

CHEM 3410: Physical Chemistry I — Fall 2009

September 21, 2009

Lecture 8: Entropy and the Second Law

References

1. Levine, *Physical Chemistry*, Sections 3.1–3.7, 5.7

Key Concepts

- The second law can be stated in several different manners, which results from the various types of systems where it has been discovered or applied.
 1. It can be thought of in terms of the direction of heat flow when two bodies are placed in contact. Heat will flow from the hot to cold body, never in the reverse direction.
 2. We can convert work to heat without any problems, but heat cannot be converted to work at 100% efficiency. There is always some dissipation when energy changes form. Another way of saying this is we cannot have perpetual motion of the “second kind”.
 3. A more practical statement of the second law is that the *entropy* of the universe (system + surroundings) must increase in any spontaneous process. Entropy remains constant in a reversible process.
- This third approach forces us to define a new thermodynamic function, entropy, given the symbol S . Entropy is a state function, which means changes for a system are completely determined by the initial and final state.
- Physically, entropy is a hard concept to get a handle on. It can be related to the number of ways a system can arrange itself, or what is called the number of microstates (Ω). The more possible equivalent microstates, the higher the entropy. This can also be thought of in terms of the probabilities of a system existing in a set of states. These two approaches form the basis for statistical thermodynamics or statistical mechanics.
- From a more macroscopic point of view, entropy is sometimes put in terms of the relative state of order or disorder of a system. The larger the disorder, the higher the entropy. From our definition of the second law, it seems then that the universe is tending towards a more disordered state.
- In mathematical terms, our third statement of the second law can be written this way for a spontaneous process:

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} > 0$$

and for a reversible process:

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} = 0$$

- In the case of a reversible process, we can write:

$$dS_{system} = \frac{\delta q_{rev}}{T}$$

This relates changes in entropy to heat flow in a reversible process.

- This definition also gives us a conjugate variable for T . Much like $-P$ and V are conjugate variables ($= PdV$), temperature and entropy are conjugate variables: TdS .
- Using a simple heat engine, or the so-called Carnot cycle, we can show that the definition of entropy above makes sense as well as entropy is a state function.

- The Carnot cycle involves a reversible cyclic process where a gas is first isothermally expanded at a high temperature (T_{hot}), then allowed to expand adiabatically as the temperature cools from T_{hot} to T_{cold} . The gas is isothermally compressed at the lower temperature (T_{cold}) and finally it is compressed adiabatically as the temperature increases from T_{cold} back to T_{hot} .

- ΔU for the cycle must be zero, since internal energy is a state function.
- We can calculate q and w for each step since we have gotten fairly good at working with the first law and applying it to ideal gases.
- We can arrive at an expression for the efficiency (ε) of an engine of this type, in terms of the temperatures (both the hot and cold temperatures). Efficiency is defined as the ratio of useful work out to the amount of heat supplied at the high temperature.

$$\varepsilon = \frac{\text{work out}}{\text{heat in}} = \frac{T_{hot} - T_{cold}}{T_{hot}} = \frac{q_{ab} + q_{cd}}{q_{ab}}$$

- This expression can be rearranged to give us something that looks remarkably like our definition of entropy:

$$\frac{q_{ab}}{T_{hot}} + \frac{q_{cd}}{T_{cold}} = 0$$

which is just ΔS for the system, and is equal to zero since the process is cyclic. It all works out!

- 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.

Related Exercises in Levine

Exercises 3.11, 3.14, 3.22