ME 24-221
Thermodynamics I

Supplementary Notes on Entropy and the Second Law of Thermodynamics

1 Reversible Process

A reversible process is one which, having taken place, can be reversed without leaving a change in either the system or the surroundings.

2 Entropy

Consider a closed system such as a piston-cylinder assembly. Let us say that a gas is contained in the cylinder, and that it consists of our system. We take our system through a closed cycle by adding (or removing) heat. We ensure that the path is *reversible*. If we think of our cycle as consisting of a series of infinitesimally small links as shown in Figure 1, and we measure the infinitesimal heat transfer to the system in that link, δQ_i, and the temperature of our system, T_i, during that infinitesimal transfer, we can evaluate the sum:

$$\sum_{i=1}^{N} \delta Q_i / T_i$$

where *i* is the ith link, and N is the number of links. If the links were made truly infinitesimally small, we would in effect be evaluating the cyclic integral

$$\int_{cycle} \delta Q / T$$

If we did an experiment of this type, we would find that this cyclic integral would always come out to be zero. Since we know that the change in a property of a system over a closed cycle is zero , we postulate that there must exist a *property* of the system, S, such that:

$$dS = \delta Q / T \quad \text{for a reversible process} \tag{1}$$

The property S is called *Entropy*. It is an extensive property whose units are J/K. The corresponding specific property is denoted by s. Its units are J/(kg K). The temperature T appearing in Equation 1 is the absolute temperature of the system. The change in entropy between two states 1 and 2 may be evaluated using:

$$\Delta S = S_2 - S_1 = \int_1^2 \delta Q_{rev} / T \tag{2}$$

It is important to understand what Equation 2 means. Since S is a property of the system, $S_2 - S_1$ is independent of the path connecting the two points 1 and 2; it is the same for *all* paths connecting the two points as long as the end points are fixed. However, we can evaluate $S_2 - S_1$ *directly* from $\delta Q / T$ only if the path connecting the two is reversible.

3 Entropy Change for an Irreversible Process

If the path connecting points 1 and 2 is irreversible, it is found that

$$dS = \delta Q / T + dS_{gen} \tag{3}$$

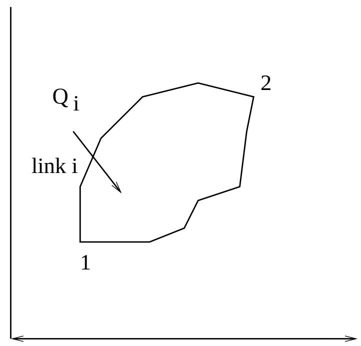

Figure 1: Cycle Integral Evaluation for Entropy

Here dS_{gen} is the entropy generated by irreversibilities such as friction, heat transfer across finite temperature differences or uncontrolled expansions, and is *always positive*. Irreversibility always increases the entropy.

The entropy change between two states 1 and 2 is given by:

$$\Delta S = S_2 - S_1 = \int_1^2 \delta Q/T + {}_1S_{2,gen} \tag{4}$$

Again, it is important to interpret Equation 4 correctly. Once the points 1 and 2 are fixed, the entropy change between them is fixed, regardless of the process connecting them. *However, this change ΔS is only equal to $\int \delta Q/T$ if the process is reversible*. If the process is irreversible, the entropy change would turn out to be *greater* than $\int \delta Q/T$ because of entropy generation due to irreversibilities. Alternatively, if we fixed $\int \delta Q/T$ for the two paths, the irreversible path would end up with a different end state than the reversible path. The end state would have a *higher* value of S_2 than the reversible path because of the extra entropy generation due to irreversibilities.

From Equation 4 we see that the entropy of a system can change because of two agents:(i) heat transfer to/from a system, and (ii) irreversibilities. Heat transfer *to* the system tends to increase its entropy; heat transfer *from* a system tends to decrease its entropy. Irreversibilities always tend to increase a system's entropy. Therefore, the entropy of a system can either increase or decrease overall; a decrease can occur if the system loses enough heat to make up for entropy increases due to irreversibilities.

Another important point is that the work done by/on the system does not appear in the entropy change expression. Work does not change the entropy directly. The doing of work may indirectly lead to friction or other irreversibilities which can generate entropy.

For an isolated system, δQ is zero. Therefore

$$dS = dS_{gen}$$

or

$$S_2 - S_1 = {}_1S_{2,gen} \geq 0 \tag{5}$$

Thus, the entropy of an isolated system can only increase (or stay the same if all processes within it are reversible). Since the universe, which is the sum of the system and its surroundings, is the ultimate isolated system, we can also say:

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} \geq 0 \tag{6}$$

This is probably the most useful operational statement of the Second Law of thermodynamics, and one which we shall use most often in our problem solving.

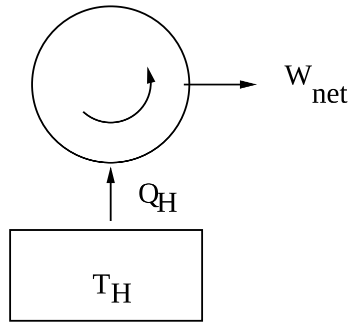

Figure 2: A Heat Engine Which Violates the Kelvin-Planck Statement

4 The Isentropic Process

Consider Equation4. If the process 1-2 is reversible, ${}_1S_{2,gen} = 0$. If the process is adiabatic, $\delta Q = 0$. Thus, for a reversible, adiabatic process, $S_2 = S_1$. Such a process is called an *isentropic* process. Remember that all reversible processes are not isentropic. Similarly, all adiabatic processes are not isentropic. It is only a reversible *and* adiabatic process which is isentropic.

5 Equivalence with the Kelvin-Planck and Clausius Statements of the Second Law

The Kelvin-Planck statement of the Second Law states:
It is impossible to construct a device that will operate in a cycle and produce no effect other than new work and the exchange of heat with a single reservoir.

Let us consider a heat engine that violates the Kelvin-Planck statement, as shown in Figure 2. Here we have a heat engine that receives Q_H at temperature T_H, and does net work W_{net}. Consider one cycle of operation. Applying the First Law and realizing that ΔE is zero in a closed cycle

$$Q_H = W_{net}$$

The total entropy change of the universe may be written as:

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_H$$

where ΔS_{system} is the entropy change of the heat engine itself and ΔS_H is the entropy change of the high-temperature reservoir. Because S is a property of the system, $\Delta S_{system} = 0$ in one complete cycle. Further, since the heat transfer occurs in an isothermal process,

$$\Delta S_H = \int \delta Q/T = \frac{1}{T_H} \int \delta Q = -\frac{Q_H}{T_H}$$

since Q_H is *removed* from the reservoir. Therefore

$$\Delta S_{universe} = 0 - \frac{Q_H}{T_H} \leq 0$$

Thus, an engine which violates the Kelvin-Planck statement of the Second Law also violates the rule that $\Delta S_{universe} \geq 0$.

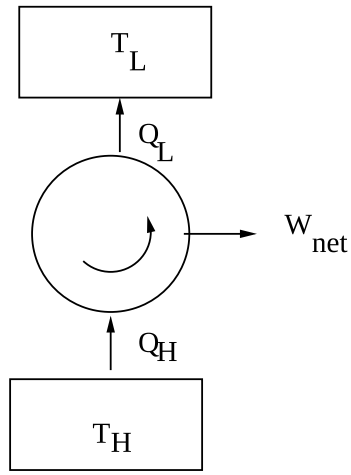

Figure 3: A Heat Engine Operating Between Two Reservoirs

Why does heat rejection Q_L to T_L fix the problem? That is, why is the engine shown in Figure 3 legal whereas the one shown in Figure 2 illegal? Consider the net entropy change of the universe for the case shown in Figure 3.

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_H + \Delta S_L$$

From the First Law, since ΔE=0 for one closed cycle of operation,

$$Q_H - Q_L = W_{net}$$

where W_{net} is the work done by the system, and is a positive number. As before, ΔS_{system} =0 in a closed cycle. Therefore

$$\begin{aligned}
\Delta S_{universe} &= 0 - \frac{Q_H}{T_H} + \frac{Q_L}{T_L} \\
&= -\frac{Q_L + W_{net}}{T_H} + \frac{Q_L}{T_L} \\
&= Q_L\left(\frac{1}{T_L} - \frac{1}{T_H}\right) - \frac{W_{net}}{T_H} \qquad (7)
\end{aligned}$$

The first term in the last equation of Equation 7 is always positive; the second term (which is itself positive) appears with a negative sign. So the sum can be negative. However, if W_{net} were small enough, we could get a net increase in entropy of the universe. Removing Q_H from T_H decreases the entropy of the universe. Adding Q_L to T_L increases it. So if we add enough Q_L to T_L to make up for the decrease due to the removal of Q_H , we can build a system for which the Second Law is not violated. It is clear we cannot do this unless there is a non-zero Q_L.

The Clausius statement of the Second Law says:

It is impossible to construct a device that operates in a cycle and produces no other effect than the transfer of heat from a cooler body to a hotter body.

That is, a heat engine of the type shown in Figure 4 is impossible.

Let us consider the entropy changes associate with an engine that violates the Clausius statement. The net entropy change

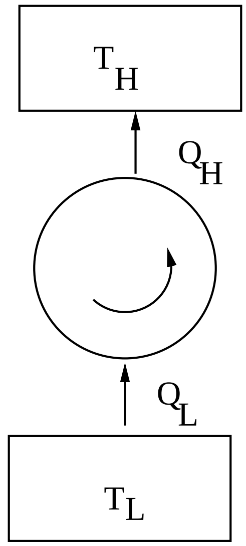

Figure 4: A Heat Engine Which Violates the Clausius Statement

of the universe for such an engine is

$$\begin{aligned}\Delta S_{universe} &= -\frac{Q_L}{T_L} + \frac{Q_H}{T_H} \\ &= Q_L\left(\frac{1}{T_H} - \frac{1}{T_L}\right)\end{aligned}$$

Since $T_L < T_H$, $\Delta S_{universe} \leq 0$. Therefore such an engine is impossible.

We see that even though we cannot prove the Kelvin-Planck or the Clausius statements of the Second Law, they are consistent with our operational statement $\Delta S_{universe} \geq 0$.

6 Heat Transfer and Irreversibility

Heat transfer between two bodies is considered reversible if it occurs across infinitesimally small temperature differences. It is irreversible if it occurs across a finite temperature difference. Let us consider the entropy changes associated with heat transfer between two bodies at T_1 and T_2 respectively, as shown in Figure 5. Here

$$\Delta S_{universe} = -\frac{Q}{T_1} + \frac{Q}{T_2}$$

If $T_1 = T_2$ (i.e. the heat transfer is across infinitesimally small differences in temperature), $\Delta S_{universe} = 0$. That is, the heat transfer is reversible. If $T_1 > T_2$, $\Delta S_{universe} > 0$. So heat transfer from a hot body to a cold one causes a net increase in the entropy of the universe. If $T_1 < T_2$, $\Delta S_{universe} < 0$. This is, of course, impossible.

7 The Carnot Cycle and Entropy Change

Consider the Carnot cycle shown in Figure 3. Recall that the Carnot cycle is a reversible cycle which involves four reversible processes:

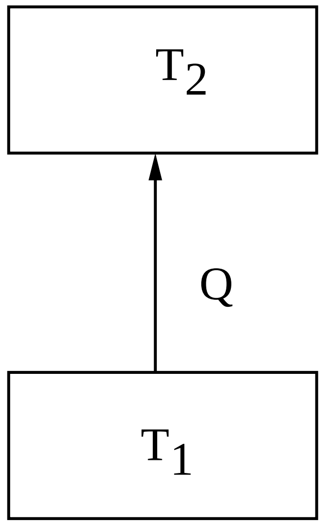

Figure 5: Heat Transfer Between Reservoirs T_1 and T_2

- 1-2 : Isothermal expansion due to heat addition Q_H from a high temperature reservoir at T_H.
- 2-3: Adiabatic expansion.
- 3-4: Isothermal compression due to heat loss Q_L to a low temperature reservoir at T_L.
- 4-1: Adiabatic compression.

Consider one closed cycle of operation. The entropy change of the universe is given by:

$$\begin{aligned} \Delta S_{universe} &= \Delta S_{system} + \Delta S_H + \Delta S_L \\ &= 0 - \frac{Q_H}{T_H} + \frac{Q_L}{T_L} \end{aligned}$$

The universe is an isolated system, so it is adiabatic. Since the Carnot cycle is reversible and all the heat transfer interactions are reversible, all processes in the universe are reversible. So the universe undergoes a reversible, adiabatic process, i.e., an isentropic process:

$$\Delta S_{universe} = 0$$

Therefore

$$\frac{Q_H}{T_H} = \frac{Q_L}{T_L}$$

Recall that we had assumed this relationship in deriving the thermal efficiency of the Carnot cycle in terms of temperature. It is valid as long as the cycle is reversible, and the heat addition and heat rejection happen isothermally at T_H and T_L respectively.