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CHEM 3410: Physical Chemistry I — Fall 2009

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Lecture 9: Calculating Entropy Changes

References

1. Engel and Reid, *Physical Chemistry*, Sections 5.1–5.7

Key Concepts

- For a spontaneous process, the change in entropy for the universe is positive. This will lead us to the fact that entropy is maximized at equilibrium. This should make some qualitative sense now, but we'll get more quantitative soon.
- We show quantitatively using $dS_{system} = \frac{\partial q_{rev}}{T}$, that heat does indeed flow for a body at higher temperature to one at a lower temperature.
- We applied some of the quantitative relationships developed for understanding ΔU, q and w to determining entropy changes for different processes involving ideal gases. Some tricks/tips:
  - For a reversible process, $\Delta S_{univ} = 0$, so $\Delta S_{sys} = -\Delta S_{surr}$.
  - For an irreversible process connecting the same initial and final states as some reversible, the change in entropy for the system must be the same as in the reversible case. This is because entropy is a state function.
  - For calculating entropy changes for the surroundings, it is essential to use the actual heat transfered to the surroundings. S is a state function, but the surroundings end up in a different final state depending on the actual path of the process, therefore ΔS_{surr} will be different.
- To find the entropy change as a function of temperature we applied a similar approach to the one we used in thermochemistry, but instead of just integrating to find the heat flow, we integrated to find the entropy change. For example to find the entropy change upon heating n moles of a solid from T_1 to T_2 we would do the following:

  $$\Delta S_{sys} = \int_{T_1}^{T_2} \frac{\partial q_{rev}}{T} = \int_{T_1}^{T_2} \frac{nC_p dT}{T}$$

  If the heat capacity is constant, then it can be removed from the integral:

  $$nC_p \int_{T_1}^{T_2} \frac{nC_p dT}{T} = nC_p \ln \frac{T_2}{T_1}$$

  If there is a phase change, for example melting, then we have to account for the entropy change of going from the solid to liquid phase at the melting point:

  $$\Delta S_{melting} = \frac{\Delta H_{melting}}{T_{melting}}$$