Chapter 5: The 2\textsuperscript{nd} Law of Thermodynamics

An Introduction

This 1000 hp engine photo is courtesy of Bugatti automobiles.
ENGINEERING CONTEXT

The presentation to this point has considered thermodynamic analysis using the conservation of mass and conservation of energy principles together with property relations. In Chaps. 2 through 4 these fundamentals are applied to increasingly complex situations. The conservation principles do not always suffice, however, and often the second law of thermodynamics is also required for thermodynamic analysis.

The **objective** of this chapter is to introduce the second law of thermodynamics. A number of deductions that may be called corollaries of the second law are also considered, including performance limits for thermodynamic cycles. The current presentation provides the basis for subsequent developments involving the second law in Chaps. 6 and 7.
Objectives:

(1) Motivate the need for and usefulness of the second law

(2) Introduce statements of the second law as point of departure for applications of second law
Motivating the Second Law

Every day experience teaches us that there is a definite or preferred direction for *Spontaneous* processes.

We know that some processes just do NOT occur “by themselves”

This is the basis for a law of nature- the Second Law of Thermodynamics

Let’s look at some examples
Warm objects spontaneously tend to cool

Is energy conserved? (i.e. is 1\textsuperscript{st} Law observed?)

What forms of energy are involved and how are they conserved?
Can the process be reversed *Spontaneously*? [ Would body in equilibrium at ambient temp heat up while environment cools? ]

Can the process be reversed at all?
Fluids move from higher to lower pressure environments spontaneously.

Is energy conserved? (i.e. is 1st Law observed?)

What forms of energy are involved and how are they conserved?
Can the process be reversed *Spontaneously*?

Can the process be reversed at all?
Objects spontaneously fall from elevated positions

Is energy conserved? (i.e. is 1st Law observed?)

What forms of energy are involved and how are they conserved?
Can the process be reversed *Spontaneously*?

Can the process be reversed at all?
Spontaneous Processes

Objects spontaneously tend to cool

Fluids move from higher to lower pressure environments spontaneously

Objects spontaneously fall from elevated positions

Spontaneous processes occur in a predictable direction, and have the potential to produce work
Restoration Processes

- **Refrigerator to cool environment**
- **Pump to force fluid into container**
- **Motor to raise weight**

*Work from auxiliary device required to restore initial condition of system. Permanent change in environment required. Not REVERSIBLE*
1st Law is not sufficient: energy conservation obeyed in all cases

Energy balance not enough to predict direction of processes

For simple, example processes- direction can be predicted

More complex processes where experience lacking or uncertain
- Direction more difficult to predict
- Guiding principle would be helpful
- Second Law provides this
When left to themselves, systems tend to undergo spontaneous changes and approach equilibrium state internally and with environment.

Equilibrium state may be achieved rapidly or slowly.

Conservation of energy always obeyed, but it doesn’t determine direction or final, equilibrium state.

Another principle required: 2nd Law.
Opportunities for Developing Work

Use $\Delta T$ to produce work

$W_{\text{cycle}} = Q_{\text{in}} - Q_{\text{out}}$
Opportunities for Developing Work

Use $\Delta P$ to produce work

Atmospheric air at $p_0$

Valve

Air at $p_i > p_0$

Flow in

Flow out

Air at $p_0 < p < p_i$

Air at $p_0$
Opportunities for Developing Work

Use $\Delta PE$ to produce work
Summary

When imbalance (non-equilibrium) between two systems exists, there is opportunity to extract work.

Opportunity is lost if systems come to equilibrium in an uncontrolled manner.

Given opportunity to extract work, 2 questions can be posed:

What is the theoretical maximum amount of work that could be extracted?

What are the factors that would preclude realizing maximum work?
Example of Ocean Temperature Differences producing work. How much is produced compared to maximum amount?

http://en.wikipedia.org/wiki/Ocean_thermal_energy_conversion

View of a land based OTEC facility at Keahole Pointe on Kona coast of Hawaii.

US Gov. - Department of Energy
Ocean thermal energy conversion, or OTEC, is a way to generate electricity using the temperature difference of seawater at different depths. Nearly all energy utilised by humans originates from some form of cyclic heat engine. A heat engine is placed between a high temperature reservoir and a low temperature reservoir. As heat flows from one to the other, the engine extracts some of the heat in the form of work.

The oceans, which constitute some 70% of the earth's surface area, contain enormous thermal reservoirs that vary in temperature. They are a huge storage unit of the solar input. This, if economically tapped on a large scale, could be a solution to some of the human population's energy problems. The energy extraction potential is one or two orders of magnitude higher than other ocean energy options.
OTEC utilizes the temperature difference that exists between the surface waters heated by the sun and the colder deep (up to 1000 m) waters to run a heat engine. This source and sink provides a temperature difference of 20°C in ocean areas within 20° of the equator. These conditions exist in tropical coastal areas, roughly between the Tropic of Capricorn and the Tropic of Cancer. Such a small temperature difference makes energy extraction difficult and expensive. Hence typically OTEC systems have an overall efficiency of only 1 to 3 %.
Experience suggests that maximum work extraction is a reality since capacity to produce unlimited amount of work would mean no energy concerns/crisis.

Experience also tells us about factors such as friction that limit potential to produce maximum amount of work.

Second Law allows:

- Defining quantitatively the maximum amount of work that can be produced.
- Quantifying the factors responsible for not attaining the maximum.
The Many Uses of the 2nd Law

• Predict process direction
• Establish equilibrium conditions
• Determine theoretical best performance
• Evaluate factors limiting best performance

• Define a temperature scale independent of properties or choice of substance
• Develop means for property evaluation for derived properties, such as $h$ and $u$
Statements of the 2\textsuperscript{nd} Law

\textbf{Clausius Statement:}

It is impossible for any system to operate in such a way that the sole result would be an energy transfer by heat from a cooler to a hotter body.

Implies that can’t have refrigerator operating without work input.
Thermal Reservoir:

Idealization of a system that remains at fixed temperature even when energy is added or removed (OK for energy content to change)

Idealization that can be approximated in reality in several ways:

1) Large systems (earth’s atmosphere, large lake, large metal block, etc)
2) Two phase system (evaporating water, condensing water, etc)
Statements of the 2nd Law

Kelvin-Planck Statement:

It is impossible for any system to operate in a thermodynamic cycle and deliver a net amount of energy by work to its surroundings while receiving energy from a single thermal reservoir.

In such a case, all Q converted to W.

Work can be produced from energy exchange with 2 reservoirs, but then not all Q from high temperature converted to Work.
1\text{st} \text{ Law OK:}

\[ Q_{\text{cycle}} = W_{\text{cycle}} \]

Cycle work could be Positive, negative or zero

Kelvin-Planck says that \( W_{\text{cycle}} \) can not be positive for energy exchange with single reservoir

Analytical form of Kelvin-Planck statement of Second Law:

\[ W_{\text{cycle}} \leq 0 \quad \oint W \leq 0 \]
Less than zero for presence of internal Irreversibilities

Equal to zero for absence of internal Irreversibilities

Concept of Irreversibilities introduced in Section 5.2
Equivalence of Clasius and Kelvin-Planck statements can be shown
Identifying Irreversibilities

One of most important engineering uses of 2\textsuperscript{nd} Law is determining best theoretical performance of systems

Comparison of actual with maximum provides insight into how much improvement can be realized

Maximum performance is associated with Idealized Systems

Actual processes are associated with Irreversibilities that limit performance

Recognizing sources of irreversibility is important
Process is **Irreversible** if system and ALL parts of the environment **CANNOT** be restored exactly to initial states after process is complete.

Process is **Reversible** if system and ALL parts of the environment **CAN** be restored exactly to initial states after process is complete.

System that has undergone **Irreversible** process **CANNOT** be restored to initial state, but it would be impossible to also restore environment to its initial state.

2\(^{nd}\) Law can be used to determine whether a process is **Reversible** or **Irreversible**.

Irreversible processes include one or more of following attributes:
Irreversibilities

- Heat transfer through a **finite** temperature difference
- Unrestrained expansion of a gas or liquid
- Spontaneous chemical reaction
- Spontaneous mixing
- Friction (sliding and flow)
- Electric current flow through a resistance
- Magnetization or polarization with hysteresis
- Inelastic deformation
- And many more …
Irreversible Processes

1 → 2 Reversible

1 → 2 Irreversible
Accounting for Irrev. in Engr. Thermo
Fundamental Characteristic of **Irreversible** Processes:

Gradients/differences in properties are involved

- Finite temperature difference
- Finite pressure difference
- Finite concentration difference

Fundamental Characteristic of **Reversible** Processes:

No gradients/differences in properties are involved

- Equilibrium (static)
- Quasi-equilibrium (quasi-static)
Distinction Between Internal and External Irreversibility

Internal: Irreversibility exists IN SYSTEM

External: Irreversibility exists IN ENVIRONMENT

Distinction somewhat arbitrary since it is a function of boundary location

Engineers should recognize irreversibilities, evaluate influence and develop means to minimize
Irreversibilities are “necessary” or tolerated in some systems

Example:

Brakes rely on friction to stop vehicles

Why are brakes irreversible? What happens to energy forms? What could have happened to energy forms?

Note that “real” processes often rapid and involve large gradients

Rapid acceleration, large temperature differences, explosions, combustion, etc

Tolerate these- otherwise too costly, too inconvenient
Example

Heat transfer between two bodies at different temperatures

Expect this to be irreversible – Why?

Could approach reversible heat transfer by reducing temperature difference

Would require long time or large area or both
Note temperature gradient within the system (small block)

=> Internal Irreversibility

Minimize Irreversibility

Is it worth it?

Can we tolerate this?
Irreversibility present in process can be demonstrated by applying Kelvin-Planck statement of 2\textsuperscript{nd} Law

(1) Assume a way to return system and surroundings to their respective initial states
(2) Show that to do so would be equivalent to devising a cycle that produces work with NO other effect than receiving heat from single heat reservoir

In most cases this procedure is cumbersome and better approach is to use concept of entropy production (to be developed)
Want to show that this process is Irreversible

System is the Green block

Assume no heat transfer occurs

No work is done ON surroundings
1\textsuperscript{st} Law for Closed System

\[ Q = \Delta E + W \]

\[ (U_f - U_i) + mg(z_f - z_i) + (KE_f - KE_i) = Q - W \]

Friction converts decrease in PE to increase in Internal Energy (Temperature)
Consider reversing this sliding process.

Block falls and warms.

Block cools and rises.
Use Kelvin-Planck to show this is Irreversible process

Assume processes to return system and environment back to respective initial states- produce a cycle

Show that net result of cycle is equivalent to Kelvin-Planck statement of Second Law

Then show that all processes in cycle except one being tested are possible/reversible

Thus, process tested is impossible/irreversible
Cycle Formed Of 3 Processes

- Process 1 (to be tested)
- Process 2
- Process 3

Heat Reservoir

Initial State, 1

Heat OUT
Work IN

W_{out} > 0

State 2

Extract Work, \( \Delta PE < 0 \)

Heat Transfer In, \( \Delta U > 0 \)

Initial State restored
Note that the net result of this cycle is: $Q_{\text{cycle}} \text{ IN and } W_{\text{cycle}} \text{ OUT}

Which Kelvin-Planck says is IMPOSSIBLE
Both of these processes we added to complete the cycle are possible (and can be made reversible).

Thus, “test” process is impossible.

Extract Work from $\Delta PE$ (No friction)

Heat Transfer to Increase $U$

Heat Reservoir
Reversible Processes

Reversible processes are idealizations

Nothing is reversible, but can be approached

• Frictionless pendulum
  What energy forms are being converted?

• Adiabatic compression and expansion of gas in frictionless piston-cylinder system

Work done ON system (compression exactly balances

Work done BY system (expansion)
Irreversible processes have Irreversibilities IN the system and/or IN the environment.

**Internally Reversible** process have no Irreversibilities IN the SYSTEM. May be Irreversibilities in Surroundings. This represents **External Irreversibilities**.

Internally reversible process: all intermediate states, all Intensive properties (T, P, u, etc) are uniform throughout system.

System is almost at equilibrium: Quasi-equilibrium, Quasi-static.
Internally reversible process: all intermediate states, all intensive properties (T, P, u, etc) are uniform throughout system

Pressure distribution for compression AND expansion

Pressure distribution for compression

Pressure distribution for expansion

Net Work for Cycle in each case?
What factors determine whether quasi-equilibrium is OK?

Velocity of Piston

compared to:

Speed of sound (propagation velocity of pressure pulse/wave)

This is for Mechanical considerations (Pressure)

What about Thermal (Temperature) or Chemical (Concentration)?
This course emphasizes Quasi-Equilibrium Processes:

- Rates of Heat Transfer, $\dot{Q}$, are NOT related to $\Delta T$
- Rates of mass flow, $\dot{m}$, are NOT related to $\Delta P$

Heat Transfer (AME432) relates $\dot{Q}$ to $\Delta T$
and allows quantification of temperature gradients
and differences within systems of interest

Similarly, Fluid Mechanics (AME331) relates mass flows
to pressure gradients and differences
Applying the Second Law to Thermodynamic Cycles

Important applications of second law related to power cycles and refrigeration and heat pump cycles are presented

• Further our understanding of implications of second law

• Provide basis for important deductions from second law in subsequent sections
Power Cycles (Heat Engines)

\[ W_{\text{cycle}} = Q_H - Q_C \]

Note: If \( Q_C = 0 \), \( W_{\text{cycle}} = Q_H \)

\[ \eta = 1.0 \]

Thermal efficiency would be 100%

Not allowed by Kelvin-Planck

Thus, Thermal efficiency of ALL Power cycles < 100%
Power Cycles (Heat Engines)

Thermal efficiency of ALL Power cycles < 100%

To arrive at this conclusion it was NOT necessary to:

1) Identify substance used in engine (steam, etc)
2) Specify series of processes in cycle
3) Indicate whether processes are actual or idealized
Carnot Corollaries

- Thermal efficiency of IRREVERSIBLE power cycle is ALWAYS less than thermal efficiency of REVERSIBLE power cycle when each operates between same two thermal reservoirs

\[ \eta_{\text{Rev}} > \eta_{\text{Irrev}} \]

- ALL REVERSIBLE power cycles operating between same two thermal reservoirs have the same thermal efficiency

\[ \eta_{\text{Rev}} = \eta_{\text{Rev}} \]
Refrigeration and Heat Pump Cycles

Second Law places limits on performance of devices which pump thermal energy “uphill” - as it does for power cycles

Refrigeration and Heat Pumps
Refrigeration and Heat Pump Cycles

Coefficients of Performance: Desired Result/Cost

**Refrigeration**

\[
\beta = \frac{Q_C}{W_{cycle}} = \frac{Q_C}{Q_H - Q_C}
\]

**Heat Pump**

\[
\gamma = \frac{Q_H}{W_{cycle}} = \frac{Q_H}{Q_H - Q_C}
\]
Carnot Corollaries for Refrigeration and Heat Pumps

• Coefficient of performance of IRREVERSIBLE refrigeration cycle is ALWAYS less than coefficient of performance of REVERSIBLE refrigeration cycle when each operates between same two thermal reservoirs

• ALL REVERSIBLE refrigeration cycles operating between same two thermal reservoirs have the same coefficient of performance

Can substitute “heat pump” for “refrigeration cycle”
Defining the Kelvin Temperature Scale

2nd Corrollary: ALL REVERSIBLE refrigeration cycles operating between same two thermal reservoirs have the same coefficient of performance (efficiency)

Work of cycle, $W_{\text{cycle}}$, is related to Heat Transfers, $Q_H$ and $Q_C$. But Heat Transfers are related to Temperatures of thermal reservoirs, $T_H$ and $T_C$.

Thus, reasonable to assume that the ratio of heat transfers is related to the thermal reservoir temperatures

$$\frac{Q_C}{Q_H} = \psi(T_C, T_H)$$
Defining the Kelvin Temperature Scale

Many choices possible for the function $\psi$

Here a very simple choice is made:

$$\psi = \frac{T_C}{T_H}$$

In which case the ratio of temperatures is directly related to the ratio of heat transfers for a reversible cycle

$$\left( \frac{Q_C}{Q_H} \right)_{\text{rev.cycle}} = \frac{T_C}{T_H}$$
Defining the Kelvin Temperature Scale

Choose Reference temperature to be 273.16 K at Triple Point (TP) of water (i.e. known and convenient state in lab)

All other temperatures directly related to this reference and the ratio of heat transfers for a reversible cycle

\[ T = 273.16 \left( \frac{Q}{Q_{TP}} \right)_{\text{rev.cycle}} \]

Independent of substances- a conceptual viewpoint with imaginary device operating in a reversible cycle. Q’s could be measured.

Q’s must be positive.
Lowest possible temperature is 0 K as Q \( \rightarrow \) 0
## International Temperature Scale

<table>
<thead>
<tr>
<th>Number</th>
<th>$T_{90}/K$</th>
<th>$t_{90}/^\circ C$</th>
<th>Substance$^a$</th>
<th>State$^b$</th>
<th>$W_r(T_{90})$</th>
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<tr>
<td>1</td>
<td>3 to 5</td>
<td>-270.15 to -268.15</td>
<td>He</td>
<td>V</td>
<td>Vapor Pressure Pt</td>
</tr>
<tr>
<td>2</td>
<td>13.8033</td>
<td>-259.3467</td>
<td>e-H$_2$</td>
<td>T</td>
<td>Triple Pt</td>
</tr>
<tr>
<td>3</td>
<td>$\sim$17</td>
<td>$\sim$-256.15</td>
<td>e-H$_2$ (or He)</td>
<td>V (or G)</td>
<td>Vapor Pressure Pt</td>
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<tr>
<td>4</td>
<td>$\sim$20.3</td>
<td>$\sim$-252.85</td>
<td>e-H$_2$ (or He)</td>
<td>V (or G)</td>
<td>Vapor Pressure Pt</td>
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<tr>
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http://www.omega.com/techref/intltemp.html
Recall Heat Engine, Refrigerator and Heat Pump Performance Coefficients in terms of $Q, s$ as basis for expressing Performance Coefficients in terms of temperatures of thermal reservoirs.
Power

\[ \eta = \frac{W_{\text{cycle}}}{Q_{\text{in}}} = \frac{Q_{\text{in}} - Q_{\text{out}}}{Q_{\text{in}}} \]

Refrigeration

\[ \gamma = \frac{Q_{\text{out}}}{W_{\text{cycle}}} = \frac{Q_{\text{out}}}{Q_{\text{out}} - Q_{\text{in}}} \]

Heat Pump

\[ \beta = \frac{Q_{\text{in}}}{W_{\text{cycle}}} = \frac{Q_{\text{in}}}{Q_{\text{out}} - Q_{\text{in}}} \]
Maximum Performance: Heat Engines

Since:
\[ \eta = \frac{W_{cycle}}{Q_H} = 1 - \frac{Q_L}{Q_H} \]

Carnot efficiency
\[ \eta_{max} = \eta_{Carnot} = 1 - \frac{T_C}{T_H} \]

And:
\[ \frac{Q_L}{Q_H} = \frac{T_L}{T_H} \]

For \( T_C = 298 \) K
Maximum Performance: Refrigerators

\[ \beta = \frac{Q_{in}}{W_{cycle}} = \frac{Q_{in}}{Q_{out} - Q_{in}} \]

\[ \beta_{\text{max}} = \frac{T_C}{T_H - T_C} \]
Maximum Performance: Heat Pumps

\[ \gamma = \frac{Q_{\text{out}}}{W_{\text{cycle}}} = \frac{Q_{\text{out}}}{Q_{\text{out}} - Q_{\text{in}}} \]

\[ \gamma_{\text{max}} = \frac{T_H}{T_H - T_C} \]
Examples

Example 5.1 Evaluating Power Cycle Performance Claim
Example 5.2 Evaluating Refrigerator Performance
Example 5.3 Evaluating Heat Pump Performance
Carnot Cycle

Carnot Cycle is specific example of reversible power cycle operating between two thermal reservoirs

Two other examples in Chapter 9: Ericsson and Sterling

All of these idealized cycles exhibit Carnot efficiency
Carnot Cycle

Reversible power cycle:
Two adiabatic processes alternated with two isothermal processes

Note where Qs occur on diagram
Carnot Cycle

For processes 1-2 & 3-4 to be reversible, requires quasi-static

For processes 2-3 & 4-1 to be reversible, requires $\Delta T \to 0$
Carnot Cycle: General & Specific

\[ W_{\text{cycle}} = Q_H - Q_C \]

General

Specific Realization

\[ \eta = \frac{W_{\text{cycle}}}{Q_H} = 1 - \frac{Q_L}{Q_H} \]
Evaluation of Work

Work done **BY** system for **process** i to j:

\[
W_{ij} = \int_{V_i}^{V_j} P \, dV
\]

Work done **BY** system for **cycle**:

\[
W_{\text{cycle}} = \oint P \, dV
\]

Work per unit mass (specific work) done **BY** system:

\[
w = \frac{W}{m}
\]
Carnot Cycle

Work considerations

Net Work OUT is produced
Carnot cycles can be devised with other “working” substances and other reversible processes

We just examined closed system of a gas as working substance in piston-cylinder assembly.

Now let’s consider overall system of water as working substance flowing through series of open components.
1-2: Work OUT during expansion through turbine. Pressure drops

2-3: Water condensed during flow through condenser, $Q_C$ OUT to cold reservoir

3-4: Work IN to pump water to high pressure in boiler

4-1: Water evaporated during flow through boiler, $Q_H$ IN from hot reservoir
Carnot Cycle: General & Specific

General

Specific Realization

\[ W_{\text{cycle}} = Q_H - Q_C \]

\[ \eta = \frac{W_{\text{cycle}}}{Q_H} = 1 - \frac{Q_L}{Q_H} \]

\[ \eta_{\text{Carnot}} = 1 - \frac{T_L}{T_H} \]
States for Carnot Vapor Power Cycle

Note 2 isothermal processes (reversible)
Note 2 adiabatic processes (reversible)
Carnot Cycle

Carnot power cycles operated in reverse may be regarded as a reversible Refrigeration or Heat Pump cycle, with maximum coefficient of performance.

Reversible power cycle:
Two adiabatic processes alternated with two isothermal processes

Note: Work done ON system to refrigerate
Carnot Cycle: Refrigeration

Reverse the processes in the power cycle: Still two adiabatic processes alternated with two isothermal processes.
Carnot Cycle: Refrigeration
Carnot Cycle: Refrigeration

How would the states change?
What components would be used?
What working substance should be used?
END