1. Second Law of Thermodynamics

The first law describes how the state of a system changes in response to work it performs and heat absorbed. The second law deals with direction of thermodynamic processes and the efficiency with which they occur. It also underlies the stability of thermodynamic equilibrium.

The second law was discovered through the study of engines. There are two equivalent formulations of the second law of thermodynamics, and are both useful in understanding the conversion of thermal energy to mechanical energy.

*Kelvin form:* It is impossible to construct a cyclic engine that converts thermal energy from a body into an equivalent amount of mechanical work without a further change in its surroundings. In an engine that takes thermal energy from a thermal reservoir cyclically and converts that energy to work, the additional effect is typically a heat flow from the engine into its lower-temperature surroundings.

The second form is: *The Clausius form:* It is impossible to construct a cyclic engine whose only effect is to transfer thermal energy from a colder body to a hotter body.

1a. The Carnot Cycle

Consider a process comprised of two isothermal legs and two adiabatic legs. If executed reversibly, this process describes a Carnot Cycle.

i. Leg 1-2 The leg from 1 to 2 is isothermal expansion at temperature $T_{12}$ so $\Delta u_{12} = 0$. Heat absorbed during this leg is:

\[
q_{12} = w_{12} = \int_1^2 p \, d\alpha = RT_{12} \ln \frac{\alpha_2}{\alpha_1}
\]
ii. Leg 2-3 Adiabatic, so \( q_{23} = 0 \). and

\[
-w_{23} = \Delta u_{23} = c_v(T_{34} - T_{12})
\]

iii. Leg 3-4 The leg from 3 to 4 is isothermal compression at temperature \( T_{34} \) so

\[
q_{34} = w_{34} = RT_{34} \ln \frac{\alpha_4}{\alpha_3}
\]

iv. Leg 4-1 Adiabatic, so \( q_{41} = 0 \). and

\[
w_{41} = \Delta u_{41} = c_v(T_{12} - T_{34})
\]

During the two adiabatic legs, the work cancels and \( dq = 0 \). The work and heat transfer over the cycle follow from the isothermal legs alone. We can relate the specific volumes to the changes in temperature along the adiabatic legs using Poisson’s identity:

\[
\frac{T_{12}}{T_{34}} = \left( \frac{\alpha_3}{\alpha_2} \right)^{\gamma-1}
\]

so

\[
\frac{\alpha_2}{\alpha_1} = \frac{\alpha_3}{\alpha_4}
\]

The heat transferred during the isothermal legs yields

\[
\int dq = RT_{12} ln \frac{\alpha_2}{\alpha_1} + RT_{34} ln \frac{\alpha_4}{\alpha_3}
\]

\[
= R(T_{12} - T_{34}) ln \frac{\alpha_2}{\alpha_1}
\]

If \( T_{12} > T_{34} \) if \( \alpha_2 > \alpha_1 \) then

\[
\int p \alpha = \int dq > 0
\]
The system performs net work which is converted from heat absorbed during the cycle. The Carnot cycle is a paradigm of a heat engine. Heat must be absorbed at high temperature $T_{12}$ during isothermal expansion, and rejected at low temperatures $T_{34}$ during isothermal compression. More heat is absorbed at high temperature than is rejected at low temperature. The first law then implies that net heat absorbed during the cycle is balanced by net work performed by the system.

If the preceding cycle is executed in reverse, the system constitutes a refrigerator. The net work and heat transfer over the cycle are proportional to the temperature difference between the heat source and heat sink. Not all of the heat absorbed by the system during expansion is converted into work, some of that heat is rejected during compression - therefore the efficiency of a heat engine is limited - even for a reversible cycle.

v. Efficiency is a measure of what fraction of the heat flow from the hotter thermal reservoir (such as burning fuel) is converted into work. If the work done in one complete cycle is $w$, then we define efficiency $\eta$ as the ratio of the work done to the total positive heat flow supplied: $q_h$. If a Carnot engine absorbing $q_h$ units of heat from a hot reservoir at a temperature $T_h$ and rejecting $q_c$ units of heat from the system to a cold reservoir at a temperature $T_c$ has an efficiency $\eta$

$$\eta = \frac{w}{q_h}$$

(9)

the first law states that $du = dq - pd\alpha$, for the two isothermal legs $0 = q_h - q_c - w$, so the efficiency is

$$\eta = \frac{q_h - q_c}{q_h} = 1 - \frac{q_c}{q_h}$$

(10)

For the Carnot Engine:

$$q_h = w_{12}$$

(11)

$$q_c = -w_{34}$$

(12)

The minus sign because we have defined $q_c$ as the heat flow from the system to the reservoir whereas in the first law the heat flow is from the thermal reservoir to the system.
\[ \eta = 1 - \frac{q_c}{q_h} \quad (13) \]
\[ = 1 - \frac{w_{34}}{w_{12}} \quad (14) \]
\[ = 1 + \frac{RT_{34} \ln \alpha_4}{RT_{12} \ln \alpha_1} \quad (15) \]
\[ = 1 - \frac{RT_{34} \ln \alpha_4}{RT_{12} \ln \alpha_1} \quad (16) \]

Because the ratio of the volumes is the same the **Efficiency of any Carnot Cycle** is:

\[ \eta = 1 - \frac{T_{34}}{T_{12}} \quad (17) \]

This means that for a Carnot engine to be efficient, the temperatures of the two reservoirs should be quite different from one another. If \( T_c \) were to be zero, the efficiency would be 1, for this reason a perfectly efficient Carnot engine is not possible.

1. All Carnot cycles that operate between the same two temperatures have the same efficiency.
2. The Carnot engine is the most efficient engine possible that operates between any two given temperatures

**1b. Entropy and the Second Law**

The second law of thermodynamics is inspired by the observation that the quantity \( q/T \) is independent of path under reversible conditions. This allows the introduction of the state variable **entropy**.

For a Carnot cycle, we have shown that \( q_c/q_h = T_c/T_h \), this relation can be expressed as:

\[ \frac{-q_c}{T_c} + \frac{q_h}{T_h} = 0 \quad (18) \]
Remember that $q_c$ is the heat flow from the carnot engine to the cold thermal reservoir, so $-q_c$ is the heat flow to the engine at the cold temperature. This means that for a Carnot cycle $\sum_i \frac{q_i}{T_i} = 0$ where $i$ labels the steps and we always regard the heat flows as the heat flow to the engine.

Let’s make this more general, consider the integral $\int_A^B \frac{dq}{T}$ on a $p-V$ diagram, then:

$$\int_A^B \frac{dq}{T} = \int_A^B \frac{du + pd\alpha}{T} = \int_A^B \frac{c_v dT}{T} + \int_A^B \frac{R d\alpha}{\alpha}$$

$$= (c_v \ln T_B + R \ln \alpha_B) - (c_v \ln T_A + R \ln \alpha_A)$$  \hspace{1cm} (19)

This implies that the value of the integral depends only on the initial and final values on the variables, and not on the path along which the integral is evaluated. This implies that there is a state function $s$ which, like the internal energy $u$, depends only on the state of the gas, and not on how it reached that state. This state function is called the entropy of the system. It is defined by:

$$s(B) - s(A) = \int_A^B \frac{dq}{T}$$

$$= c_v \ln \frac{T_B}{T_A} + R \ln \frac{\alpha_B}{\alpha_A}$$

This immediately leads to the generalization that for a reversible cycle:

$$\oint \frac{dq}{T} = 0$$  \hspace{1cm} (21)

Remember that this result is valid over a cycle i.e. a closed path. This result is known as Clausius’ theorem. Another way to express this is as:

$$ds = \frac{dq}{T}$$

Entropy Change for a Reversible Process
Reversible and Irreversible Processes

Reversible Process  Idealized process for which the system can be restored to its initial state without leaving a net influence on the system or its environment.

Natural Process  Proceeds freely, where the system can be out of equilibrium and cannot be reversed entirely without leaving a net influence on either the system or its environment. The natural process is inherently “irreversible”.

1. A gas acted on by a piston maintained at a constant temperature (through contact with heat reservoir.

2. Gas expands isothermally from state 1 to state 2.

3. Gas is restored to state 1 through isothermal compression.

i. Reversible Process  If this process is executed very slowly without friction $p_s$ is uniform and equals the pressure exerted by the piston. Work performed by the system during expansion:

$$ w_{12} = \int_{1}^{2} p_{p} d\alpha $$

$$ = \int_{1}^{2} \frac{RT_{12}}{\alpha} d\alpha $$

$$ = RT_{12} \ln \frac{\alpha_2}{\alpha_1} $$

The work performed during compression:

$$ -w_{21} = -\int_{2}^{1} p_{p} d\alpha $$

$$ = RT_{12} \ln \frac{\alpha_2}{\alpha_1} $$

Consequently, the work performed on the system vanishes and because $du = 0$ for this isothermal process,

$$ \oint dq = \oint p d\alpha = 0 $$
Heat absorbed is zero and system and environment are restored to their original states. The process is entirely reversible.

ii. Irreversible Process However, if the process is executed rapidly and \( p_s \) is not able to adjust to \( p_p \), \( \Delta u \) vanishes, so:

\[
\oint dq = \oint p d\alpha < 0 
\]  

Net work is performed on the system, which must be compensated by a rejection of heat to the environment. Reversibility minimizes the work that must be performed on a system and maximizes the work that is performed by the system.

1d. How Entropy Changes for Irreversible or Spontaneous Processes

Irreversible processes (e.g. processes with friction) lead to increased inefficiency in any otherwise reversible engine. Efficiency for any system is:

\[
\eta = 1 - \frac{q_{rejected}}{q_{absorbed}}
\]  

Efficiency is reduced if if the heat flow to the system is reduced, or the algebraic sum of the heat flows into the system to decrease. But this is exactly the effect of irreversibilities that occur anywhere along the cycle. For example in a car, there is additional heat flow out due to the heating of the pistons and other parts of the engine. We can say that for an irreversible cycle

\[
\oint \frac{dq}{T} < 0
\]  

This is known as Clausius inequality. We can also combine the equations:

\[
\oint \frac{dq}{T} \leq 0
\]  

\[
ds \geq \frac{dq}{T}
\]  

Generalized Entropy Change for a Reversible (equality holds) and Irreversible (inequality holds) Process

This is perhaps the most common form of the Second Law of Thermodynamics.
Now consider the cycle in which leg 1-2 is irreversible and leg 2-1 is reversible

$$ 0 > \oint \frac{dq}{T} = \int_1^2 \frac{dq}{T} + \int_2^1 \frac{dq}{T} $$  \hspace{1cm} (31) 

Since the first term is $s_A - s_B$, then

$$ s_B - s_A > \int_A^B \frac{dq}{T} $$  \hspace{1cm} (32) 

**The difference in entropy between two points is greater than the integral of $dq/T$ over an irreversible change.**

**i. What does this mean for the efficiency of an engine?** The process must satisfy the entropy formulations of the second law:

$$ -\frac{q_h}{T_h} + \frac{q_c}{T_c} \geq 0 $$  \hspace{1cm} (33)

$$ \frac{q_c}{q_h} \geq \frac{T_c}{T_h} $$

This leads to:

$$ \eta \leq 1 - \frac{T_c}{T_h} $$  \hspace{1cm} (34) 

The equality applies for the reversible Carnot cycle. For cycles with irreversibility the inequality sign holds. Thus, the entropy formulation of the second law implies that the Carnot engine is the most efficient type of engine.

**ii. The Entropy of an Isolated System Never Decreases** In any reversible adiabatic process the change in entropy is zero. If there is no heat flow, but irreversibility, $\Delta s > 0$. (like a free gas expansion in an isolated container). Spontaneous processes in an isolated system increase the system's entropy. For this reason, for an isolated thermal system **the state of maximum entropy is the state of stable equilibrium.**
1e. Restricted Forms of the Second Law

For certain processes, the change of entropy implied by the second law is simplified. For an adiabatic process

\[ ds_{ad} \geq 0 \]  

(35)

For a reversible adiabatic process \( ds = 0 \), this process is isentropic.

For an isochoric process, wherein expansion work vanishes, the first law transforms into:

\[ ds_\alpha = c_v \left( \frac{dT}{T} \right)_\alpha \]  

(36)

This actually holds whether the process is reversible or irreversible.

We can conclude that changes in entropy follow from:

1. Irreversible work (only increases \( s \))
2. Heat transfer (can increase or decrease \( s \))
If. Calculations of Entropy Change

\[
\begin{align*}
    ds & = \frac{dq}{T} \text{ reversible} \quad (37) \\
    ds & > \frac{dq}{T} \text{ irreversible} \quad (38)
\end{align*}
\]

HOWEVER, \( s \) is a state variable and only depends on endpoints. \( \Delta s_{\text{irrev}} \) can be found by devising a series of reversible transformations.

Reversible processes

Reversible Adiabatic Process \( dq_{\text{rev}} = 0, \Delta s = 0 \)

Reversible Phase Change at constant \( T \) and \( p \) \( \Delta s = \frac{1}{T} \int dq_{\text{rev}} = \frac{q_{\text{rev}}}{T} = \frac{l}{T} \).

Where \( l \) is the latent heat. We can also do it for extensive properties (depend on mass) \( \Delta S = \frac{ln}{m} m \) is the mass.

Reversible Change of State for Ideal Gas \( dq_{\text{rev}} = du + dw = c_v dT + pd\alpha \)

consequently, \( ds = \frac{dq_{\text{rev}}}{T} = c_v dlnT + R dln\alpha \)

\( \Delta s = c_v ln(T_2/T_1) + R ln(\alpha_2/\alpha_1) \) or for extensive properties \( \Delta S = mc_v ln(T_2/T_1) + nR*ln(\alpha_2/\alpha_1) \) where the first term is the temperature term and the second term is the volume term.

Reversible Constant Pressure Heating \( dq_{\text{rev}} = c_p dT - \alpha dp \) (second term cancels)

consequently \( \Delta s = c_p ln(T_2/T_1) \) or \( \Delta S = mc_p ln(T_2/T_1) \)

Irreversible processes

Irreversible change of state of an ideal gas from \( p_1, T_1, \alpha_1 \) to \( p_2, T_2, \alpha_2 \). We can break this down into two processes

1. slow expansion to \( \alpha_2 \) at constant \( T_1 = \Delta s_1 \)
2. heat to \( T_2 \) at constant \( \alpha_2 = \Delta s_2 \)

\( \Delta S = \Delta S_1 + \Delta S_2 = nR*ln(\alpha_2/\alpha_1) + mc_v ln(T_2/T_1) \)

Irreversible phase change (such as supercooled water turning into ice. It is irreversible because intermediate states consist of mixtures of ice and water that are not at equilibrium - as it would have to be at 0C. Also because a small amount of heat will not cause the ice at temperatures less that 0C to turn into water at less than 0C). We can break this down into three processes.
1. Isobaric heating of water \[ \Delta S = m c_p(\text{water}) \ln(T_2/T_1). \]

2. Phase change under constant \( p \) and \( T \). \[ \Delta S = \frac{L_{fm}}{T} \]

3. Isobaric cooling of ice \[ \Delta S = m c_p(\text{ice}) \ln(T_2/T_1) \]

**1g. Adiabats as Isentropes**

If a process is adiabatic, \( d\theta = 0 \) and \( ds \geq 0 \). The entropy remains constant or it can increase through irreversible work (associated with frictional dissipation of kinetic energy). In the case of an air parcel, the conditions for adiabatic behavior are closely related to those for reversibility. Adiabatic behavior excludes turbulent mixing and irreversible expansion work, consequently the conditions for adiabatic behavior are equal to conditions of isentropic behavior. Under these circumstances potential temperature surfaces \( \theta = \text{constant} \) coincide with isentropic surfaces \( s = \text{constant} \).

**i. Diabatic conditions** which imply a change of potential temperature proportional to the heat absorbed by an air parcel.

Using the potential temperature definition

\[ d\ln \theta - d\ln T = -\kappa dp \]  \hspace{1cm} (39)

Using the first law

\[ d\ln T - \kappa d\ln p = \frac{dq}{c_p T} \]  \hspace{1cm} (40)

So

\[ d\ln \theta = \frac{dq}{c_p T} \]  \hspace{1cm} (41)

Since \( ds \geq dq/T \)

\[ d\ln \theta \leq \frac{ds}{c_p} \]  \hspace{1cm} (42)

\[ d\ln \theta = \frac{ds}{c_p} \]  \hspace{1cm} (43)

Last equality because it involves only state variables and the equality must hold irrespective of whether or not the process is reversible.
This means that the change in potential temperature is directly related to the change in entropy.

1h. *The Fundamental Relations*

Substituting the second law into the two forms of the first law leads to:

\[
\begin{align*}
\text{du} & \leq Tds - pd\alpha \\
\text{dh} & \leq Tds + \alpha dp
\end{align*}
\]

(44) \hspace{2cm} (45)

(46)

For a reversible process these lead to

\[
\begin{align*}
\text{du} &= Tds - pd\alpha \\
\text{dh} &= Tds + \alpha dp
\end{align*}
\]

(47) \hspace{2cm} (48)

(49)

It is convenient to introduce a new state variable the *Gibbs function* \((g)\) defined by:

\[
g = h - Ts = u + pv - Ts
\]

(50)

In terms of this variable the fundamental relations become:

\[
\begin{align*}
\text{dg} &= -sdT + \alpha dp
\end{align*}
\]

(51)