $p-T$ diagram exhibits a larger slope. Repeating the calculation of Eq. (4.8) we find

$$p_2 = p_1 \exp\left[-\frac{\Delta H_{sub,m}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right] \tag{4.11}$$

As an example the $p-T$ diagram of CO_2 is shown in Fig. 4.3. Since the sublimation curve is always steeper than the vaporization curve an intersection between both curves is a must and a new phase line between solid and liquid is a must as well. This explains the existence of a triple point.
Now we will use this phase diagram to describe the sublimation of CO_2 when opening a CO_2 flask:

1. CO_2 in a gas flask is under high pressure, hence it is in liquid and vapor state.
2. When releasing CO_2 gas it cools by the Joule-Thompson effect thus forming solid CO_2 which appears as snow-like dry ice by so-called de-sublimation.
3. The triple point at 5.11 atm (cf. Fig. 4.3) indicates sublimation of solid CO_2 and not melting under atmospheric pressure.

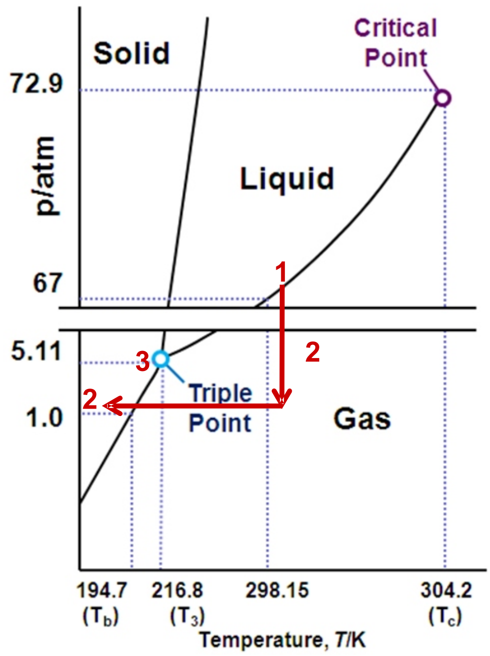

Figure 4.3: $p-T$ diagram of CO_2.