Lecture 18

Introduction to 2nd Law and Entropy
Example

Consider an adiabatic compressor steadily moving R125,

\[ P_2 = 430 \text{ psia} \]
\[ T_2 = 138^\circ\text{F} \]

\[ P_1 = 5 \text{ psia} \]
\[ T_1 = 100^\circ\text{F} \]
\[ m = 0.15 \text{ lbm/s} \]

\[ -\dot{W} + m(h_1 - h_2) = 0 \quad \rightarrow \quad \dot{W} = m(h_1 - h_2) \]

\[ \dot{W} = \left(0.15 \frac{\text{lbm}}{\text{s}}\right)(160.22 - 150.09) \frac{\text{Btu}}{\text{lbm}} \left(\frac{3600 \text{ s}}{\text{hr}}\right) \left(\frac{\text{hp-hr}}{2545 \text{ Btu}}\right) = 2.15 \text{ hp} \]

**Really?** A compressor that compresses a refrigerant and delivers power? Can I invest my money in this idea?
The Second Law of Thermodynamics

Before you invest in the contraption on the previous slide, recall the Second Law of Thermodynamics.

Energy can only be transformed. The transformation of energy always proceeds from a condition of very useful energy to less useful energy.

The Second Law dictates how energy can be transformed.

Conclusions with the compressor example …

- **The First Law analysis is correct!**
  - The First Law is an energy book keeper
- **The Second Law is not being obeyed!**
  - The Second Law is the energy transformation police
What is Entropy?

• A thermodynamic property
  – Total entropy = $S$ (upper case letter)
  – Specific entropy = $s$ (lower case letter)

• An indication of molecular disorder
  – High values = high molecular disorder
    • Gases
  – Low values = low molecular disorder
    • Solids

• A quantity that can be produced but not destroyed within a system undergoing a process
  – Entropy is not a conserved quantity!
What is Entropy?

• Entropy is produced in a process by virtue of irreversibilities
  – mechanical friction, fluid friction, heat transfer, mixing, electrical resistance, chemical reactions ...

• Irreversibilities are present in all real-world systems and processes

• Reversible processes
  – Free of entropy production
  – Do not exist – they are idealizations

• The Third Law of Thermodynamics
  – The entropy of a perfect crystalline substance at absolute zero is zero!
    • Provides a universal datum state for entropy
The Second Law Pioneers

Sadi Carnot (1786-1832)

William Thomson (Lord Kelvin) (1824-1907)

William Rankine (1820-1872)

Rudolph Clausius (1822-1888)

Carnot Cycles

\[
\left( \frac{Q_H}{Q_L} \right)_{rev} = \frac{T_H}{T_L}
\]

Defined Entropy
The Kelvin-Planck Statement

It is impossible to construct a device that operates in a thermodynamic cycle and delivers a net amount of energy as work to its surroundings while receiving energy by heat from a single reservoir.

Implication: No heat engine can ever operate with an energy conversion efficiency of 100%.
Carnot’s Heat Engine

Carnot hypothesized ...

- The energy conversion (thermal) efficiency of an irreversible heat engine is always less than the thermal efficiency of a reversible heat engine operating between the same thermal energy reservoirs
- Reversible engines operating between the same thermal energy reservoirs have the same thermal efficiency
  - The reversible engine is not dependent on the working fluid
Analysis of the Carnot Heat Engine

Kelvin and Rankine suggested that,

\[
\left( \frac{|Q_{out}|}{Q_{in}} \right)_{rev} = \frac{T_L}{T_H}
\]

Temperatures must be on the absolute scale!

Therefore, the thermal efficiency of a Carnot Heat Engine is,

\[
\eta_{th,\text{Carnot}} = 1 - \frac{T_L}{T_H}
\]

This is the maximum efficiency of a heat engine!
The Clausius Statement

It is impossible for any system to operate in such a way that the energy transfer by heat from a cooler body to a hotter body occurs without the input of work.

\[
\begin{align*}
\text{Cold} & \quad Q \quad \text{System} \\
\text{Hot} & \quad Q
\end{align*}
\]

This is impossible!
Carnot’s Refrigerator

Carnot hypothesized ...

- The thermal efficiency of an irreversible refrigerator is always less than the thermal efficiency of a reversible refrigerator operating between the same thermal energy reservoirs.
- Reversible refrigerators operating between the same thermal energy reservoirs have the same thermal efficiency.
  - The reversible refrigerator is not dependent on the working fluid.
Analysis of the Carnot Refrigerator

For the Refrigeration cycle ...

\[ \eta_{th} = \text{COP}_R = \frac{Q_{in}}{|W_{cycle}|} = \frac{Q_{in}}{|Q_{out} - Q_{in}|} = \frac{1}{|Q_{out}| / |Q_{in}| - 1} \]

\[ \text{COP}_{R,\text{Carnot}} = \frac{1}{\left(|Q_{out}| / |Q_{in}|\right)_{rev} - 1} = \frac{1}{T_H / T_L - 1} \]

\[ \text{COP}_{R,\text{Carnot}} = \frac{T_L}{T_H - T_L} \]

For the Heat Pump cycle ...

\[ \eta_{th} = \text{COP}_H = \frac{Q_{out}}{|W_{cycle}|} = \frac{Q_{out}}{|Q_{out} - Q_{in}|} = \frac{1}{1 - Q_{in} / |Q_{out}|} \]

\[ \text{COP}_{H,\text{Carnot}} = \frac{1}{1 - \left(Q_{in} / |Q_{out}|\right)_{rev}} = \frac{1}{1 - T_L / T_H} \]

\[ \text{COP}_{H,\text{Carnot}} = \frac{T_H}{T_H - T_L} \]
My colleagues, Kelvin and Rankine, have proposed that for a Carnot heat engine,

\[
\left( \frac{Q_H}{|Q_L|} \right)_{rev} = \frac{T_H}{T_L}
\]

I can rewrite this expression as,

\[
\frac{Q_{H,rev}}{T_H} = \frac{Q_{L,rev}}{T_L}
\]

An alternative way to write this is,

\[
\frac{Q_{H,rev}}{T_H} - \frac{Q_{L,rev}}{T_L} = 0
\]
I have to remember that these expressions have been developed for a Carnot cycle. Since we are considering a cycle that is reversible, it must be true that,

\[
\int \left( \frac{\bar{d}Q}{T} \right)_{\text{rev}} = \frac{Q_{H,\text{rev}}}{T_H} - \frac{Q_{L,\text{rev}}}{T_L} = 0
\]

I know that if the cyclic integral of a differential quantity is zero, the quantity must be a property. Therefore, it must be true that,

\[
\left( \frac{\bar{d}Q}{T} \right)_{\text{rev}} \quad \text{is the differential of a property!}
\]
I know that $dQ$ is not a property, but $(\overline{dQ} / T)$ for a reversible process is a property! Since I discovered this property, I choose to call it entropy and give it the symbol, $S$. Therefore,

$$dS = \left( \frac{\delta Q}{T} \right)_{\text{rev}}$$

In 1865, Clausius wrote,

“We might call $S$ the transformational content of the body, just as we have termed the quantity $U$ the heat and work content of the body. But since I believe it is better to borrow terms for important quantities from the ancient languages so that they may be adopted unchanged in all modern languages, I propose to call the quantity $S$ the entropy of the body, from the Greek $\eta$ тροπη, meaning a transformation.”
The Inequality of Clausius

Clausius demonstrated that for a closed reversible process,

\[ dS = \left( \frac{\delta Q}{T} \right)_{\text{rev}} \]

It can be shown that for a closed irreversible process (Sec 7.7)

\[ dS > \left( \frac{\delta Q}{T} \right) \]

Therefore, for any closed process,

\[ dS \geq \left( \frac{\delta Q}{T} \right) \]

This is known as the Inequality of Clausius