The Second Law of Thermodynamics

We observe that heat always flows spontaneously from a warmer object to a cooler one, although the opposite would not violate the conservation of energy.

This direction of heat flow is one of the ways of expressing the second law of thermodynamics:

The Second Law of Thermodynamics:

When objects of different temperatures are brought into thermal contact, the spontaneous flow of heat that results is always from the high temperature object to the low temperature object. Spontaneous heat flow never proceeds in the reverse direction.
Heat Engines

A heat engine is a device that converts heat into work. A classic example is the steam engine. Fuel heats the water; the vapor expands and does work against the piston; the vapor condenses back into water again and the cycle repeats.

All heat engines have:
- a working substance
- a high-temperature reservoir
- a low-temperature reservoir
- a cyclical engine
Efficiency of a Heat Engine

Assumption:
\( \Delta U = 0 \) for each cycle, else the engine would get hotter (or colder) with every cycle.

An amount of heat \( Q_h \) is supplied from the hot reservoir to the engine during each cycle. Of that heat, some appears as work, and the rest, \( Q_c \), is given off as waste heat to the cold reservoir.

\[
W = Q_h - Q_c
\]

The efficiency is the fraction of the heat supplied to the engine that appears as work.

\[
e = \frac{W}{Q_h}
\]
Efficiency of a Heat Engine

The efficiency can also be written:

\[
e = \frac{W}{Q_h} = \frac{Q_h - Q_c}{Q_h} = 1 - \frac{Q_c}{Q_h}
\]

SI unit: dimensionless

In order for the engine to run, there must be a temperature difference; otherwise heat will not be transferred.
The maximum-efficiency heat engine is described in Carnot’s theorem:

If an engine operating between two constant-temperature reservoirs is to have maximum efficiency, it must be an engine in which all processes are reversible. In addition, all reversible engines operating between the same two temperatures, \( T_c \) and \( T_h \), have the same efficiency.

This is an idealization; no real engine can be perfectly reversible.
The efficiency of the Carnot Cycle:

\[ e_{\text{max}} = 1 - \frac{T_c}{T_h} \]
Maximum Work from a Heat Engine Cycle

**Maximum Efficiency of a Heat Engine**

\[ e_{\text{max}} = 1 - \frac{T_c}{T_h} \]

The maximum work a heat engine can do is then:

\[ W_{\text{max}} = e_{\text{max}} Q_h = \left(1 - \frac{T_c}{T_h}\right)Q_h \]

If the two reservoirs are at the same temperature, the efficiency is zero.

The smaller the ratio of the cold temperature to the hot temperature, the closer the efficiency will be to 1.
Refrigerators, Air Conditioners, and Heat Pumps

While heat will flow spontaneously only from a higher temperature to a lower one, it can be made to flow the other way if work is done on the system. Refrigerators, air conditioners, and heat pumps all use work to transfer heat from a cold object to a hot object.
If we compare the heat engine and the refrigerator, we see that the refrigerator is basically a heat engine running backwards – it uses work to extract heat from the cold reservoir (the inside of the refrigerator) and exhausts to the kitchen. Note that

\[ Q_h = Q_c + W \]

- more heat is exhausted to the kitchen than is removed from the refrigerator.
Refrigerators

An ideal refrigerator would remove the most heat from the interior while requiring the smallest amount of work. This ratio is called the coefficient of performance, COP:

\[
\text{Coefficient of Performance for a Refrigerator, COP} \quad \text{COP} = \frac{Q_c}{W}
\]

SI unit: dimensionless

Typical refrigerators have COP values between 2 and 6. Bigger is better!

An air conditioner is essentially identical to a refrigerator; the cold reservoir is the interior of the house, and the hot reservoir is outdoors.
Finally, a heat pump is the same as an air conditioner, except with the reservoirs reversed.

Heat is removed from the cold reservoir outside, and exhausted into the house, keeping it warm.

Note that the work the pump does actually contributes to the desired result (a warmer house) in this case.
Heat Pump Efficiency

In an ideal heat pump with two operating temperatures (cold and hot), the Carnot relationship holds; the work needed to add heat $Q_h$ to a room is:

$$W = Q_h - Q_c = Q_h \left(1 - \frac{Q_c}{Q_h}\right) = Q_h \left(1 - \frac{T_c}{T_h}\right)$$

The COP for a heat pump:

**Coefficient of Performance for a Heat Pump, COP**

$$\text{COP} = \frac{Q_h}{W}$$

SI unit: dimensionless
Performance measures

Engine: we want work with minimum energy (heat) input

Refrigerator: we want maximum $Q_c$ removed for minimum cost of $W$

Heat Pump: we want maximum $Q_H$ added for minimum cost of $W$

Efficiency of a Heat Engine, $e$

$$e = \frac{W}{Q_h} = \frac{Q_h - Q_c}{Q_h} = 1 - \frac{Q_c}{Q_h}$$

SI unit: dimensionless

Coefficient of Performance for a Refrigerator, COP

$$COP = \frac{Q_c}{W}$$

SI unit: dimensionless

Coefficient of Performance for a Heat Pump, COP

$$COP = \frac{Q_h}{W}$$

SI unit: dimensionless
A reversible engine has the following relation between the heat transferred and the reservoir temperatures:

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

Rewriting,

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

This quantity, \(Q/T\), is the same for both reservoirs. This conserved quantity is defined as the change in entropy.
Entropy

Like internal energy, entropy is a state function.

Unlike energy, entropy is NOT conserved.

In a reversible heat engine, the entropy does not change.
Entropy

A real engine will operate at a lower efficiency than a reversible engine; this means that less heat is converted to work.

\[
1 - \frac{Q_c}{Q_h} < 1 - \frac{T_c}{T_h}
\]

\[
\frac{Q_c}{T_c} > \frac{Q_h}{T_h}
\]

\[
\Delta S_{\text{total}} = -\frac{Q_h}{T_h} + \frac{Q_c}{T_c} > 0 \quad \text{for irreversible processes}
\]

Any irreversible process results in an increase of entropy.
To generalize:

- The total entropy of the universe increases whenever an irreversible process occurs.
- The total entropy of the universe is unchanged whenever a reversible process occurs.

Since all real processes are irreversible, the entropy of the universe continually increases. If entropy decreases in a system due to work being done on it, a greater increase in entropy occurs outside the system.
Entropy
Order, Disorder, and Entropy

Entropy can be thought of as the increase in disorder in the universe.

In this diagram, the end state is less ordered than the initial state – the separation between low and high temperature areas has been lost.
Entropy

As the total entropy of the universe increases, its ability to do work decreases.

The excess heat exhausted during an irreversible process cannot be recovered into a more organized form of energy, or temperature difference.

Doing that would require a net decrease in entropy, which is not possible.

It's the Second Law of Thermodynamics: Sooner or later everything turns to sh**.