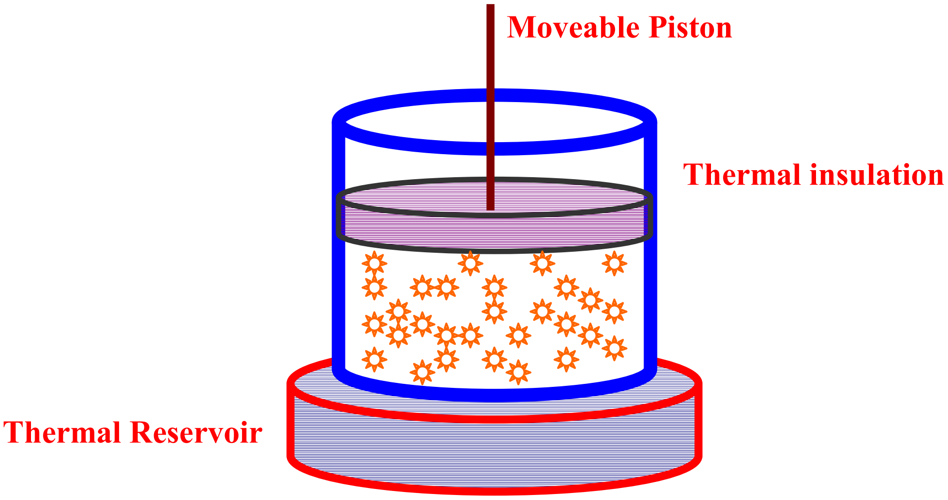
First Law of Thermodynamics

Consider a thermodynamic system consisting of a thermally insulated container of gas molecules that can absorb heat from or transfer heat into a **thermal reservoir**.

A piston with cross-sectional area **A** can either do work **on** the system or extract work **from** the system.

The gas has **intrinsic parameters {P, T, V, N}**



Systems evolve from initial equilibrium **{P, T, V, N specified}** to a final equilibrium configuration with **{P, T, V, N specified}**.

State functions depend only on intrinsic variables and changes in these functions depend on the starting point and ending point with path independence in between.

Internal energy is a state function, depending only on **T**

Heat and work are not state functions and therefore path dependent quantities.

The 'path' referred to is in **P-V space**, i.e., Pressure vs. Volume. The evolution of the system may be graphed P versus V.

To see why **work** is not a state function, consider the **work done by the system** during an expansion. For this evaluate the piston displacement:

$$W = \vec{F} \bullet \vec{d} = F\frac{A}{A}d = PV$$

Isobaric (constant pressure) process.

In general,

$$W = \int_{V_i}^{V_f} PdV$$

➔ **Work is the area underneath the P-V curve.**

Since this area depends on the path taken, **work is path dependent**.

Work, internal energy, and heat are related by the **1st Law of Thermodynamics**:

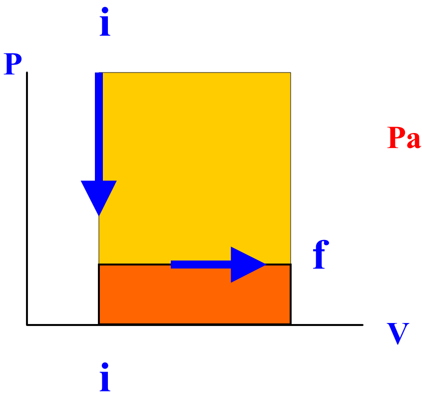
$$U = Q - W$$

{W **is work done by the system**}

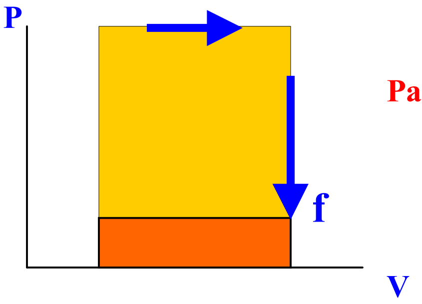
Then since internal energy is a state function **heat must also be path dependent**.

Path dependence and P-V diagrams

An example shows the path dependence of W:



Path 1 here gives W as the orange area Pa*m^3 = Joules



Path 2 gives W as the orange+gold areas Pa*m^3 =Joules

1) **Q positive ➔ System absorbs energy; Q negative ➔ System gives off energy**
2) **W is positive for expansions against external force; W is negative for $V_f < V_i$**
3) **U increases with increasing T and U decreases as temperature is reduced.**

Special Cases of the 1st Law of Thermodynamics

Adiabatic Process: Transition from initial to final states take place either very rapidly or in a well insulated system such that **$Q = 0$**, No heat is exchanged.

The 1st Law ➔

$$\Delta U = -W$$

If the system does work, $W > 0$ ➔ decreasing U
If work is done on the system, $W < 0$ ➔ increasing U

In **throttling** a gas confined in a container under pressure undergoes a **free expansion** into an evacuated container by route of a small orifice.

In aerosol throttling, liquid expands passing through a small orifice and vaporizes into a gas. The phase change requires heat and since the process is adiabatic, this heat comes from the liquid reducing its temperature. The can cools.

Isochoric or Isovolumetric Process: Volume is held constant such that **$W = P\Delta V = 0$**.

The 1st Law ➔

$$\Delta U = Q$$

All changes in **U** are due to heat input or extracted from the system.

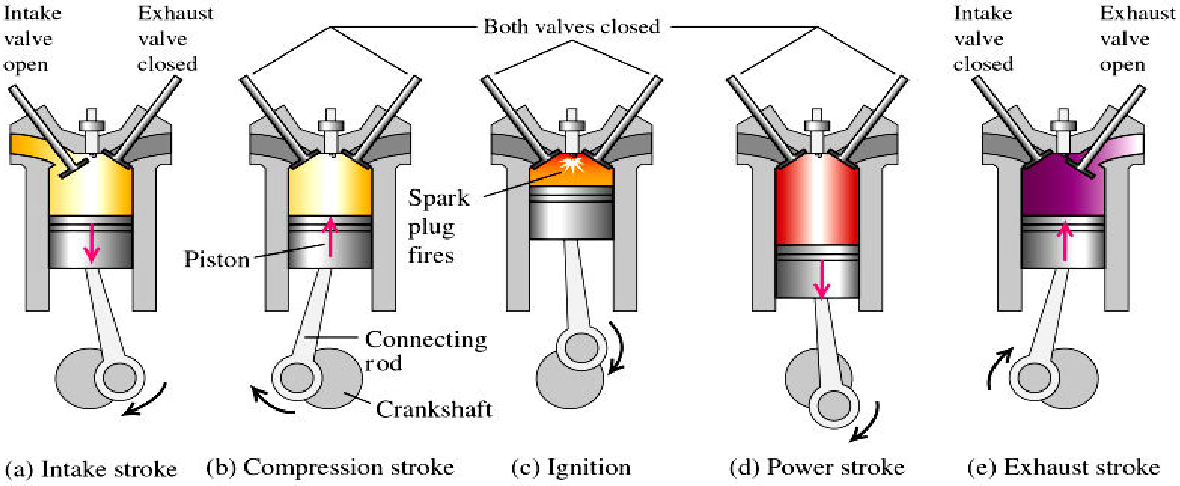
Sealed beverages in a refrigerator are cooled isochorically as heat is extracted.

Cyclic Processes A cyclic process is represented by a closed loop in P-V space. As the system evolves through the cycle **$\Delta U = 0$.**

The 1st Law ➔ $$W = Q$$

Cyclic processes are of general importance in **heat engines** that take a working substance, like gasoline/air, through a closed series of thermodynamic steps to extract work output from heat input.

1) **Intake of fuel and air**
2) **Compression of the mixture**
3) **Ignition by spark causing expansion and work done**
4) **Exhaust of combustion products.**



The compression stroke and power strokes are approximately adiabatic.

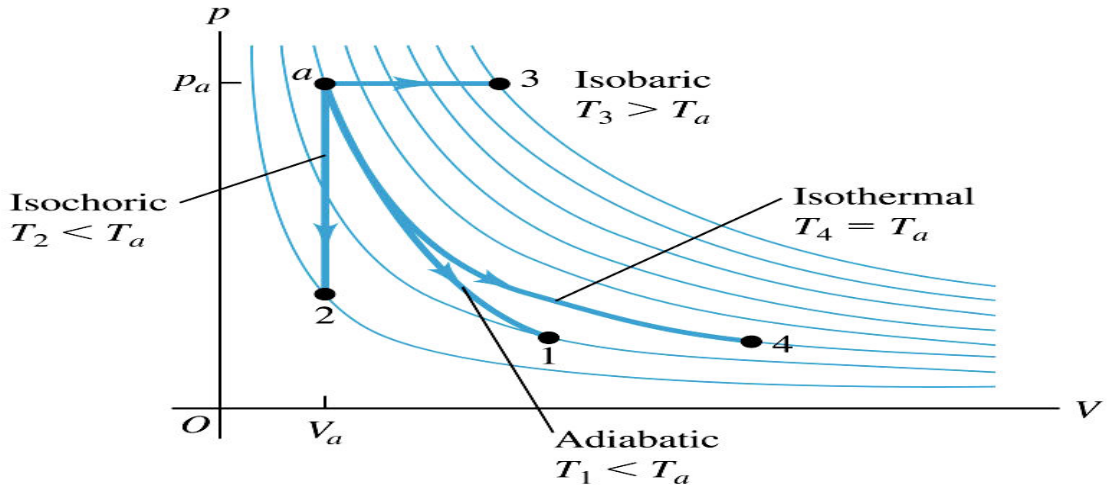
A **pV diagram** of the four-stroke process is the **Otto Cycle**:

Free Expansion: Gas expanding adiabatically into a vacuum does no work since there isn't any pressure resisting the expansion. Since the process is adiabatic, heat exchange is also zero.

The 1st Law ➔ $$Q = W = \Delta U = 0$$

Thermodynamic Processes

Thermodynamic processes of interest currently are summarized in the figure below.



Note the difference between an adiabatic curve and an isothermal curve.

Adiabatic Expansion of an Ideal Gas

Adiabatic processes either takes place in a well-insulated enclosure or at such a fast rate that in either case, zero heat is exchanged with the environment.

$$PV^{\gamma} = Const \qquad \gamma = \frac{C_P}{C_V} = \frac{5}{3}$$ Ideal monatomic gas.

$$TV^{\gamma-1} = Const$$

Process	Constant Quantity	Relation Between Parameters
Isobaric	**Pressure**	$Q = nC_P\Delta T$ **And** $W = P\Delta V$
Isothermal	**Temperature**	$Q = W = nRT\ln\left\{\frac{V_f}{V_i}\right\}$ **And** $\Delta U = 0$
Isochoric	**Volume**	$Q = \Delta U = nC_V\Delta T$ **And** $W = 0$
Adiabatic	PV^{γ} **And / Or** $TV^{\gamma-1}$	$Q = 0$ **And** $\Delta U = -W$

Entropy & the 2nd Law of Thermodynamics

Nature spontaneously tends to disorder. Thermodynamic processes evolve towards an equilibrium state via a route by which final state **entropy** will be maximized.

Entropy is a state function. $\Delta S_{Cycle} = 0$ **Reversible processes**

For **irreversible processes,** system evolution moves beyond **quasi-equilibrium** and paths in thermodynamic space are not retraceable. Information is lost.

Since entropy is a state function, ΔS may be quantitatively evaluated by using a **reversible** evolution between the same initial and final states.

Change in entropy is related to the amount of heat added to or extracted from a system and the temperature at which that addition or extraction takes place.

$$\Delta S = \frac{\Delta Q}{T}$$

Isothermal Process

If the process **isn't** isothermal, but ΔT is small relative to temperatures involved, then:

$$\Delta S = S_f - S_i \cong \frac{Q}{T_{avg}}$$

Small ΔT Process

Entropy changes generally result from volume changes, temperature changes, or number of molecules. Keeping n fixed, the first law of thermodynamics gives:

$$\Delta S = S_f - S_i = nC_V \ln\frac{T_f}{T_i} + nR\ln\frac{V_f}{V_i}$$

For all thermodynamic processes and the universe,

1) $$\Delta S = S_f - S_i \geq 0$$ **Equality true only for reversible processes**

2) **Most if not all real processes are irreversible.**

3) **Time's arrow may be indicated by entropy.**

Statistical Entropy

The **Boltzmann** definition of entropy is in terms of accessible **microstates** and characterizes entropy using the **multiplicity** of microstates for a given **configuration.**

Entropy is $S = k \ln W$ where W is the **multiplicity** of microstates.

The **configuration** with greatest multiplicity maximizes entropy and is equilibrium.

Let four molecules be distributed into two halves of a thermally insulated container. There are $2^N = 2^4 = 16$ ways to arrange the molecules:

Left Side of Container	**Right Side of Container**
None	**1,2,3,4**
1	**2,3,4**
2	**1,3,4**
3	**1,2,4**
4	**1,2,3**
1,2	**3,4**
1,3	**2,4**
1,4	**2,3**
2,3	**1,4**
2,4	**1,3**
3,4	**1,2**
1,2,3	**4**
1,2,4	**3**
1,3,4	**2**
2,3,4	**1**
1,2,3,4	**None**

There are two ways for which all the molecules are in one side only.

There are six ways for the molecules to be split evenly between the two sides.

Multiplicities for these configurations are the binomial factors:

$(4\_choose\_2) = \frac{4!}{2!*2!} = 6$ And $(4\_choose\_4) = \frac{4!}{4!*0!} = 1$

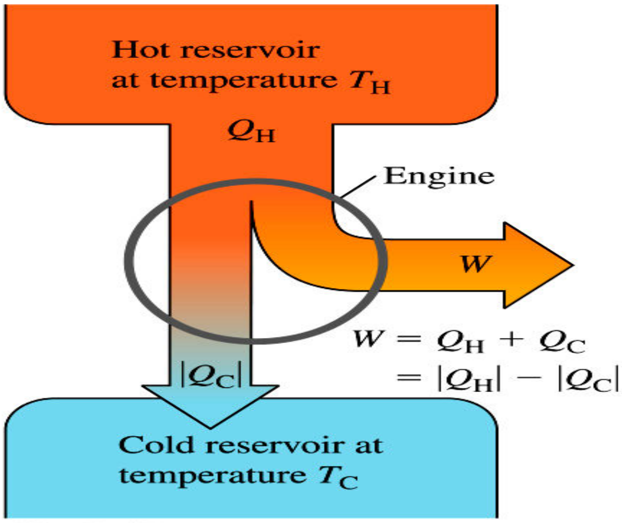
As systems evolve to equilibrium, free energy is reduced and the number of accessible states consistent with energy constraints is maximized. This configuration becomes the most probable and is therefore the configuration of maximum entropy.

All microstates are equally probable, not all configurations are equally probable:

Given the 16 possible states total, the probability that all molecules are in the left side of the container is 1 / 16 = 0.0625. For a 50/50 split, the probability is 6/16 = 0.375. The latter is the most probable configuration.

Heat Engines

Heat engines operate between a high and low temperature gradient to transform heat into work or mechanical energy.



The engine **working substance** receives heat $\mathbf{Q_H}$ at $\mathbf{T_H}$ and ejects heat $\mathbf{Q_C}$ at $\mathbf{T_C}$. The work done by the engine is:

$$W = Q_H - Q_C$$

$$\Delta S = \Delta S_H - \Delta S_C = \frac{Q_H}{T_H} - \frac{Q_C}{T_C}$$

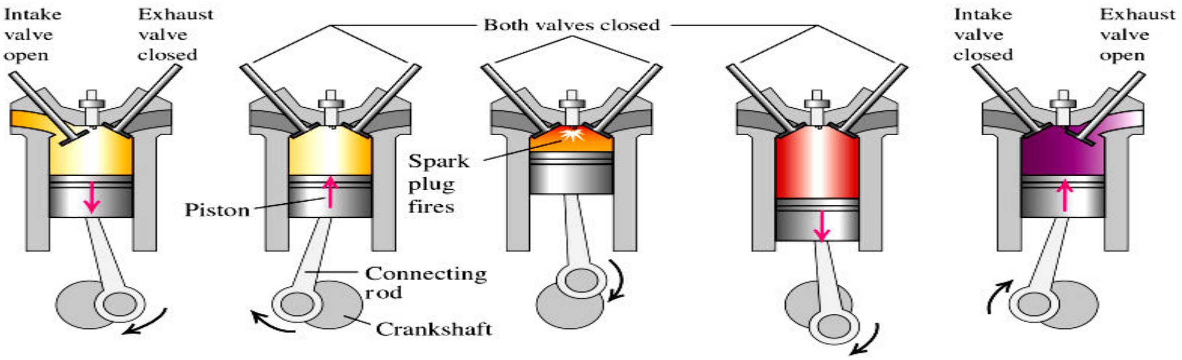
Efficiency is defined:

$$\varepsilon = \frac{W}{Q_H} = 1 - \frac{Q_C}{Q_H}$$

For an ideal engine all processes are reversible and $\Delta S = S_f - S_i = 0$

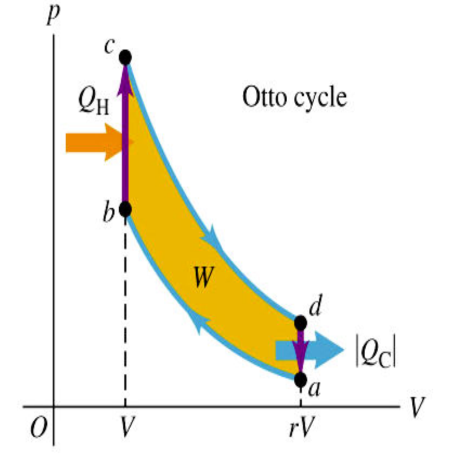
The efficiency for an ideal engine is then: $\varepsilon = \frac{W}{Q_H} = 1 - \frac{T_C}{T_H}$

A non-ideal automobile 4-cycle engine can be approximated by the **Otto cycle**:



(a) Intake stroke (b) Compression stroke (c) Ignition (d) Power stroke (e) Exhaust stroke

The **Otto Cycle**:



$a \rightarrow b$: Compression stroke
(adiabatic compression)
$b \rightarrow c$: Ignite fuel
(heating at constant volume)
$c \rightarrow d$: Power stroke
(adiabatic expansion)
$d \rightarrow a$: Reject heat to environment
(cooling at constant volume)

The compression stroke and power strokes are approximately adiabatic.

The efficiency is found by evaluating: $\varepsilon = \dfrac{W}{Q_H} = 1 - \dfrac{Q_C}{Q_H}$

$$Q_H = nC_V(T_c - T_b)$$

$$Q_C = nC_V(T_d - T_a)$$

$$\varepsilon = 1 - \frac{Q_C}{Q_H} = 1 - \frac{T_d - T_a}{T_c - T_b}$$

For the adiabatic compression and power strokes:

$$T_a(rV)^{\gamma-1} = T_b V^{\gamma-1} \qquad T_d(rV)^{\gamma-1} = T_c V^{\gamma-1}$$

$$\varepsilon = 1 - \frac{T_d - T_a}{T_c - T_b} = 1 - \frac{1}{r^{\gamma-1}}$$

For a compression ratio of eight and $\gamma=1.4$ this efficiency is ~56%. This is greater than efficiencies seen in real engines where losses due to friction and incomplete combustion are significant.

In **diesel engines**, compression ratios are a factor of two greater than in normal gas engines. Diesel fuel injected just before the power stroke ignites spontaneously due to high temperatures generated during the compression stroke.

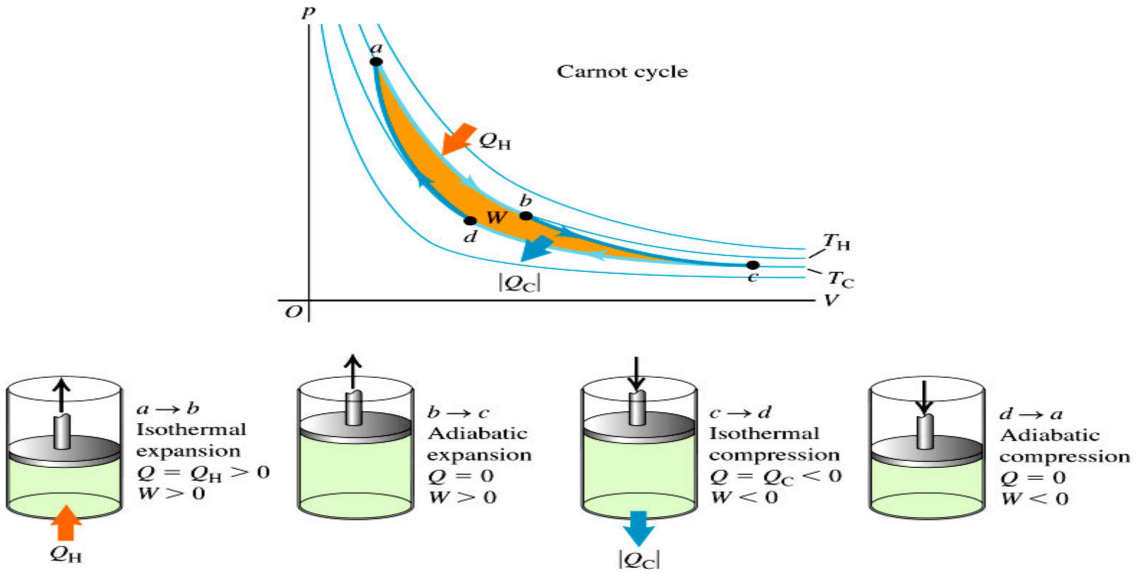
The 2nd Law of Thermodynamics stated by Kelvin and Planck is:

It is impossible to construct a heat engine that converts all heat input into an equal amount of work output. ε is never unity.

A **reversible** heat engine is known as a **Carnot** engine.

Carnot Cycle

Carnot engines cycle reversibly through two isothermal / adiabatic steps as shown.



Heat is added and extracted from the gas isothermally making the process reversible.

On the isotherms, $\Delta U = 0$

$$Q_H = W_{ab} = nRT_H \ln\frac{V_b}{V_a} \qquad Q_C = W_{cd} = nRT_C \ln\frac{V_d}{V_c}$$

Adiabatically $T_H V_b^{\gamma-1} = T_C V_c^{\gamma-1}$ $\qquad T_H V_a^{\gamma-1} = T_C V_d^{\gamma-1}$

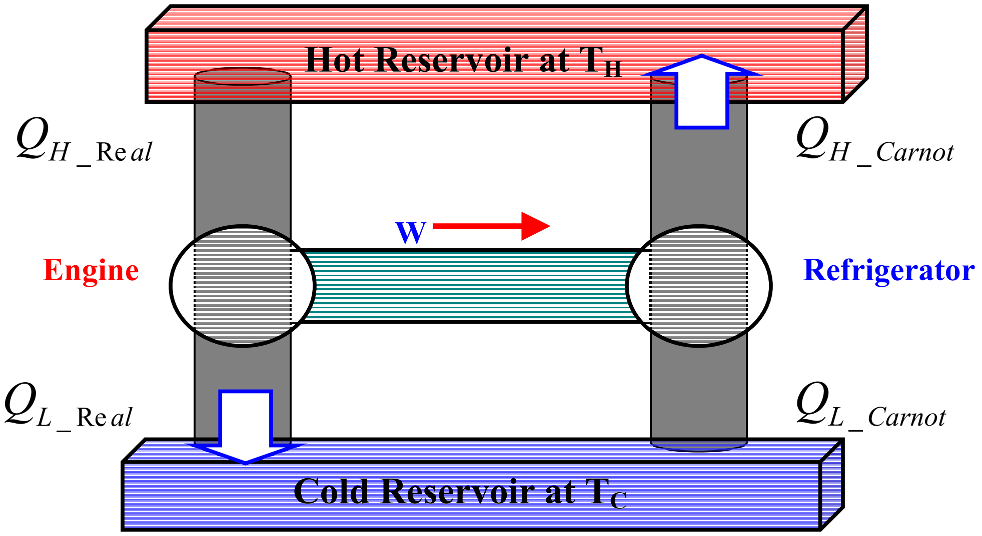
$$\varepsilon = 1 - \frac{Q_C}{Q_H} = 1 - \frac{T_C}{T_H} * \frac{\ln(V_c/V_d)}{\ln(V_b/V_a)}$$

$$\varepsilon_{Carnot} = 1 - \frac{T_C}{T_H}$$

No **real engine** is more efficient than a Carnot engine.

Imagine a **real engine** (work output as heat is moved from high→low) attached to a **Carnot** refrigerator (input work in order to move heat from low to high).

Let these two engines run from the **same** temperature reservoirs.



If $\varepsilon_{Real} > \varepsilon_{Carnot}$

$$\frac{W}{Q_{H\_Real}} > \frac{W}{Q_{H\_Carnot}}$$

$$Q_{H\_Real} < Q_{H\_Carnot}$$

The work output from the real engine is the work input to the Carnot refrigerator.

$$Q_{H\_\mathrm{Real}} - Q_{L\_\mathrm{Real}} = Q_{H\_Carnot} - Q_{L\_Carnot}$$

$$Q_{H\_\mathrm{Real}} - Q_{H\_Carnot} = Q_{L\_\mathrm{Real}} - Q_{L\_Carnot} < 0$$

Leading to the two conditions

$$Q_{H\_\mathrm{Real}} < Q_{H\_Carnot} \qquad\qquad Q_{L\_\mathrm{Real}} < Q_{L\_Carnot}$$

More heat is going into the high reservoir than is extracted by the real engine and more heat is leaving the low reservoir than is input from the real engine. Heat appears to be spontaneously transferred from the cold to the hot reservoir.

This violates Clausius' statement of the 2nd Law of Thermodynamics:

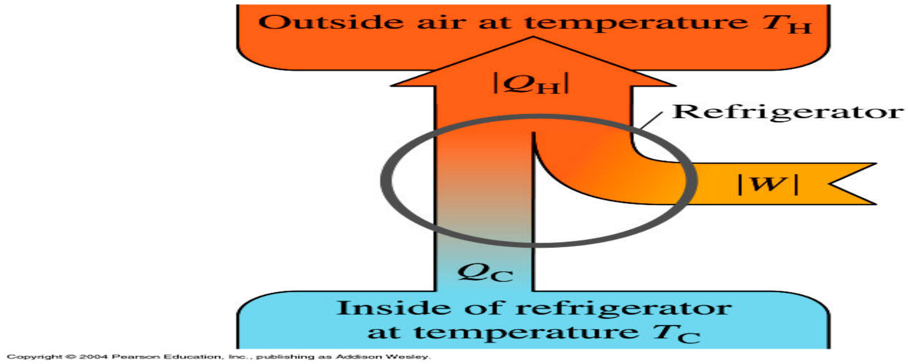
It is impossible for any process to have as its sole result the transfer of heat from a cooler to a hotter body.

Real engines are irreversible due to friction and the speed with which the working substance is cycled both of which lead to non-equilibrium conditions.

Refrigerators

Operated in reverse the heat engine becomes a refrigerator or air conditioner. Work is input in order to move heat from a low temperature into a high temperature reservoir.

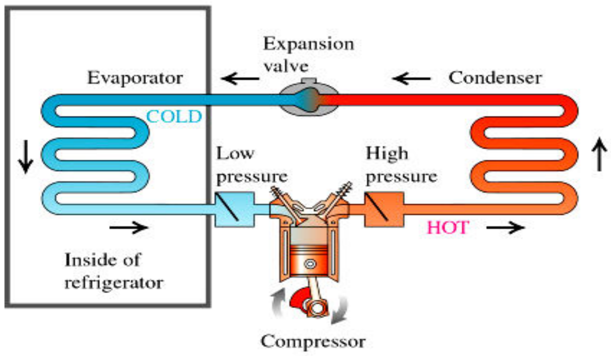
Schematically:



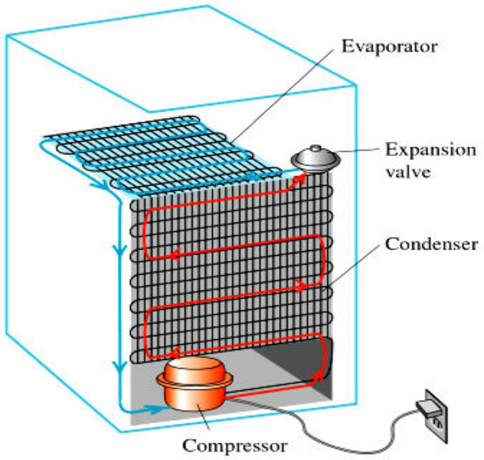
The **coefficient of performance** for a refrigerator is $K = \dfrac{Q_C}{W} = \dfrac{Q_C}{Q_H - Q_C}$

The working substance in a refrigerator, the refrigerant, is compressed to high pressure and high temperature and passed through a condenser where it gives off heat and **partially** condenses.

An expansion valve controls the rate at which the refrigerant undergoes expansion into an internal evaporator where it now expands, cools, absorbs heat from the interior and **partially** vaporizes.



(a)



(b)

Third Law of Thermodynamics

The Kelvin-Planck statement of the Second Law indicates that ε can never equal unity.

Since the most efficient engine has $\varepsilon = \dfrac{W}{Q_H} = 1 - \dfrac{T_L}{T_H}$ the second law is implying the **3rd Law of Thermodynamics** $T_L \equiv 0$ **is impossible**.

Lowering a given temperature may be accomplished by placing the system in thermal contact with a system at lower temperature. To lower the temperature again requires another system at even lower temperature and so on ad infinitum. Absolute zero cannot be reached in a finite number of steps.

Quantum Mechanics also restricts simultaneous measurement of arbitrary precision of the location and momentum of an atom. At absolute zero, all motion would cease and we would have momentum and position knowledge simultaneously with absolute precision.