3.7 Third law

We now will state fundamental laws regarding the entropy when the temperature gets close to its absolute zero, i.e. $T \to 0$ K (later on we discuss the consequences). First we have the Nernst theorem:

$$\lim_{T\to 0} \Delta S_{trans} = 0 \tag{3.14}$$

Some observations regarding the Nernst theorem:

- For $T \to 0$ K: $\Delta G \approx \Delta H$
- The DIFFERENCES of the heat capacities of educts and products of any reaction / transition goes to zero for $T \to 0$ K (e.g. rhombic and monoclinic sulfur)
- Diagrams $\Delta G/T$ and $\Delta H/T$: slope of both state functions goes zero for $T \to 0$ K

$$\begin{aligned} \Delta G_{T\to 0} = \Delta H_{T\to 0} \Rightarrow &\quad \left(\frac{\partial \Delta G}{\partial T}\right)_{p,T\to 0} = \left(\frac{\partial \Delta H}{\partial T}\right)_{p,T\to 0} \\ \Rightarrow &\quad \Delta S_{T\to 0} = \Delta C_{p,T\to 0} \end{aligned} \tag{3.15}$$

  Here we have used for the first time $(\partial G/\partial T)_p = -S$ (Guggenheim).

According to the Nernst theorem $S(T = 0)$ need not be zero!
BUT: According to the Planck theorem (= Third law),

$$\lim_{T\to 0} S = 0 \tag{3.16}$$

- "The entropy of any homogenous substance, which is in complete internal equilibrium, may be taken as zero at 0 K", e.g. if the heat capacity change goes to zero, the structure essentially remains the same; thus, entropy change = 0.
- This implies absolute values of the "third-law entropies".
- BUT: Residual entropies ($S > 0$) based on configurational contribution (disorder) may exist. A) molecules (CO), B) presence of isotopes, C) spin configurations: $S = k \ \ln(2^n)$.

The most important consequence of the third law is that $T = 0$ K can never be reached; according to Planck: "If the heat capacity goes to zero, each minimum action serves for an enhancement of T inside the sample; thus, it appears practically impossible to approach 0 K".
$S = 0$ is never fulfilled in real systems due to the intrinsic disorder of the crystals. As we will see later from the statistical approach of Boltzmann $S = 0$ means that only one configuration is possible, however real crystals contain defects. They cannot be removed at $T = 0$ because of missing thermal activation.