The Second Law of Thermodynamics

Chemistry CHEM 213W

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The second law of thermodynamics gives information concerning the direction of spontaneous change. If the second law says that a certain process is impossible, you will not be able to get the process to go. On the other hand, note that if the second law says that a process is possible, you still have to worry about kinetics--you have to find a way in which to carry out the process in a reasonable amount of time.

There are a number of equivalent physical statements of the second law of thermodynamics. According to Kubo (Thermodynamics, North Holland Publishing Co., 1976) they are:

1. **Clausius principle:** A process which involves no change other than the transfer of heat from a hotter body to a cooler body is irreversible; or, it is impossible for heat to transfer spontaneously from a colder to a hotter body without causing other changes.

2. **Thompson’s (or Kelvin’s) principle:** A process in which work is transformed into heat without any other changes is irreversible; or, it is impossible to convert all the heat taken from a body of uniform temperature into work without causing other changes.

3. **Impossibility of perpetual motion of the second kind:** (due to Max Planck) It is impossible to devise an engine operating in a cycle which does work by taking heat from a single heat reservoir without producing any other change.

4. **Caratheodory’s principle:** For a given thermal equilibrium state of a thermally uniform system, there exists another state which is arbitrarily close to it, but which can never be reached from it by an adiabatic change.

Any of these physical statements can be used to prove the others, and to finally prove the mathematical statement of the second law of thermodynamics:

5. There exists a state function, the entropy (denoted by the letter S) which for any spontaneous process satisfies the Clausius inequality:

\[ \Delta S \geq \int \frac{dQ}{T} \]

where the equality holds when the process is reversible.

Before showing how 1.-4. imply 5., let’s first consider how the different physical statements imply one another. For example, how does one show that Clausius’ principle implies Thompson’s? Suppose it didn’t; i.e., Clausius’s principle is correct, but Thompson’s is not. This means that you can build an engine which produces work, and which is connected to a single heat reservoir. If so, consider the following device:
where, E is the Thompson violator, and R is a Carnot refrigerator.

If we adjust the sizes of E and R such that all the work is used to run the Carnot refrigerator, and view the combined E-R apparatus as the system, we have succeeded in creating a device, which spontaneously pumps heat from cold to hot without any work input from the surroundings. This violates Clausius’ principle and thus we have proved Thompson’s principle by contradiction.

Similarly, we can use Thompson’s principle to prove Clausius’. Again, the proof is by contradiction. If Clausius’s principle is untrue, then you can find a device which spontaneously (i.e., without any work input) transfers heat from a colder body to a hotter one. Consider the following apparatus:
What is the net result after one cycle? Work has been produced in the surroundings, but there is no net change in the heat content in the cooler reservoir. Hence, it is as if the system were operating in contact with a single reservoir and producing work in the surroundings, in contradiction to Thompson’s principle.

These kind of arguments can be used to prove the equivalence of the other physical formulations of the second law.