Chapter 19 – The Second Law of Thermodynamics

Heat Engines and the Second Law of Thermodynamics

No system can absorb heat from a single reservoir and convert it entirely into work without additional net changes in the system or its surroundings: Kelvin

For practical purposes, this means that the energy losses (eventually, into heat) are inevitable and the ideal engines cannot exist.

A process whose only net result is to absorb heat from a cold reservoir and release the same amount of heat to a hot reservoir is impossible: Clausius

For practical purposes, this means that the energy losses (eventually, into heat) are inevitable and the ideal refrigerators cannot exist.

A heat engine is a cyclic device whose purpose is to convert as much heat into work as possible. The heart of a heat engine is a working substance that absorbs heat $Q_h > 0$, does work $W > 0$, and releases heat $Q_c > 0$ as it returns to its initial state.
Schematics of a steam engine. All engines have more or less the same main components: a heat source ("burning fuel"), working substance, load to work on, and a heat exchanger for cooling.

Schematics of a thermodynamic cycle for an Internal combustion engine (the Otto cycle).  
a – b: adiabatic compression  
b – c: heating at constant volume  
c – d: work done during adiabatic expansion  
d – a: release of heat
Second law of thermodynamics (heat engine formulation): *It is impossible for a heat engine working in a cycle to produce only the effect of absorbing heat from a single reservoir and performing an equivalent amount of work.*

Rules:

1. In each full cycle the change in internal energy $\Delta E_{int} = 0$.
2. The energy conservation law dictates that $Q_h = W + Q_c$.
3. The efficiency of the heat engine is the ratio of benefit to cost, $e = \frac{W}{Q_h}$.
4. The work in each step in a cycle $W = \int_{V_i}^{V_f} P \, dV$, $P = \frac{nRT}{V}$.
5. The heat absorbed by the gas during a step $Q = C\Delta T$. 

*Schematics of a generic heat engine*
Example 1. Find the efficiency of an engine which absorbs 400 J and dumps 350 J of heat during a cycle.
The work \( W = Q_h - Q_c = (400 - 350) \) J = 50 J.
The efficiency \( e = W/Q_h = 50J/400J = 12.5\% \)

Example 1. Find the efficiency of an internal combustion engine (the Otto cycle).

The efficiency \( e = W/Q_h = (Q_h - Q_c)/Q_h = 1 - Q_c/Q_h \)
The heat is released on a \( d - a \) step of the cycle,
\( Q_c = C_v |T_a - T_d| = C_v(T_a - T_a) \)
The heat is absorbed on a \( b - c \) step of the cycle,
\( Q_h = C_v(T_c - T_b) \), and the efficiency
\( e = 1 - (T_d - T_a)/(T_c - T_b) \).
The processes \( a - b \) and \( c - d \) are adiabatic,
\( T_a V_a^{\gamma-1} = T_b V_b^{\gamma-1}, T_c V_c^{\gamma-1} = T_d V_d^{\gamma-1}, \)
and \( T_b = T_a r^{\gamma-1}, T_c = T_d r^{\gamma-1} \) where \( r = V_a/V_b \)
Finally, the efficiency
\( e = 1 - (T_d - T_a)/(T_c - T_b) = 1 - (T_d - T_a)/(T_d r^{\gamma-1} - T_a r^{\gamma-1}) \)
\( = 1 - 1/r^{\gamma-1} = e \)
Refrigerators and the Second Law of Thermodynamics

It is impossible for a refrigerator working in a cycle to produce only the effect of absorbing heat from a cold object and releasing the same amount of heat to a hot object.

A measure of refrigerator’s performance is not the efficiency $e$, but the coefficient of performance (COP) which is given by the ratio of the benefit to cost,

\[
\text{COP} = \frac{\text{benefit}}{\text{cost}} = \frac{Q_c}{W}
\]
Example 2. How long will it take to freeze 1L of water, initially at 10°C, in a freezer of a refrigerator with COP = 6 and power ratings 400W assuming that only 10% of power is used by the freezer?

The extracted heat $Q_c$ required to cool 1L of water from 10°C to 0°C and to freeze it is equal to

$$Q_c = mc\Delta T + mL_f = (1\text{kg})(4.18\text{kJ/kg} \times \text{K})(10\text{K}) + (1\text{kg})(333.5\text{kJ/kg}) = 41.8\text{kJ} + 333.5\text{kJ} = 375.3\text{kJ}$$

With COP = 6 = $Q_c/W$, this requires energy $W = Q_c/\text{COP} = 375.3\text{kJ}/6 = 62.6\text{kJ}$.

Since available power is $400\text{W} \times 0.1 = 40\text{W}$, the required time is

$$t = \frac{62.6 \times 10^3\text{J}}{40\text{W}} = 1565\text{s} = 26.1\text{min}$$

The Carnot Engine (Cycle)

*No engine working between given hot and cold heat reservoirs can be more efficient than the reversible engine such as the Carnot engine*

The Carnot cycle consists of 4 steps:
1. A quasi-static isothermal absorption of heat from a hot reservoir $T_h$
2. A quasi-static adiabatic expansion to a lower temperature $T_c$
3. A quasi-static isothermal heat release to a cold reservoir at $T_c$
4. A quasi-static adiabatic compression back to the original state $T_h$
The efficiency \( e = 1 - Q_c/Q_h \) of the Carnot engine

Since the internal energy of the gas does not change during an isothermal step 1, the absorbed heat \( Q_h \) is equal to the work done by the gas,

\[
Q_h = W_{by \text{ gas}} = \int_{V_1}^{V_2} P \, dV = \int_{V_1}^{V_2} \left( \frac{nRT_h}{V} \right) \, dV = nRT_h \int_{V_1}^{V_2} \frac{dV}{V} = nRT_h \ln \frac{V_2}{V_1}
\]

Similarly, the heat is released during another isothermal step 3:

\[
Q_c = nRT_c \ln \frac{V_3}{V_4}.
\]

The steps 1 and 3 are connected via adiabatic steps 2 and 4:

\[
T_h V_2^{\gamma-1} = T_c V_3^{\gamma-1}, \quad T_h V_1^{\gamma-1} = T_c V_4^{\gamma-1}
\]

meaning that

\[
\frac{V_2}{V_1} = \frac{V_3}{V_4}
\]

and the efficiency

\[
e = 1 - \frac{Q_c}{Q_h} = 1 - T_c \ln \frac{V_3}{V_4}/T_h \ln \frac{V_2}{V_1} = 1 - \frac{T_c}{T_h} = e.
\]

Since the maximum possible efficiency is the Carnot efficiency, the efficiency of any real engine

\[
e \leq 1 - \frac{T_c}{T_h}
\]
Example 3. If 500kJ of heat is transferred between heat reservoirs at 400K and 293K. What is the maximal amount of work that might be produced using this heat (the amount of “lost work”)?

The maximal efficiency of a heat engine operating between these two reservoirs

\[ e = 1 - \frac{T_c}{T_h} = 1 - \frac{293K}{400K} = 1 - 0.73 = 0.27 \]

Out of 500kJ of heat the engine operating with this efficiency would produce

\[ W = eQ_h = 0.27 \times 500kJ = 135kJ \]

The Thermodynamic (Absolute) Temperature Scale

Since the efficiency of a reversible (Carnot) engine does not depend on the nature of the working substance,

\[ e = 1 - \frac{Q_c}{Q_h} = 1 - \frac{T_c}{T_h}, \]

this can be used as a thermodynamic or absolute definition of temperature,

\[ \frac{T_c}{T_h} = \frac{Q_c}{Q_h} \]
Heat Pumps

A heat pump is a refrigerator built not with a purpose to cool objects inside of it, but with a purpose to heat the region outside of it.

Essentially, it uses the external energy $W$ to extract the Heat $Q_c$ from the cold Reservoir and dump $Q_h$ into the hot reservoir ("room"). Energy conservation dictates $Q_h = Q_c + W$.

And the COP is defined as

$$\text{COP}_{\text{HP}} = \frac{Q_h}{W} = \frac{Q_h}{(Q_h - Q_c)}.$$

This COP is different from a standard COP of refrigerator,

$$\text{COP}_{\text{R}} = \frac{Q_c}{W} = \text{COP}_{\text{HP}} - 1.$$

If the heat pump is operated by an ideal reversible engine,

$$\text{COP}_{\text{HP max}} = \frac{T_h}{(T_h - T_c)}$$
Irreversibility, Disorder, and Entropy

Irreversibility of thermodynamic process is related to the degree of disorder in thermodynamic states – order cannot be restored by itself and requires external energy. A thermodynamic function that is a measure of disorder in thermodynamic systems is called **entropy** $S$.

The change in entropy $dS$ as the system goes between the states

$$dS = \frac{dQ_{rev}}{T}$$

where $dQ_{rev}$ is the amount of heat absorbed in a **reversible** process.

**Entropy of an Ideal Gas**

If the gas is a subject of a reversible process, then the change in its internal energy is

$$dE_{int} = dQ_{rev} + dW_{on} = dQ_{rev} - PdV = C_V dT$$

Using the gas law, we get

$$C_V \frac{dT}{T} = dQ_{rev} / T - nRdV / V \rightarrow dS = C_V \frac{dT}{T} + nR \frac{dV}{V}.$$ 

After integration between the states this yields

$$\Delta S = CV \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}.$$
Entropy change for an isothermal *expansion* of an ideal gas

\[ \Delta S = \int \frac{dQ_{rev}}{T} = nR \ln \frac{V_2}{V_1} > 0 \]

The amount of heat released by the reservoir and absorbed by the gas is equal to the work done by the gas,

\[ Q_{rev} = W = \int_{V_1}^{V_2} P \, dV = nR \ln \frac{V_2}{V_1} \]

\[ \Delta S \] for a free expansion of an ideal gas

Since a free expansion is always an irreversible process, we cannot use the definition of the entropy via \( dQ_{rev} \). The change in entropy is related to the change in volume and

\[ \Delta S = nR \ln \frac{V_2}{V_1} > 0 \]

\[ \Delta S \] for a constant pressure processes

At constant pressure

\[ dS = dQ/T = C_p dT/T \]

\[ \Delta S = C_p \int_{T_1}^{T_2} dT/T = C_p \ln \frac{T_2}{T_1} \]
**Example 4.** Find the changes in the entropy of the system and the universe if you mix 2kg of water at 20°C with 4kg of water at 80°C. The pressure is constant, 1atm.

The temperatures of hot and cold samples were $T_h = 353K$ and $T_c = 293K$. The amount of heat lost by the 4kg of hot water $cm_4(T_h - T_f)$ is equal to the amount of heat gained by the 2kg of cold water, $cm_4(T_h - T_f) = cm_2(T_f - T_c) \rightarrow T_f = 333K$

For each part of the system the change in entropy is

$$\Delta S = mcp \int_{T_i}^{T_f} \frac{dT}{T} = mcp \ln \frac{T_f}{T_i}.$$ 

For the 2kg portion this means that

$$\Delta S_2 = mcp \ln \frac{T_f}{T_i} = 2kg \times \frac{4.184}{\text{kJ/(kg} \times \text{K)}} \times \ln \frac{333K}{293K} = 8.368 \text{kJ/K} \times \ln 1.34 = 2.45 \text{kJ/K.}$$

For the 4kg portion

$$\Delta S_4 = mcp \ln \frac{T_f}{T_i} = 4kg \times \frac{4.184}{\text{kJ/(kg} \times \text{K)}} \times \ln \frac{333K}{353K} = 16.736 \text{kJ/K} \times \ln 0.943 = -0.982 \text{kJ/K}$$

and the overall change of entropy of water $\Delta S = 2.45 \text{kJ/K} - 0.982 \text{kJ/K} = 1.468 \text{kJ/K.}$ Since the calorimeter is insulated, the entropy of the surroundings does not change and the total change of the entropy of the universe is also 1.468kJ/K.
$\Delta S$ for a perfectly inelastic collision

If a body of mass $m$ falls from a height $h$ and and stops (an inelastic fall),

$$\Delta S = Q/T = mgh/T$$

$\Delta S$ for heat transfer between the reservoirs

Assuming that the temperature of each large reservoir does not change as a result of this heat transfer,

$\Delta S_h = -Q/T_h$, $\Delta S_c = Q/T_c$ \rightarrow \Delta S = \Delta S_h + \Delta S_c = Q/T_c - Q/T_h = Q(T_h - T_c)/T_h T_c$

$\Delta S$ for a Carnot cycle

Because a Carnot cycle is reversible, the entropy change should be zero. The entropy change of the hot reservoir $\Delta S_h = -Q_h/T_h$, and for the cold reservoir $\Delta S_c = Q_c/T_c$. Since the temperatures $T_{c,h}$ by the definition of the thermodynamic temperature are related to each other as $T_c/T_h = Q_c/Q_h$,

$$\Delta S = \Delta S_{engine} + \Delta S_h + \Delta S_c = 0 -Q_h/T_h + Q_c/T_c = 0.$$
The Second Law of Thermodynamics

For any process the entropy of any insulated closed system (including the universe) never decreases.

For any irreversible process the entropy of any insulated closed system (including the universe) always increases.

During an irreversible process energy equal to $T\Delta S$ becomes unavailable to do work ($T$ is the temperature of the coldest reservoir and $\Delta S$ is the entropy increase due to irreversibility).

Entropy and Probability

Reversing the irreversible processes is not impossible - it is just highly improbable because of an extremely large number of particles.

Consider the possibility (probability) of a gas spontaneously contracting from a larger volume $V_1$ to a smaller volume $V_2$. If the gas contains $N$
molecules, then the probability of finding all of them simultaneously in the smaller volume $V_2$ is

$$p = \left(\frac{V_2}{V_1}\right)^N$$

The logarithm of this probability

$$\ln p = N \ln \left(\frac{V_2}{V_1}\right) = nN_A \ln \left(\frac{V_2}{V_1}\right)$$

Comparing this with the change in entropy of the gas $\Delta S$ we get

$$\Delta S = nR \ln \left(\frac{V_2}{V_1}\right) = (R/N_A) \ln p = k \ln p$$

where $k = R/N_A$ is Boltzmann’s constant.

*(photo courtesy of Dr. Kaufman)*
Review of Chapter 19.

Efficiency of a heat engine \( e = \frac{W}{Q_h} = \frac{(Q_h - Q_c)}{Q_h} = 1 - \frac{Q_c}{Q_h} \)

Coefficient of performance of a refrigerator \( \text{COP} = \text{benefit}/\text{cost} = \frac{Q_c}{W} \)

COP of a heat pump \( \text{COP}_{\text{HP}} = \frac{Q_h}{W} = \frac{Q_h}{(Q_h - Q_c)} \)

A Carnot engine is a reversible engine working in Carnot cycle,
1. A quasi-static isothermal absorption of heat from a hot reservoir \( T_h \)
2. A quasi-static adiabatic expansion to a lower temperature \( T_c \)
3. A quasi-static isothermal heat release to a cold reservoir at \( T_c \)
4. A quasi-static adiabatic compression back to the original state \( T_h \)

Conditions for reversibility of processes:
1. No dissipative losses such as friction, viscous forces, etc.
2. Heat transfer occurs only between objects with (almost) equal temperatures
3. The process is quasistatic so that the system is always in an equilibrium state

**The above make the reversible processes extremely slow!**
Carnot efficiency,
\[ e = \frac{W}{Q_h} = 1 - \frac{Q_c}{Q_h} \]
\[ e = 1 - \frac{T_c}{T_h} \]
is the highest possible efficiency of an engine operating between the hot and cold reservoirs with temperatures \( T_c \) and \( T_h \).

The ratios of thermodynamic temperatures of two reservoirs is defined by the ratio of the heat released and absorbed by the Carnot engine operating between these two reservoirs,
\[ \frac{T_c}{T_h} = \frac{Q_c}{Q_h} \]

The temperature of the triple point of water is \( T_{\text{triple}} = 273.16 \text{K} \).

Entropy is a measure of disorder and is related to the probability. The entropy difference between two nearby states is determined by the heat \( dQ_{\text{rev}} \) absorbed during the reversible transition between these two states,
\[ \Delta S = \frac{dQ_{\text{rev}}}{T} \]

The entropy is always positive. The entropy change can be positive or negative.
The increase in entropy by $\Delta S$ makes the amount of energy

$$W_{\text{lost}} = T \Delta S$$

unavailable for doing work

The entropy of any closed insulated system (including the universe!) remains the same if the process is reversible and always increases as a result of ANY irreversible process!