School of Physics and Astronomy

Junior Honours **Thermodynamics** $\boxed{\text{GJA 2019-2020}}$

Lecture TOPIC 4 (Finn: 4.1, 4.2, 4.3, 4.4, 4.5, 4.6)

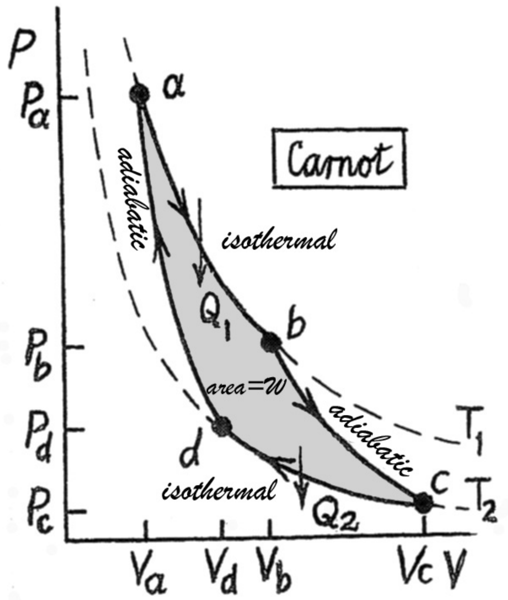
Synopsis: Cyclic processes: Carnot cycle; heat engines. The Second Law of Thermodynamics. Time. Carnot's Theorem.

Cyclic processes - introduction to the Carnot cycle and engine

A *reversible cyclic* process is one where the cycled system returns to its initial (equilibrium) state on the completion of each cycle with all processes quasi-static and reversible. During the cycle the values of the state variables change, with the system exchanging heat as well as mechanical energy with its surroundings. The simplest reversible cycle is the Carnot cycle comprising sequentially isothermal expansion, adiabatic expansion, isothermal compression, and adiabatic compression. This is particularly simple because heat is only exchanged along the two isotherms. In the sketch (which is for a system consisting of an ideal gas) the net work done is represented by the area inside the closed curve. The Carnot cycle is useful for illustrating general principles and describing heat engines, heat pumps and refrigerators. We will analyse a single cycle, but note that engine power depends on the number of cycles/sec. Isothermal processes tend to be slow, so the Carnot cycle is not useful for practical engines.

The Carnot cycle and engine

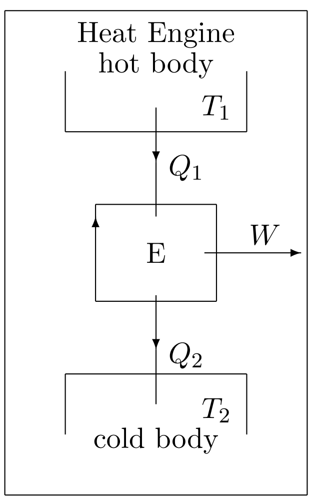
The four-stage Carnot cycle is shown. Any fluid known as the **working substance** may be taken around the cycle. The surroundings consist of two constant temperature heat reservoirs, one at T_1 and the other at $T_2 < T_1$, and some means (such as pistons) to allow the exchange of mechanical energy with other devices. The system and surroundings comprise the hypothetical *Carnot engine*. It operates reversibly between the two heat reservoirs, with, in each cycle, heat Q_1 entering at T_1, Q_2 leaving at T_2 and work W being delivered. If the working substance is not an ideal gas, the shapes of the isotherms and adiabatics will be (slightly) different from those shown.



The efficiency of a heat engine

A generalised engine is illustrated schematically opposite. *This engine still operates in cycles, with its working substance always returning to the same thermodynamic state at the end of each cycle.* Thermodynamic efficiency analysis is done in work/heat *per cycle*: in reality the *power* produced is often more important:

$$\text{Power} = \text{Work per cycle} \times \text{cycles per second}$$



Q_1, Q_2 and W are heat supplied to, heat rejected by and work done **by** the working substance. The work done **on** the working substance is $-W$, and the First Law takes the form $\Delta U = Q_1 - Q_2 + (-W) = 0$ for each complete cycle. From this, $W = Q_1 - Q_2$, and the efficiency η of the engine is defined by

$$\boxed{\eta = W/Q_1 = 1 - Q_2/Q_1}$$

The Second Law of Thermodynamics

The Second Law puts restrictions on which processes may occur, or more particularly which processes can never occur even though they are energetically possible. The properties of heat engines provide the imagery to help visualise which processes are not allowable. There are two statements of the second law that you need to know, one due to Clausius, and the other due to Kelvin modified by Planck. In contemporary language, these are:

The Clausius statement:

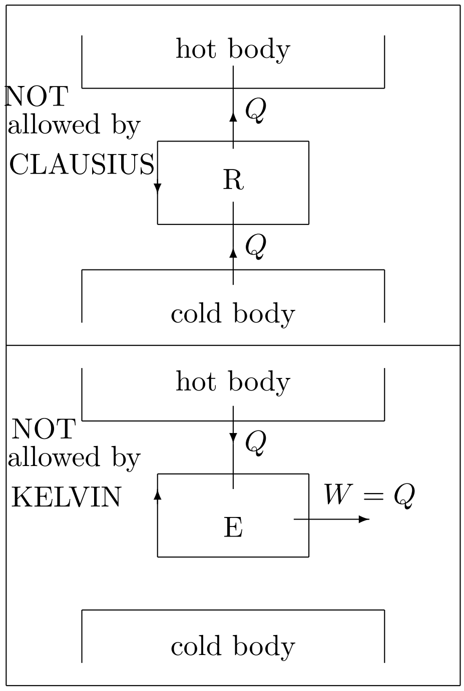
> *It is impossible to construct a device that, operating in a cycle, produces no effect other than the transfer of heat from a colder to a hotter body.*

The "R" on the diagram of the forbidden device, denotes "refrigerator".

The Kelvin-Planck statement

> *It is impossible to construct a device that, operating in a cycle, produces no effect other than the extraction of heat from a single body at a uniform temperature and the performance of an equivalent amount of work.*

The "E" on the diagram of the forbidden device, denotes "engine".

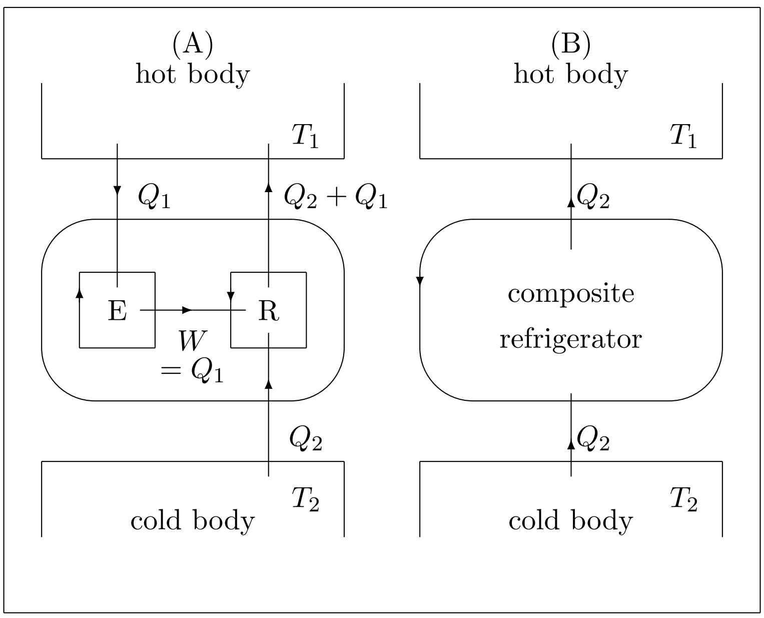


Note the use of *body* rather than *heat reservoir*, meaning that engines can be considered to operate between two bodies (one a source and the other a sink of heat) of which the hotter one cools and the colder one heats up whilst the engine is running.

The equivalence of the Clausius and the Kelvin-Planck statements

This is traditionally proved by showing that if either statement is false, so is the other.

Suppose Kelvin-Planck's statement is false. Then an engine (E) can drive a refrigerator (R), as sketched opposite, where W (equal to $Q_1$from the 1st law applied to E) is just sufficient to operate one cycle of R. If R extracts Q_2 from the cold body, it will deliver heat $Q_1 + Q_2$ (1st law applied to R) to the hot body, each cycle. E+R can be treated as a composite refrigerator, whose only effect is to transfer heat Q_2 from a colder to a hotter body, requiring Clausius's statement to also be false.
(The similar proof that if Clausius's statement is false so too is Kelvin's is left as an exercise).

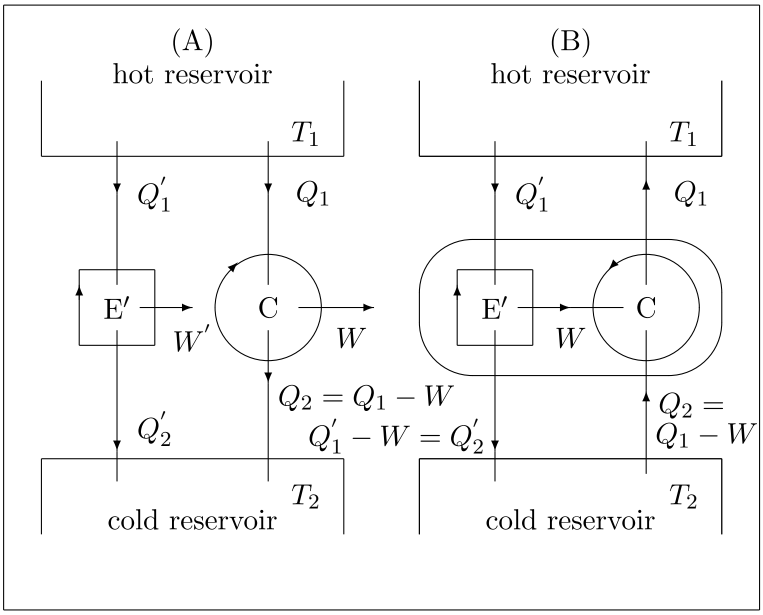


Carnot's theorem and a corollary

These are preliminaries to deducing the existence of a new state function, entropy.
Carnot's Theorem is

No engine operating between two reservoirs can be more efficient than a Carnot engine operating between the same two reservoirs.

To prove this we will examine how the efficiency of a hypothetical engine E' is restricted by Clausius's statement of the $2^{\rm nd}$ law.



Let the hypothetical engine E′ (efficiency η') and a Carnot engine C (efficiency η_C) operate between the same heat reservoirs at temperatures T_1 and $T_2 < T_1$; sketch (A) above. All stages of the Carnot engine are reversible, so it can be driven backwards. If the engines are adjusted so that $W' = |W|$, then, **assuming** $\eta' > \eta$, $W'/Q_1' = W/Q_1' > W/Q_1$ **leads to** $Q_1 > Q_1'$. That means (see diagrams) that the composite device (sketch (B))would act as a refrigerator which each cycle extracts heat $Q_1 - Q_1'$ from the lower temperature reservoir and delivers exactly the same heat to the higher temperature reservoir *without exchanging mechanical work with any other device.* This contradicts Clausius's statment of the $2^{\rm nd}$ law, so the assumption $\eta' > \eta_C$ cannot be valid. It is necessary to consider also the possibility $\eta' = \eta_C$, for which, from the diagram, $Q_1' = Q_1$. The composite device achieves nothing: heat flows are zero and there is no work exchanged. The conclusion is that the efficiency η for any real engine must therefore satisfy

$$\boxed{\eta \le \eta_C}$$

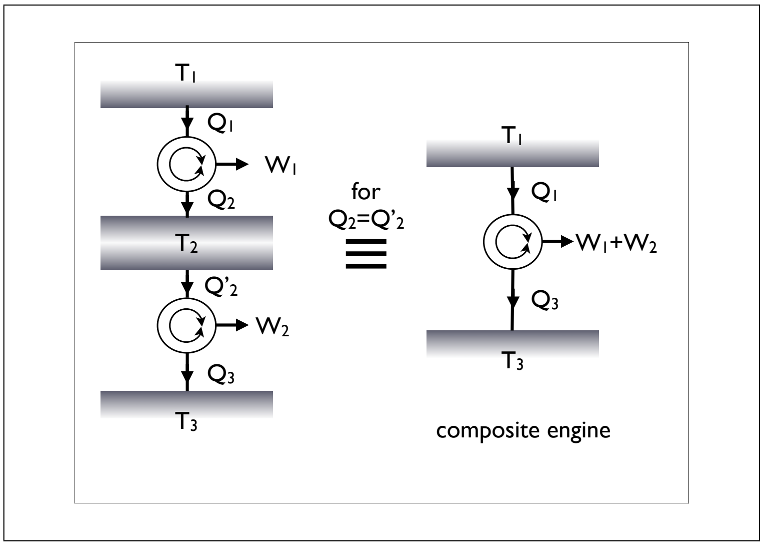
The corollary follows: make the composite device from two Carnot engines, C_a and C_b, with the first one, efficiency η_{c_a} driving the second one, efficiency η_{c_b}, backwards. Carnot's Theorem leads to $\eta_{c_a} \le \eta_{c_b}$. However, for C_b driving C_a backwards, $\eta_{c_b} \le \eta_{c_a}$. The only option is $\eta_{c_a} = \eta_{c_b}$, hence the corollary:

All Carnot engines operating between the same two reservoirs have the same efficiency (INDEPENDENT of the working substance).

Another Corollary: Unification of Temperature Definitions

We have shown that the thermodynamic efficiency of all *reversible* heat engines operating between the same two temperature reservoirs is equal (independent of the choice of working substance or process). This efficiency, $\eta = 1 - \frac{Q_2}{Q_1}$, can therefore only depend on the temperature of the reservoirs. The ratio Q_1/Q_2 is therefore some universal function f of T_1 and T_2: $Q_1/Q_2 = f(T_1, T_2)$. We can say more about the functional form of f by considering the following:

Consider two reversible engines as shown (any working substance). Per cycle, the first removes heat from reservoir at T_1 and rejects heat at T_2 doing work W_1. The size and rate of the processes of the second engine are scaled so that it is synchronised with the first engine removing heat $Q'_2 = Q_2$ per cycle from the reservoir at T_2 doing some work W_2 and rejecting heat Q_3 to a reservoir at T_3 with $T_1 > T_2 > T_3$.



For this arrangement the heat entering and leaving the reservoir at T_2 balance and so no reservoir is in fact required. The overall process is thus equivalent to the composite engine shown on the right of the figure. For the two individual engines:

$$\frac{Q_1}{Q_2} = f(T_1, T_2) \qquad (1)$$

$$\frac{Q_2}{Q_3} = f(T_2, T_3) \qquad (2)$$

While for the composite

$$\frac{Q_1}{Q_3} = f(T_1, T_3) \qquad (3)$$

with f the same universal function in all 3 expressions. Multiplying EQN 1 by EQN 2, Q_2 cancels giving an expression for Q_1/Q_3 that can be compared with EQN 3:

$$\frac{Q_1}{Q_3} = \boxed{f(T_1, T_2).f(T_2, T_3) \;=\; f(T_1, T_3)}$$

The only way the boxed expression can be satisfied is if the function f factorises,

$$f(T_1, T_2) = \frac{\theta(T_1)}{\theta(T_2)}$$

with $\theta(T)$ a universal function of temperature for a given choice of temperature scale. We have thus found a 'natural' temperature scale, θ, that can be expressed as a function of our arbitrary practical temperature scale.

Remarkably, the 'temperature' which determines engine efficiency, is the same as the one which determines direction of heat flow, and the one in the ideal gas equation, and the one in kinetic theory of gasses, and the one in statistical mechanics. If system A has higher temperature than system B according to one definition, then A will have higher temperature than B according to all definitions.