3.9 ΔS for first-order phase transitions

The general equation for calculating ΔS is

$$\Delta S = \int \frac{\delta q_{rev}}{T} \tag{3.17}$$

For first order phase transitions $T = const.$ while ΔH changes. Using here ΔH instead of δq implies that the pressure is kept constant. Thus we find

$$\Delta_{trs} S = \frac{\Delta_{trs} H}{T_{trs}} \quad \text{thus for an endothermic process} \quad \Delta_{trs} S > 0 \tag{3.18}$$

According to Trouton's rule the standard entropy for vaporization of liquids is

$$\Delta_{vap} S = \Delta S(gas) - \Delta S(liquid) \approx 85 \text{ J/(K mol)} \tag{3.19}$$

The main assumption for this rule is that the structures of all liquids and of all gases is roughly the same, thus, $\Delta_{vap} S$ is roughly the same. Essentially one looks at the liquid state as being less chaotic compared to vapor.

	$\Delta_{vap} H^0$ [kJ mol^{-1}]	Θ_B [°C]	$\Delta_{vap} S^0$ [kJ K^{-1} mol^{-1}]
Benzene	30.8	80.1	87.2
Carbon tetrachloride	30.0	76.7	85.8
Cyclohexane	30.1	80.7	85.1
Hydron sulfide	18.7	-60.4	87.9
Methane	8.18	-161.5	73.2
Water	40.7	100	109.1

As can be seen in the table above Trouton's rule holds for a number of liquids quite well. Water has a significantly larger value for $\Delta_{vap} S^0$ since the liquid state is more ordered than expected, thus more entropy change is found. In contrast e.g. methane shows a negative deviation since the energy in the vapor state is not as dispersed as expected (due to a low population of higher rotational energy levels for light molecules at low T).