Thermodynamic Principles of Energy Conversion

What is Thermodynamics?

Thermodynamics is the study of the effects of work, heat, and energy on a system. Thermodynamics is only concerned with large scale observations.

- Zeroth Law: Thermodynamic Equilibrium and Temperature
- First Law: Work, Heat, and Energy
- Second Law: Entropy

Ideal Carnot Cycle

$p-V$ diagram

$T = 300$ K

$T = 200$ K

$W = Q_1 - Q_2$

$V = Volume$

$p = pressure$

$T = Temperature$

$W = Work$
Forms of Energy:
1. Potential energy = the energy that is stored in an object due to its position relative to some zero position.
2. Kinetic energy = the energy a body has because it is moving.

\[ \text{PE} \equiv -\int_{0}^{r} F(r) \, dr \quad \text{and} \quad \text{KE} \equiv \frac{1}{2}MV^2 \]

\[ E \equiv \text{KE} + \text{PE} = \text{constant} \quad \text{(principle of conservation of energy)} \]

3. Internal energy = \( U = \) sum of the energy of atoms and molecules
4. Chemical Energy = new molecular species formed = \( E_{\text{chem}} \)
5. Nuclear Energy = formation of new atomic nuclei = \( E_{\text{nuc}} \)
6. Electric Energy = electric dipole moment = \( E_{\text{el}} \)
7. Magnetic Energy = magnetic dipole moment = \( E_{\text{mag}} \)

Total energy of a material body

\[ E \equiv KE + PE + U + E_{\text{chem}} + E_{\text{nuc}} + E_{\text{el}} + E_{\text{mag}} \]

In any practical process only a few of these terms are significant.

First Law of Thermodynamics – for an isolated system \( E = \) constant.

Changes in internal energy = heat transferred into the system minus work done by the system.
The Second Law of Thermodynamics

In a CLOSED system:

\[ \Delta S \geq 0 \]

- \( = \): reversible process
- \( > \): irreversible process

There exists a useful thermodynamic variable called entropy (S). A natural process that starts in one equilibrium state and ends in another will go in the direction that causes the entropy of the system plus the environment to increase for an irreversible process and to remain constant for a reversible process.

\[ S_2 - S_1 \quad \text{(reversible)} \]
\[ S_2 > S_1 \quad \text{(irreversible)} \]
Thermodynamic properties (1)

• Intensive properties – they are the same everywhere in the system. Pressure (p) and Temperature (T) are intensive variables.

• Extensive properties – vary with the mass of the substance. Energy (E), volume (V), and entropy (S) are extensive variables.

• Extensive properties can be divided by the mass (M) of the system to produce specific properties which are independent of mass.

  Specific energy: \( e \equiv E/M \)
  Specific volume: \( v \equiv V/M \)
  Specific entropy: \( s \equiv S/M \)

• Enthalpy (h) = total heat content of a system.

  \( h \equiv e + pv \)
  \( de = dh - pdv \) (constant pressure process. 1\(^{st}\) Law \( E = Q - W \))
  \( de = dq - pdv \) (\( q \) = amount of heat added to system)

  At constant pressure: \( dq = de + pdv \)
  At constant volume: \( dq = de \) (\( pdv = 0 \), no change in volume)
Thermodynamic properties (2)

• Heat capacity – the amount of heat required to raise the temperature of one kilogram of a substance by 1°C. In SI units heat capacity is equal to joules per kilogram.

• Calorie = the amount of heat energy required to raise one gram of water from 14.5°C to 15.5°C ≡ 4.184 J/g

• Heat capacity at constant pressure (C_{p}) versus heat capacity at constant volume (C_{v}).

• Free energy - Helmholtz free energy is the maximum amount of work a system can do a constant volume and temperature while the Gibbs free energy is the maximum amount of work a system can do at constant pressure and temperature.

\[ f \equiv h - Ts = e + pv - Ts \]
\[ df = dh - sdT \]

• Steady flow – mass flow rate (\dot{m}) is invariant with time

\[ \dot{m} \ h_{\text{out}} = \dot{m} \ h_{\text{in}} + \dot{Q} - \dot{W} \quad (\text{first law}) \]
\[ h_{\text{out}} = h_{\text{in}} = q - w \quad (\text{where } q \equiv \frac{\dot{Q}}{\dot{m}} \text{ and } w = \frac{\dot{W}}{\dot{m}}) \]
Heat transfer and heat exchange – consider the exchange of heat energy between two environments – one hot and the other cold.

\[
\dot{Q} = UA(T_h - T_c)
\]

\(\dot{Q}\) = rate of heat transfer

\(U\) = heat transfer coefficient = \(W/(m^2 \cdot K)\) \(\Delta T\)

\(A\) = surface area of the material that separates the two environments

\((T_h - T_c)\) is the temperature difference between the two environments

Why do we care? If we are trying to maximize the flow of heat to the working fluid we need to maximize \(\dot{Q}\).
Ideal Heat Engine Cycles

In a cyclic process the heat energy can be provided from the external environment or internally. A coal-fired power plant which heats water to form steam that drives a turbine is an example of an external combustion system. Gas turbines and automobile engines derive their energy internally, hence they are called Internal Combustion Engines (ICE).

Thermodynamic efficiency = $\eta_{th} \equiv w/q$ (This is what we want to maximize)
The Carnot cycle - the ideal case of the conversion of heat energy to mechanical work in which the heat transfers occurs across infinitesimally small temperature differences and the adiabatic steps have zero energy transfer. The processes is reversible.

$$\eta_{\text{th}} \equiv \frac{w}{q} = 1 - \frac{T_c}{T_h}$$

The efficiency of the ideal heat engine only depends on the difference in temperature between the hot and cold reservoirs.

The net work is the area enclosed by the cycle path.

$$w = \int p \, dv = \int T \, ds$$
Rankine cycle – external combustion system that generates steam to drive a turbine.

**The Simple Ideal Rankine Cycle**

Steps in Rankine cycle
1. Ambient temperature water pumped to high pressure and injected into a boiler
2. Water heated to boiling point
3. Water completely turned into steam
4. Heated further to a higher temperature
5. Steam flows through a turbine and generates mechanical power. There is a reduction in pressure
6. The low pressure steam leaving the turbine is cooled to an ambient temperature liquid.
7. Pumped back into boiler completing the cycle

\[ w_t = h_1 - h_2 = \Delta h = v \Delta p \]

A high-pressure high-temperature steam cycle is one in which steam \( t \) and \( p \) exceed the critical point of water. One can also superheat the steam to increase the efficiency. The thermodynamic efficiency for the Rankine cycle is between 30 – 45%
Otto Cycle – closed cycle versus the open Rankine cycle. Energy is generated internally through the combustion of a fuel. The process is considered to be adiabatic.

$$n_{th} = 1 - \frac{1}{(v_e/v_c)c_p}1$$

$v_c$ = volume after compression stroke and $v_e$ = volume after expansion.

Ideal efficiency ≈ 44%
Real efficiency ≈ 28%
Energy Processing: First and Second Law Constraints

First Law: \( h_{out} - h_{in} = q - w \)

Second Law: \( f_{out} - f_{in} = q - w - T(S_{out} - S_{in}) \)

\[ T(S_{out} - S_{in}) \geq q \]

\[ w \leq f_{out} - f_{in} \]

Fuel Heating Value (FHV) = amount of heat released during the combustion process starting with the fuel at 25°C.

\( \text{HHV} = \text{return to 150°C} \quad \text{LHV} = \text{return to 25°C} \)

\[ \dot{m}_f = \frac{P}{\eta_f (FHV)} \]

\( \dot{m}_f \) = fuel mass consumption rate of an engine.

P = power output

\( \eta_f \) = fuel efficiency = ratio of the work produced to the heating value of the fuel consumed.

**Fuel (Thermal) Efficiencies of Current Power Technologies**

<table>
<thead>
<tr>
<th>Type</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steam electric power plant</td>
<td></td>
</tr>
<tr>
<td>Steam at 62 bar, 480°C</td>
<td>30</td>
</tr>
<tr>
<td>Steam at 310 bar, 560°C</td>
<td>42</td>
</tr>
<tr>
<td>Nuclear Power plant</td>
<td></td>
</tr>
<tr>
<td>Steam at 70 bar, 286°C</td>
<td>33</td>
</tr>
<tr>
<td>Automotive gasoline engine</td>
<td>25</td>
</tr>
<tr>
<td>Automotive diesel engine</td>
<td>35</td>
</tr>
<tr>
<td>Gas turbine electric power plant</td>
<td>30</td>
</tr>
<tr>
<td>Combined cycle electric power plant</td>
<td>43</td>
</tr>
<tr>
<td>Fuel cell electric power</td>
<td>45</td>
</tr>
</tbody>
</table>