The Second Law of Thermodynamics

April 24, 2012
Chapter 20
Chapter Overview

- This chapter will deal with the definition and discussion of *reversible* and *irreversible* thermodynamic processes.
  - Examples, what characterizes them,…
- We will be able to understand these processes within the framework of the 2nd Law of Thermodynamics and the introduction of the concept of *Entropy*.
- Lastly, with the help of the 2nd Law, we will be able to study the ultimate efficiencies of various types of heat engines and power plants.
Heat Engine

Q is positive when it enters the working substance. Q is negative when leaving the working substance.

We can define the efficiency of an engine in the following way:

\[ e = \frac{W}{Q_H} \]
\[ = \frac{(Q_H + Q_C)}{Q_H} \]
\[ = 1 - \left| \frac{Q_C}{Q_H} \right| \]
Refrigerators

Evaporator

Condenser

Compressor

Outside air at temperature $T_H$

$|Q_H|$

$|W|$

Inside of refrigerator at temperature $T_C$

$Q_C$
Coefficient of Performance

\[ K = \frac{|Q_c|}{|W|} = \frac{|Q_c|}{(|Q_H| - |Q_C|)} \]

Note for a refrigerator both \( W \) and \( Q_H \) are negative and \( Q_C \) is positive.
2nd Law of Thermodynamics

- It is impossible for any system to undergo a process in which it absorbs heat from a reservoir at a single temperature and converts the heat completely into mechanical work, with the system ending in the same state in which it began. (Kelvin-Planck)

- It is impossible for any process to have as its sole result the transfer of heat from a cooler to a hotter body. (Clausius)

- These both point to the inherent one-way aspect of many thermodynamic processes (irreversible processes).
2nd Law examples

(a) If a workless refrigerator existed, it could be used to make a 100% efficient engine.

(b) If a 100% efficient engine existed, it could be used to make a workless refrigerator.
Carnot posited that the maximum heat engine efficiency would happen only when the heat engine avoided ALL irreversible processes. Thus, his cycle allowed only isothermal and adiabatic steps.
The Carnot Cycle

- Step 1- The gas expands isothermally at $T_H$ absorbing heat $Q_H$.
- Step 2- The gas expands adiabatically until its temperature drops to $T_C$.
- Step 3- The gas is now compressed isothermally at $T_C$ rejecting heat $|Q_C|$.
- Step 4- Finally the gas is compressed adiabatically back to its initial state at temperature $T_H$. 
Carnot Refrigerator

- Run the Carnot Heat Engine in Reverse, since it is a chain of reversible steps.
Carnot Cycle and the 2nd Law

No engine can be more efficient than a Carnot Engine operating between the same two temperatures.
Entropy and the 2\textsuperscript{nd} Law

- Entropy is a quantitative measure of the disorder of a system.

\[ dS = \frac{dQ}{T} \] (for an infinitesimal reversible process)

\[ \Delta S = S_2 - S_1 = \frac{Q}{T} \] (for a reversible isothermal process)
The total entropy change during any reversible cycle is zero. As a result we conclude that the entropy of a system is independent of the path taken to get it to that state.
Entropy and the 2nd Law

- No process is possible in which the total entropy decreases, when all systems taking part in the process are included.

\[ \Delta S \geq 0 \]
The Microscopic Interpretation of Entropy

For any system, the most probable macroscopic state is the one with the greatest number of corresponding microscopic states, which is the macroscopic state with the greatest disorder and therefore the greatest entropy.

\[ S = k \ln w \] (where \( w \) is the number of possible microscopic states for a given macroscopic state).

<table>
<thead>
<tr>
<th>Macroscopic state</th>
<th>Corresponding microscopic states</th>
</tr>
</thead>
<tbody>
<tr>
<td>Four heads</td>
<td><img src="image1" alt="Four heads" /></td>
</tr>
<tr>
<td>Three heads, one tails</td>
<td><img src="image2" alt="Three heads, one tails" /></td>
</tr>
<tr>
<td>Two heads, two tails</td>
<td><img src="image3" alt="Two heads, two tails" /></td>
</tr>
<tr>
<td>One head, three tails</td>
<td><img src="image4" alt="One head, three tails" /></td>
</tr>
<tr>
<td>Four tails</td>
<td><img src="image5" alt="Four tails" /></td>
</tr>
</tbody>
</table>

Image credit: Pearson Education, Inc., publishing as Addison Wesley.