Introduction to Chemical Engineering Thermodynamics

Chapter 5
Thermodynamics is concerned with transformations of energy

First law tells you that energy is conserved but second law imposes restrictions on the process direction.

There is a difference between heat and work: (1) work is readily transformed into other forms of energy such as potential or kinetic energy (2) complete heat conversion into mechanical energy has failed. Cannot have conversion efficiencies superior to 40%.
Second law:

(1) cannot convert heat absorbed by system completely into work done by the system.

(2) cannot have a process where there is solely a transfer of heat from a cold body to a hot body.

(3) it is impossible by a cyclic process to convert heat absorbed by the system completely into work done by the system.
Second law does not prohibit product of work from heat. It only sets some restriction on how much of the heat can be converted into work.

We talk about an efficiency of conversion.
Heat engine: produces work from heat in a cyclic process

- Liquid water pumped into a boiler at high pressure

- Heat of combustion of a fuel converts water into high temperature steam

- Energy is transferred as shaft work in a turbine

- Exhaust steam is condensed and liquid water return to the boiler
\[ |W| = |Q_H| - |Q_C| \]

\[ \eta = \frac{|W|}{|Q_H|} = 1 - \frac{|Q_C|}{|Q_H|} \]

Cannot be equal to 100%
a-b adiabatic compression T rises from $T_C$ to $T_H$

b-c isothermal expansion with absorption of heat $Q_H$

c-d adiabatic expansion until $T_C$

d-a isothermal compression to initial state rejection of heat $Q_C$

**Figure 5.3:** $PV$ diagram showing Carnot cycle for an ideal gas.
Carnot cycle is reversible and maximum value for the efficiency is 0.5 based on $T_H=600$ K and $T_C=300$ K for actual heat engines efficiencies rarely exceed 0.35
change of entropy of any system undergoing a finite reversible process

\[ \Delta S = \int \frac{dQ_{\text{rev}}}{T} \]
\[
\frac{\Delta S}{R} = \int_{T_0}^{T} \frac{C_P^{ig}}{R} \frac{dT}{T} - \ln \left( \frac{P}{P_0} \right)
\]

textentropy change of an ideal gas derived for a mechanically reversible process but can use it for any process since S is a state function
Mean heat capacity defined as follows:

\[
\int_{T_0}^{T} C_P^i g \, \frac{dT}{R} \frac{dT}{T} = \frac{\langle C_P^i g \rangle}{R} \ln \left( \frac{T}{T_0} \right)
\]

\[
\frac{\Delta S}{R} = \frac{\langle C_P^i g \rangle}{R} \ln \left( \frac{T}{T_0} \right) - \ln \left( \frac{P}{P_0} \right)
\]