Chapter 16

Thermodynamics
Another area of physics is **thermodynamics**.

Continues with the principle of conservation of energy.

Will investigate rules that govern the flow of heat and exchange of other forms of energy.

Will deal with many types of systems.

Will be interested in fundamental limits on how heat can flow from one system to another.
Exchanges of Energy

- Quantities used to describe systems
  - Temperature
  - Pressure
  - Volume
- These are used to describe systems and their interactions
Properties of Systems

- Systems of many particles can be described by macroscopic quantities.
- Two systems are in the same state if their macroscopic properties are the same.
  - The microscopic properties are not identical.

Two systems are in the same state if their macroscopic properties are the same.
Interactions

• One system may be much larger than the other
• The larger system is often referred to as the environment
• Interactions generally involve forces and the transfer of energy
Laws

- Thermodynamics is based on a small set of physical laws
- There are four laws
- When the laws are put together, they yield remarkable results
  - One result includes fundamental limits on what is and is not possible
Zeroth Law

- The zeroth law is a statement about the concept of temperature.
- The zeroth law states: *If two systems A and B are both in thermal equilibrium with a third system, then A and B are in thermal equilibrium with each other.*
- Based on the idea of thermal equilibrium.
- The zeroth law restatement: Suppose the temperature of system A is equal to the temperature of system C; that is, $T_A = T_C$ (so that A and C are in thermal equilibrium). In addition, the temperature of system B is equal to the temperature of system C, that is $T_B = T_C$. Then $T_A = T_B$. 

Section 16.2
Zeroth Law, cont.

- If $T_A = T_C$ and $T_B = T_C$, then $T_A = T_B$
- The zeroth law declares that a property called temperature actually exists
- Temperature determines the way heat flows between systems

**Zeroth Law:**
If $T_A = T_C$ and $T_C = T_B$, then $T_A = T_B$. 

Section 16.2
First Law of Thermodynamics

• Internal energy, $U$, is the total energy associated with all the particles in a system.
• For an ideal monatomic system, all this energy resides in the kinetic energy of the particles.
• In other systems, the chemical bonds or interaction between the particles also contribute to $U$.
• The internal energy is a function of just a few macroscopic variables.
  - $U = \frac{3}{2} N k_B T$ or $U = \frac{3}{2} n R T$.
  - The internal energy of an ideal gas depends only on the temperature and number of particles.
First Law, cont.

- A system can be described as in an initial state by temperature $T_i$, pressure $P_i$ and volume $V_i$
- The system interacts with its environment
- As a result of the interaction, the system ends up in some final state with temperature $T_f$, pressure $P_f$ and volume $V_f$
First Law, Statement

- The change in the system from some initial state to some final state is called a **thermodynamic process**
- The first law of thermodynamics is an application of the principle of conservation of energy to such processes
- First law statement: *If an amount of heat Q flows into a system from its environment and an amount of work W is done by the system on its environment, the internal energy of the system changes by an amount* $\Delta U = U_f - U_i = Q - W$
First Law: Q and W

- Assume heat flows into the system
  - Q is +
  - Energy is added
  - Internal energy increases
    - $\Delta U$ is positive
- Assume a force acts between the system and the environment
  - W is + if work is done by the system on its environment
  - The internal energy decreases
    - $\Delta U$ is negative

Section 16.3
First Law: Sign Summary for $Q$

**FIRST LAW:**
$$\Delta U = Q - W$$

- **Q** = heat flow into system
- **W** = work done by system

**Q > 0,** heat into system

**Q < 0,** heat out of system

- Positive **Q** indicates heat flows *into* the system
  - Energy increases and $\Delta U$ is positive
- Negative **Q** indicates heat flows *out of* the system
  - Energy decreases and $\Delta U$ is negative

Section 16.3
First Law: Sign Summary for $W$

- Positive sign for $W$ indicates that the system does a positive amount of work *on* its environment.
  - Energy of the system decreases and the energy of the environment increases.
- Negative values of $W$ lead to an increase in the internal energy of the system.
  - $W > 0$, system does positive work on environment.
  - $W < 0$, environment does positive work on system.

$\Delta U = Q - W$

$Q =$ heat flow into system

$W =$ work done by system

Section 16.3
Thermodynamics Processes

- The environment can act as a \textit{thermal reservoir}.
- A reservoir is much larger than the system to which it is connected.
  - There is essentially no change in the temperature of the reservoir when heat enters or leaves it.
- The notion of a thermal reservoir comes up often in discussions of thermodynamic processes.
Calculating Work

- The container is filled with gas
- One wall is a movable piston
- Due to its pressure, the gas exerts a force on the piston
- The piston moves through a distance $\Delta x$

Section 16.4
Calculating Work, cont.

- If $F$ is the force exerted by the gas on the piston, the work done by the gas on the piston is $W = F \Delta x$
  - The piston is part of the environment of the gas
  - Work is done by the gas on the environment
- If the pressure in the gas is $P$ and the area of the piston is $A$, then $F = P A$
  - The work is $W = P A \Delta x = P \Delta V$
    - The force and pressure are constant
To analyze situations with large changes in volume, plot the process.

The initial state is a point on the diagram.

The process is the line or curve.

The final state is another point.

The entire process can be thought of as a series of small steps where \( W = P \Delta V \) can be applied.

\[ \Delta W = P \Delta V \]

In Section 16.4,

- \( W > 0 \) when \( \Delta V > 0 \) (work done by the system)
- \( W < 0 \) when \( \Delta V < 0 \) (work done on the system)
Work on P-V Diagram, cont.

- The total work is equal to the area under the corresponding curve in the P-V plane
- If the gas expands
  - $\Delta V$ is positive
  - The force is parallel to $\Delta x$
  - $W$ is positive
- If the gas compresses
  - $\Delta V$ is negative
  - The force is in the opposite direction than the displacement, such as a person pushing on the piston
  - $W$ is negative

Section 16.4
Thermodynamic Processes

- Thermodynamic processes are classified according to how the quantities P, V and T change during the course of the process.
- Types of processes include:
  - Isobaric
  - Isothermal
  - Adiabatic
  - Isochoric
An isobaric process is one with constant pressure.

On a P-V diagram, an isobaric process is a horizontal line.

\[ W = P \Delta V = P (V_f - V_i) \]

For an expansion, \( \Delta V \) and work are positive.

For a compression, \( \Delta V \) and work are negative.

Section 16.4
An isothermal process is one with constant temperature.

On a P-V diagram, an isothermal process is a curved line:
- Both pressure and volume may change.
- From the ideal gas law, $P$ is inversely proportional to $V$.

$$ W = nRT \ln\left(\frac{V_f}{V_i}\right) $$

Section 16.4
Isothermal Processes, cont.

• Expansion
  • The volume increases, $V_f > V_i$
  • $\ln \left( \frac{V_f}{V_i} \right)$ is positive
  • Work is positive

• Compression
  • The volume increases, $V_f < V_i$
  • $\ln \left( \frac{V_f}{V_i} \right)$ is negative
  • Work is negative
An adiabatic process is one with no heat flowing into or out of the system.
- The system is thermally isolated from its surroundings.
- On a P-V diagram, an adiabatic process is a curved line.
- \( P \propto \frac{1}{V^\gamma} \) or \( P V^\gamma = \text{constant} \)
- For a dilute monatomic gas, \( \gamma = 5/3 \)
Adiabatic Processes, cont.

- For an adiabatic process, $Q = 0$
- $W$ is equal to the area under the P-V diagram
- From the First Law of Thermodynamics, $\Delta U = -W$
- Expansion
  - Work is positive
  - Internal energy decreases
- Compression
  - Work is negative
  - Internal energy increases

Section 16.4
An isochoric process is one with constant volume
- Also called an *isovolumic* process
- On a P-V diagram, an isochoric process is a vertical line
- \( W = P \Delta V = 0 \)
Properties of $W$

- Many paths can connect the same initial and final states
- $\Delta U$ is the same for any path that connects the same initial and final states
- $W_A = P_i (V_f - V_i)$
- $W_B = P_f (V_f - V_i)$
- The amount of work depends on the path

The change in internal energy is the same:
$\Delta U_A = U_f - U_i = \Delta U_B$
but $W_A \neq W_B$ and $Q_A \neq Q_B$
Properties of Q

• We can also look at the heat added to the system
• Along path A, $\Delta U_A = Q_A - W_A$
• Along path B, $\Delta U_B = Q_B - W_B$
• $\Delta U_A = \Delta U_B$
  • Changes in internal energy is independent of the path
• $Q_A \neq Q_B$ since $W_A \neq W_B$
  • *The heat added to a system depends on the path taken*
Conclusions from Conservation of Energy

• The internal energy of a system depends only on the current state of the system
  • Changes in the internal energy are thus independent of the path taken in a thermodynamic process
  • The change in internal energy $\Delta U$ depends only on the internal energies of the initial and final states
• The work done during a thermodynamic process depends on the path taken
  • Even with the same initial and final states, two different thermodynamic paths can have different values of $W$
More Conclusions from Conservation of Energy

- The heat added to a system during a thermodynamic process depends on the path taken
  - Even with the same initial and final states, two different thermodynamic paths can have different values of $Q$
Cyclic Processes

- A cyclic process begins and ends at the same state
- The work done is equal to the area enclosed by the path in the P-V diagram

Section 16.4
Reversible Process

- In a reversible process, the system and the environment are brought back to precisely their original states.
- In this example, the gas expands and does some amount of work and takes heat from the environment.
- The system could also be compressed and have work done on the system while putting heat into the environment.

Section 16.5
Irreversible Process

• In this example, the hockey puck slides across the floor with friction
  • The kinetic energy of the puck is converted to heat energy
• It is not possible to bring both the system and the environment back to their original states
• This is an example of an irreversible process
  • Irreversible processes usually involve friction

Section 16.5
Second Law of Thermodynamics

- The distinction between reversible and irreversible processes is the subject of the second law.
- There are several different ways of stating the second law.
- The simplest statement of the second law says heat flows spontaneously from a warm body to a colder one.
  - It is not possible for heat to flow spontaneously from a cold body to a warmer one.
Heat Engines

- A heat engine takes heat energy and converts it into work
- An amount of heat $Q_H$ is extracted from a hot reservoir
- The energy is fed into some mechanical device
- It then does some amount of work, $W$
- In an imaginary heat engine, $Q_H = W$
Heat Engine, cont.

- Sadi Carnot showed that the imaginary heat engine was impossible
- All heat engines take energy in from a reservoir, do work and expel some energy into a cold temperature reservoir

Real heat engines all expel some heat to a cold reservoir.

Real heat engines all expel some heat to a cold reservoir.

[Diagram showing heat flow from a hot reservoir, through a heat engine, and into a cold reservoir.]

Section 16.6
Heat Engines, Equations

- From conservation of energy, $W = Q_H - Q_L$
- The goal is to have the most work possible out of the engine
- *Efficiency* can be defined as
  \[
  e = \frac{W}{Q_H}
  \]
- A larger $e$ means a larger fraction of $Q_H$ is converted to work
Other ways to express the efficiency come from combining the definition of efficiency with the equation from conservation of energy

\[ e = \frac{W}{Q_H} = \frac{Q_H - Q_C}{Q_H} = 1 - \frac{Q_C}{Q_H} \]
Carnot Engine

- To maximize the efficiency, $Q_c$ must be as low as possible
- Carnot considered a heat engine that makes use of the reversible compression and expansion of an ideal gas
  - An example of a reversible heat engine
- He was able to prove that all reversible heat engines have the same efficiency as his design
Carnot showed that for a hot temperature reservoir at $T_H$ and a cold temperature reservoir at $T_C$,

$$\frac{Q_C}{Q_H} = \frac{T_C}{T_H}$$

• The temperatures must be measured in Kelvin units

• The efficiency can be expressed in terms of temperatures

$$e = 1 - \frac{T_C}{T_H}$$

• This is the efficiency of a reversible heat engine
Carnot Engine, final

- The efficiency applies to all reversible engines
  - It doesn’t matter how they are constructed
- Carnot also discovered that no engine can have an efficiency that is better than the efficiency of a reversible engine
- In practice, all heat engines will always be irreversible to some extent
- Carnot’s result sets an absolute limit on the efficiency of all real heat engines

Section 16.6
Second Law, Alternative Form

- Carnot’s results are the basis for an alternative statement of the second law of thermodynamics.
- The efficiency of a reversible heat engine is given by:

  \[ e = 1 - \frac{T_c}{T_H} \]

  No heat engine can have a greater efficiency than this.
- The two statements of the second law are completely equivalent.
  - Given either of them as a starting point, the other one can be derived.
Examples of Heat Engines

- The internal combustion engine in most cars is a type of heat engine.
- A diesel engine is also a heat engine.
  - The higher operating temperature of a diesel engine gives it a higher theoretical limit for its efficiency.
Perpetual Motion and the Second Law

• One design of a perpetual motion machine is shown
• Carnot’s work and the second law tell us that this machine is impossible
  • Some heat energy must always be expelled to a cold reservoir
• The second law of thermodynamics rules out all perpetual motion machines

Section 16.6
Carnot showed how to use an ideal gas and piston to make a reversible heat engine.

The engine goes through four states and is cyclical.

Section 16.6
Carnot Cycle, Processes

- **State 1 to state 2**
  - The system is placed in contact with the hot reservoir
  - The gas absorbs an amount of heat $Q_H$
  - The gas expands to state 2
  - There is an isothermal expansion at $T_H$
    - Because of the contact with the hot reservoir

- **State 2 to state 3**
  - The system is isolated from its surroundings and allowed to expand
  - No heat is absorbed or expelled
  - This is an adiabatic expansion

Section 16.6
Carnot Cycle, Processes, cont.

- **State 3 to state 4**
  - The system is in contact with the cold reservoir at $T_C$
  - An amount of heat, $Q_C$, flows out of the gas and into the cold reservoir
  - The volume decreases
  - It is an isothermal compression
    - Because of the contact with the cold reservoir

- **State 4 to state 1**
  - The system is again isolated from its surroundings
  - It is adiabatically compressed back to state 1

Section 16.6
Carnot Cycle, final

- The cyclic path on the P-V diagram is called a *Carnot cycle*
- Each step involves a reversible process
- Each process can be analyzed individually
- The total work done by the gas during one cycle is the area enclosed by the path on the P-V diagram
Refrigerator

- Since the Carnot heat engine is reversible, it is possible to run it in reverse.
- $Q_C$ is extracted from the cold reservoir and $Q_H$ is expelled into the hot reservoir.
- An amount of work is done on the gas.
Refrigerator, cont.

- A heat engine run in reverse is a **refrigerator**
- Typically an electric engine does the work on the refrigeration unit
- From conservation of energy, $W + Q_C = Q_H$
The efficiency can also be determined as:

\[ e_{\text{refrig}} = \frac{Q_c}{W} \]

This efficiency is also called the coefficient of performance of the refrigerator. Another way to express the efficiency of a refrigerator is:

\[ e_{\text{refrig}} = \frac{T_c}{1 - \left(\frac{T_c}{T_H}\right)} = \frac{T_c}{T_H - T_c} \]
Typically, you want a low value for $T_C$ and a high efficiency.

However, a low value for $T_C$ leads to a low efficiency.

This is an unavoidable consequence of the second law.
Second Law and Refrigerators

- A refrigerator causes heat energy to flow from a cold body to a warm body.
- This does not violate the second law of thermodynamics, since it is not a spontaneous heat flow.
- The heat flow in a refrigerator is possible because of the work done on it.
Heat Pumps

- A heat pump is a device that can be used to heat homes and other buildings.
- It “pumps” heat from a cold reservoir into the building (the hot reservoir).
- A heat pump is thermodynamically identical to a refrigerator.
Heat Pumps, cont.

• For an effective heat pump, the amount of heat going into the house should be as high as possible while the amount of $W$ needed is as small as possible.

\[ e_{\text{pump}} = \frac{Q_H}{W} = \frac{1}{1 - \left(\frac{T_c}{T_H}\right)} \]

• The work needed to run a heat pump is given by

\[ W = Q_H \left(1 - \frac{T_c}{T_H}\right) \]

• Efficiency values much greater than 1 are mathematically possible and achievable in practice.
Entropy

- Entropy, $S$, is a macroscopic property of a system.
- If a small amount of heat $Q$ flows into a system, its entropy changes by
  \[ \Delta S = \frac{Q}{T} \]
- SI unit of entropy is J/K.

\[ \Delta S_1 = -\frac{Q}{T_1} \]
\[ T_1 > T_2 \]
\[ \Delta S_2 = +\frac{Q}{T_2} \]
Entropy and Processes

- The total entropy change is zero for all reversible processes.
- The total energy change is positive for all irreversible processes.
- The entropy form of the second law:
  - In any thermodynamic process, $\Delta S_{universe} \geq 0$.
- All three statements of the second law are equivalent:
  - Each one can be used to prove the other two.
  - Each version gives different insights into the meaning and consequences of the second law.
• In microscopic terms, entropy is a measure of the amount of disorder or randomness in a system.
• Increasing the temperature of a gas or liquid increases the kinetic energy of the molecules and increases the amount of disorder.
• Adding heat to a system always increases its entropy.
Entropy and Probability

$N = \text{number of molecules}$

Two possible states

$N = 1$

Molecule 1

$N = 2$

Molecule 2

Four possible states

$N = 4$

Sixteen possible states

Section 16.7
Entropy and Probability, cont.

- One molecule would have two possible distributions
- The probability of finding the molecule on one side is $p = \frac{1}{2}$
- With two molecules, there are four possible states
- With more molecules, the possible states increase rapidly
- A key assumption of thermodynamics is that each of these state is equally likely
• The probability can also be graphed
• Large values of entropy correspond to a greater amount of randomness distributed throughout the box
• As the number of molecules grows, the probability peak becomes narrower
• The most likely state has the highest probability and the greatest entropy
Absolute Zero

- The Kelvin scale is closely connected to kinetic theory and thermodynamics
  - The ideal gas law involves temperature in kelvins
  - The definition of entropy also involves temperature in kelvins
- When $T = 0$ K, the kinetic energy of a gas molecule is zero
  - $KE = \frac{3}{2} k_B T$
- Since the KE cannot be less than zero, this implies temperatures below absolute zero are not possible

Section 16.8
Absolute Zero and Third Law

- Carnot’s statement that all heat engines must expel some heat to a cold reservoir implies that a reservoir with $T = 0$ K is not possible.
- The third law of thermodynamics puts these ideas together.
- The third law states that it is impossible for the temperature of a system to reach absolute zero.
The process of photosynthesis is similar to a heat engine.
- \( Q_H \) is from the Sun.
- The plant does work by storing chemical energy.
- \( Q_C \) is expelled back to the surroundings.
- Ideally, \( e_{\text{photosyn}} = 0.95 \).
- In reality, \( e < 48\% \).
Heat and Mechanical Energy

- One key of thermodynamics is that heat is a form of energy.
- The second law also tells us that heat energy is different from kinetic and potential energies.
- It is possible to convert all of the mechanical energy to heat.
- The second law tells us that only a fraction of the heat energy can be converted to mechanical energy.
  - The fraction is equal to the efficiency of a reversible heat engine.
Consider an example of the compression of an ideal gas.

All the mechanical energy used to move the piston can be converted to heat energy.

Consider the impossibility of running the process in reverse.

Piston does work on molecules and increases their KE.

Cold reservoir

$Q$

$\Delta x$
Heat and Mechanical Energy, final

- To run in reverse, all the gas molecules would have to collide with the piston in synchrony so as to exert a force on the piston.
- The randomness of the gas makes such perfect synchrony impossible.
- Some molecules may collide with the piston, but the inherent disorder associated with the energy prevents all the molecules from simultaneously giving energy back to the piston.
- It is not possible to extract all the heat energy from the gas.
- The disordered motion of the gas molecules makes it impossible to convert heat energy completely to mechanical energy.