3.10 Changes of entropy with T

We will now discuss the change of entropy with temperature as illustrated in Fig. 3.8 b). Thus we have to apply successively the general Eq. (3.17). For the first-order phase transitions with constant T_{trs} we already found the mathematical solution by Eq. (3.18). To perform the integration if the changes in dH are continuous and if T is not constant we apply the heat capacity.
We get

$$\begin{aligned} S(T) = \; & S(0\,\mathrm{K}) + \int_0^{T_f} \frac{C_p(solid)}{T} dT \\ & + \frac{\Delta_{fus} H}{T_f} \\ & + \int_{T_f}^{T_b} \frac{C_p(liquid)}{T} dT \\ & + \frac{\Delta_{vap} H}{T_b} \\ & + \int_{T_b}^{T} \frac{C_p(vapor)}{T} dT \end{aligned} \tag{3.20}$$

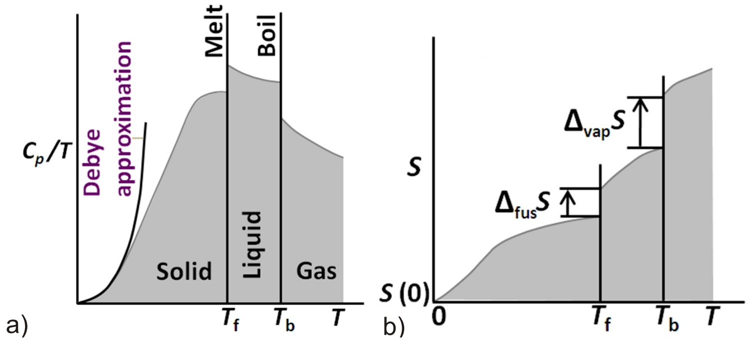

Figure 3.8: Entropy vs. T dependence: a) $C_p/T - T$ diagram; b) $S - T$ diagram.

Obviously ΔS correlates with area of the C_p/T-curve. At low T we find a solid for which we can use the Debye model to describe the heat capacity to simplify the first line in Eq. (3.20).

$$S(T) = 0 + \int_0^{T_f} \frac{aT^3}{T} dT = \frac{1}{3} a\, T_f^3 = \frac{1}{3} C_p(T_f) \tag{3.21}$$

Similarly one can describe the contribution of electrons to the heat capacity (usually assumed to be linear) leading to $S(T) = S(0\,\mathrm{K}) + C_p(T)$