Chapter 15: Thermodynamics

Heat is energy transferred from one object to another because of a difference in temperature.

Work is energy transferred from one object to another by mechanical means.

FIRST LAW OF THERMODYNAMICS

The change in internal energy of a closed system is equal to the energy added to the system minus the work done by the system on its surroundings.

\[ \Delta U = Q - W \]

Careful with signs: for example, if work is done TO the system use Q+W.

U, V, P, T, m, n are quantities that describe a state of the system: state variables. Q and W change state of the system, they are not state variables.

Ex. 15-1 2500 J of heat is added to a system, and 1800 J of work is done on the system. What is the change in internal energy of the system? 4300 J
An isothermal process is one where the temperature does not change.

In order for an isothermal process to take place, we assume the system is in contact with a heat reservoir.

In general, we assume that the system remains in equilibrium throughout all processes (process very slow).

\[ \Delta U = \frac{3nR\Delta T}{2} \]

PV=constant curves are isotherms
System starts at A. If Q is added, then P and V change, the gas expands and do work on the surroundings. Since T is constant, internal energy does not change and so Q=W
An **adiabatic** process is one where there is no heat flow into or out of the system, $Q=0$. -- system is very isolated or process is very fast (diesel engine)

$$\Delta U = -W$$

Internal energy decreases as gas expands; hence $T$ decreases and so does $PV$, which explains why C is below B

An **isobaric** process (a) occurs at constant pressure; an **isovolumetric** one (b) at constant volume.
If the pressure is constant, the work done is the pressure multiplied by the change in volume:

\[ W = Fd = PAd \Rightarrow W = P \Delta V \]

In an isovolumetric process, the volume does not change, so the work done is zero.

Work done is the area under the $P$-$V$ curve -- only way to solve it if $P$ varies as in isothermal processes.

### TABLE 15–1 Simple Thermodynamic Processes and the First Law

<table>
<thead>
<tr>
<th>Process</th>
<th>What is constant:</th>
<th>The first law predicts:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isothermal</td>
<td>$T = \text{constant}$</td>
<td>$\Delta T = 0 \text{ makes } \Delta U = 0, \text{ so } Q = W$</td>
</tr>
<tr>
<td>Isobaric</td>
<td>$P = \text{constant}$</td>
<td>$Q = \Delta U + W = \Delta U + P \Delta V$</td>
</tr>
<tr>
<td>Isovolumetric</td>
<td>$V = \text{constant}$</td>
<td>$\Delta V = 0 \text{ makes } W = 0, \text{ so } Q = \Delta U$</td>
</tr>
<tr>
<td>Adiabatic</td>
<td>$Q = 0$</td>
<td>$\Delta U = -W$</td>
</tr>
</tbody>
</table>
Exercises

Ex. 15-3 Suppose the initial volume is the same in both an isothermal and an adiabatic process. If the final volume is also the same, in which process was more work done by the gas?

In the isothermal process – larger area

Ex. 15-4 Example of an adiabatic process: hold a thin rubber with two hands and gauge its temperature with your lips. Stretch the rubber band suddenly and again touch it with your lips. Why the temperature increases?

Q=0 because the process is fast, no time for heat to enter or leave the system. We do work on the system, \( \Delta U = +W \) so the temperature increases

Ex. 15-5 An ideal gas is slowly compressed at a constant pressure of 2.0 atm from 10.0 L to 2.0 L (B to D in figure). In this process some heat flows out of the gas and the temperature drops. Heat is then added to the gas, holding the volume constant (line DA) until initial T is reached. Calculate (a) the total work done by the gas in the process BDA, and (b) the total heat flow into the gas

\[
W = -1.6 \times 10^3 \, J \quad (b) \Delta U = 0 \Rightarrow Q = -1.6 \times 10^3 \, J \text{(out of gas)}
\]
Exercises

Ex. 15-6  In an engine, 0.25 moles of an ideal monatomic gas in the cylinder expands rapidly and adiabatically against the piston. In the process, the temperature of the gas drops from 1150 K to 400 K. How much work does the gas do?

$$\Delta U = 3nR(T_f - T_i) / 2 \Rightarrow W = 2300 J$$

Ex. 15-7  Determine the change in internal energy of 1.00 liter of water (mass 1.00 kg) at 100°C when it is fully boiled from liquid to gas, which results in 1671 liters of steam at 100°C. The process is done at atmospheric pressure.

$$1 \text{atm} = 1.01 \times 10^5 \text{ N/m}^2 \quad 1 \text{L} = 10^{-3} \text{ m} \quad L_v = 22.6 \times 10^5 \text{ J/kg}$$

$$Q = mL, \; W = P\Delta V \Rightarrow \Delta U = 20.9 \times 10^5 J$$
Second Law

According to the first law, energy is conserved. There are however processes that would conserve energy, but never happens. Examples: heat flow from cold to hot object; salt and pepper separating in water.

Lack of reversibility – 2nd law of thermodynamics

The second law of thermodynamics is a statement about which processes occur and which do not. There are many ways to state the second law; here is one:

Heat can flow spontaneously from a hot object to a cold object; it will not flow spontaneously from a cold object to a hot object.

But we need a more general statement applied to other processes too.

The development of a general statement derived from the study of heat engines

A heat engine is any device that changes thermal energy into mechanical work.
Heat Engines

Easy to produce thermal energy doing work, the other way round is more difficult -- 1700: 1\(^{st}\) steam engine

As heat flows from high to low temperature, some of the heat can be transformed to mechanical work.

We will discuss only engines that run in a repeating cycle; the change in internal energy over a cycle is zero, as the system returns to its initial state.

The high temperature reservoir transfers an amount of heat \(Q_H\) to the engine, where part of it is transformed into work \(W\) and the rest, \(Q_L\), is exhausted to the lower temperature reservoir. Note that all three of these quantities are positive.

\[
Q_H = W + Q_L
\]
Steam Engine

Steam heated by combustion of coal, oil, gas, or nuclear energy

(a) Reciprocating type

(b) Turbine (boiler and condenser not shown)
Internal Combustion Engine

High temperature is achieved by burning the gasoline-air mixture in the cylinder.

Temperature difference is necessary for net work to be different from zero, otherwise the work done on the system in one part of the cycle would be equal to the work done by the system in another part, and the net work will be zero.
The efficiency of the heat engine is the ratio of the work done to the heat input:

$$e = \frac{W}{Q_H} \quad Q_H = W + Q_L$$

Ex. 15-9 An automobile engine has an efficiency of 20% and produces an average of 23000J of mechanical work per second during operation. (a) How much heat input is required, and (b) how much heat is discharged as waste heat from this engine per second?

$$Q_H = \frac{W}{e} = 115 \text{kJ}$$

$$\frac{Q_L}{Q_H} = 1 - e = 92 \text{kJ}$$
The Carnot engine was created to examine the efficiency of a heat engine. It is idealized, as it has no friction. Each leg of its cycle is reversible.

The Carnot cycle consists of:

- Isothermal expansion
- Adiabatic expansion
- Isothermal compression
- Adiabatic compression
Exercises

For an **ideal reversible engine**, the efficiency can be written in terms of the temperature:

\[ e_{\text{ideal}} = \frac{T_H - T_L}{T_H} = 1 - \frac{T_L}{T_H} \]

100% efficiency can be achieved only if the cold reservoir is at absolute zero, which is impossible.

Real engines have some frictional losses; the best achieve 60-80% of the Carnot value of efficiency.

**Ex. 15-10** A steam engine operates between 500°C and 270°C. What is the maximum possible efficiency of this engine?

\[ e_{\text{ideal}} = 0.30 = 30\% \]

Realistically an engine might achieve 0.70 of this value=21%

**Ex. 15-11** An engine manufacturer makes the following claims: An engine’s heat input per second is 9.0kJ at 435 K. The heat output per second is 4.0kJ at 285K. Do you believe these claim? (compare the efficiency with the ideal one)

\[ e = 0.56 \]

\[ e_{\text{ideal}} = 0.34 \]

It violates the 2nd law of thermodynamics
Refrigerators, Air Conditioners

They are just the reverse of heat engines

By doing work, heat is extracted from the cold reservoir and exhausted to the hot reservoir.

Refrigerator performance is measured by the coefficient of performance (COP):

$$\text{COP} = \frac{Q_L}{W} = \frac{Q_L}{Q_H - Q_L}$$

For a heat pump

$$\text{COP}_{\text{ideal}} = \frac{T_L}{T_H - T_L}$$

$$\text{COP} = \frac{Q_H}{W}$$
Exercises

Ex. 15-12 A freezer has a COP of 3.8 and uses 200 W of power. How long would it take to freeze an ice-cube tray that contains 600 g of water at 0°C? 

\[ L = 333 \text{ kJ/kg} \]

\[
P = \frac{W}{t} \Rightarrow t = \frac{W}{200 J/s} = \frac{Q_L}{COP} = \frac{200 J/s}{200 J/s} = 260 s
\]

Ex. 15-13 A heat pump has a coefficient of performance of 3.0 and is rated to do work at 1500 W. (a) How much heat can it add to a room per second? (b) If the heat pump were turned around to act as an air conditioner in the summer, what would you expect its coefficient of performance to be, assuming all else stays the same?

\[ Q_H = COP \times W = 4500 J \]

\[ Q_L = Q_H - W = 3000 J \Rightarrow COP = \frac{Q_L}{W} = 2.0 \]
Entropy and the 2\textsuperscript{nd} Law of Thermo

Thus a living organism continually increases its entropy—or, as you may say, produces positive entropy—and thus tends to approach the dangerous state of maximum entropy, which is of death. It can only keep aloof from it, i.e. alive, by continually drawing from its environment negative entropy—which is something very positive as we shall immediately see.


General statement of the second law of thermodynamics:

The total entropy of any system plus that of its environment increases as a result of any natural process.

\[ \Delta S = \frac{Q}{T} \]

T is KELVIN

Entropy is a measure of the disorder of a system. Natural processes tend to move toward a state of greater disorder. Examples: salt+pepper, falling object. Thermal equilibrium is a similar process – the uniform final state has more disorder than the separate temperatures in the initial state.

The 2\textsuperscript{nd} law of thermodynamics define an ARROW OF TIME – processes occur that are NOT REVERSIBLE

The ideas of entropy and disorder are made clearer with the use of a statistical analysis of the molecular state of a system - Boltzmann
Exercises

Ex. 15-14 An ice cube of mass 56 g is taken from a storage compartment at 0°C and placed in a paper cup. After a few minutes, exactly half of the mass of the ice cube has melted, becoming water at 0°C. Find the change in entropy of the ice/water.

\[ \Delta S = 34 \text{ J} / \text{ K} \]

L=333 kJ/kg

Ex. 15-15 A sample of 50.0 kg of water at 20.00°C is mixed with 50.0 kg of water at 24.00°C. Estimate the change in entropy.

Final temperature will 22.00°C – same amounts of water

\[ Q = mc\Delta T = (50.0 \text{ kg})(4186 \text{ J/kg°C})(2.00°C) = 4.186 \times 10^5 \text{ J} \]

\[ \Delta S = \Delta S_H + \Delta S_C \]

\[ \Delta S_H \approx \frac{4.186 \times 10^5 \text{ J}}{(23 + 273)\text{K}} = -1414 \text{ J/ K} < 0 \]

Net change in entropy of the whole system is positive

\[ \Delta S = \Delta S_H + \Delta S_C \approx 10 \text{ J/ K} > 0 \]

\[ \Delta S_C \approx \frac{4.186 \times 10^5 \text{ J}}{(21 + 273)\text{K}} = 1424 \text{ J/ K} > 0 \]
A **macrostate** of a system is specified by giving its macroscopic properties – temperature, pressure, and so on.

A **microstate** of a system describes the position and velocity of every particle. There are too many particles in a system to be able to provide all microstates. Many different microstates correspond to the same macrostate. We deal with probabilities.

**Example**: tossing 4 coins. Macrostates describe how many heads and tails there are; the microstates list the different ways of achieving that macrostate.

All heads or all tails: most orderly arrangement but lowest probability

<table>
<thead>
<tr>
<th>Macrostate</th>
<th>Possible Microstates (H = heads, T = tails)</th>
<th>Number of Microstates</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 heads</td>
<td>H H H H</td>
<td>1</td>
</tr>
<tr>
<td>3 heads, 1 tail</td>
<td>H H H T, H H T H, H T H H, T H H H</td>
<td>4</td>
</tr>
<tr>
<td>2 heads, 2 tails</td>
<td>H H T T, H T H T, T H H T, H T T H, T H T H, T T H H</td>
<td>6</td>
</tr>
<tr>
<td>1 head, 3 tails</td>
<td>T T T H, T T H T, T H T T, H T T T</td>
<td>4</td>
</tr>
<tr>
<td>4 tails</td>
<td>T T T T</td>
<td>1</td>
</tr>
</tbody>
</table>
## Statistical Interpretation

### TABLE 15–3
Probabilities of Various Macrostates for 100 Coin Tosses

<table>
<thead>
<tr>
<th>Macrostate</th>
<th>Number of microstates</th>
<th>Probability</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 heads</td>
<td>0</td>
<td>$8.0 \times 10^{-31}$</td>
</tr>
<tr>
<td>99 heads</td>
<td>1</td>
<td>$8.0 \times 10^{-29}$</td>
</tr>
<tr>
<td>90 heads</td>
<td>10</td>
<td>$1.0 \times 10^{-17}$</td>
</tr>
<tr>
<td>80 heads</td>
<td>20</td>
<td>$4.0 \times 10^{-10}$</td>
</tr>
<tr>
<td>60 heads</td>
<td>40</td>
<td>0.01</td>
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<tr>
<td>55 heads</td>
<td>45</td>
<td>0.05</td>
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<tr>
<td>50 heads</td>
<td>50</td>
<td>0.08</td>
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<tr>
<td>45 heads</td>
<td>55</td>
<td>0.05</td>
</tr>
<tr>
<td>40 heads</td>
<td>60</td>
<td>0.01</td>
</tr>
<tr>
<td>20 heads</td>
<td>80</td>
<td>$4.0 \times 10^{-10}$</td>
</tr>
<tr>
<td>10 heads</td>
<td>90</td>
<td>$1.0 \times 10^{-17}$</td>
</tr>
<tr>
<td>1 head</td>
<td>99</td>
<td>$8.0 \times 10^{-29}$</td>
</tr>
<tr>
<td>0 heads</td>
<td>100</td>
<td>$8.0 \times 10^{-31}$</td>
</tr>
</tbody>
</table>
The second law does not forbid certain processes; however, some of them have an extraordinarily low probability of occurring – a lake freezing on a hot summer day, broken crockery re-assembling itself; all the air in a room moving into a single corner.

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**TABLE 15–3**

Probabilities of Various Macrostates for 100 Coin Tosses

<table>
<thead>
<tr>
<th>Macrostate</th>
<th>Number of microstates</th>
<th>Probability</th>
</tr>
</thead>
<tbody>
<tr>
<td>heads</td>
<td>tails</td>
<td>100</td>
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<tr>
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<td>90</td>
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<td>10</td>
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<tr>
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<td></td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>Form of Electric Energy Production</td>
<td>U.S.</td>
<td>World</td>
</tr>
<tr>
<td>-----------------------------------</td>
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</tr>
<tr>
<td>Fossil-fuel steam plants: burn coal, oil, or natural gas to boil water, producing high-pressure steam that turns a turbine of a generator (Figs. 15–12b, 15–21); uses heat engine.</td>
<td>87</td>
<td>86</td>
</tr>
<tr>
<td><strong>Nuclear energy:</strong></td>
<td></td>
<td></td>
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<tr>
<td><strong>Fission:</strong> nuclei of uranium or plutonium atoms split (“fission”) with release of energy (Chapter 31) that heats steam; uses heat engine.</td>
<td>8</td>
<td>6</td>
</tr>
<tr>
<td><strong>Fusion:</strong> energy released when isotopes of hydrogen (or other small nuclei) combine or “fuse” (Chapter 31).</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Hydroelectric: Falling water turns turbines at the base of a dam.</td>
<td>4</td>
<td>7</td>
</tr>
<tr>
<td>Geothermal: natural steam from inside the Earth comes to the surface (hot springs, geysers, steam vents); or cold water passed down into contact with hot, dry rock is heated to steam.</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Wind power: 3-kW to 5-MW windmills (varies up to 50 m wide) turn a generator.</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Solar energy: <strong>Active solar heating:</strong> rooftop solar panels absorb the Sun’s rays, which heat water in tubes for space heating and hot water supply.</td>
<td>&lt;0.1</td>
<td>&lt;1</td>
</tr>
<tr>
<td><strong>Passive solar heating:</strong> architectural devices—windows along southern exposure, sunshade over windows to keep Sun’s rays out in summer.</td>
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<tr>
<td>Solar cells (photovoltaic cells): convert sunlight directly into electricity without use of heat</td>
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</table>