4 ENGINES.

4.1 Heat Engines.

We now know that in taking a fluid around a closed cycle on a PV diagram

(i) The internal energy is unchanged, $\Delta U = 0$

(ii) The work done on/by the system depends on the details of the path taken. In a clockwise cycle work is done by the system whereas the same cycle counter clockwise results in work done on the system.

(iii) The heat flow into/from the system depends on the details of the path taken. In a clockwise cycle heat flows into the system whereas the same cycle counter clockwise results in heat flowing from the system.

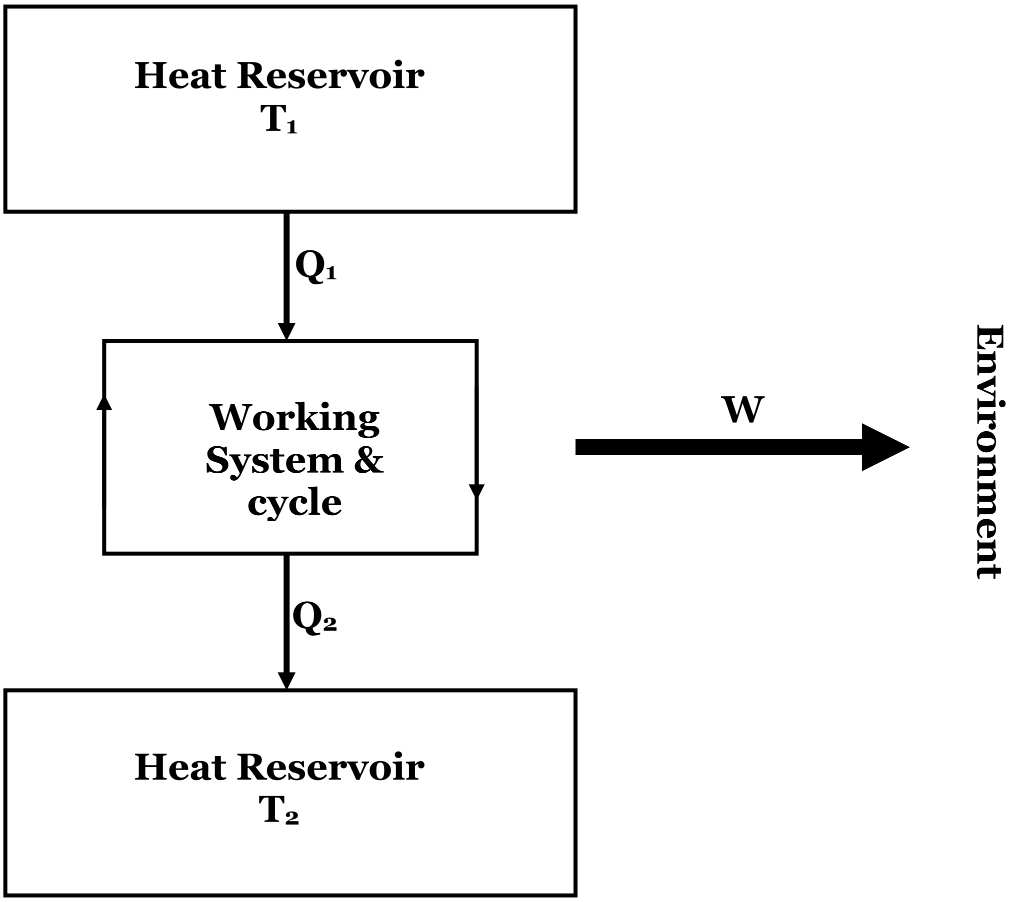
(iv) From the first law, $\not{\Delta} Q = -\not{\Delta} W$

A reversible cycle is any cycle that can be operated reversibly, in one sense absorbing heat and giving out work. For true reversibility **the heat flow must take place with infinitesimal temperature differences between the system and surroundings**. In real engines which are not reversible (friction, finite pressure, leaky valves and temperature differences) normally heat is fed in at high temperature and waste heat is discarded at low (usually ambient) temperature.
eg.

STEAM ENGINE	Superheated steam in.	Condensed water out
PETROL ENGINE	Hot ignited petrol vapour + air in	Cooler exhaust gases out.

As all engines may be thought of as heat engines with a hot source reservoir and a cold reservoir for discarded heat we are going to idealise the concept of an engine to make it easier to analyse. The idealisation involves a hot heat reservoir at temperature T_1 and a low temperature heat reservoir at temperature T_2. A working system will extract heat, Q_1 , from the former, deliver heat, Q_2 , to the latter and do an amount of work, W.

NB. The heat reservoirs by definition can lose or accept heat without their temperature changing,



Above is the schematic of the engine, this schematic and similar will be used frequently in the following discussions/descriptions of **heat engines, refrigerators** and **heat pumps**. All three of these devices use a working substance to alter the environment in some way, by doing work, extracting heat or delivering heat respectively.

Efficiency of a Heat Engine

It is easy to devise a meaningful measure of the efficiency or figure of merit for an engine. As its name suggests the larger it is the better also

$$\eta = efficiency\ =\ figure\ \ of\ \ merit = \frac{What\ \ we\ \ get\ \ out}{What\ \ we\ \ put\ \ in}$$

In the case of the engine we get out work, W. What we put in is heat from the hot reservoir, Q_1. It follows from our definition of efficiency or figure of merit that this is given by

$$\eta_E = \frac{W}{Q_1}$$

We can use the first law to adapt this as follow. The system operates in a cycle and therefore

$$\Delta U = 0 = \Delta Q + \Delta W = (Q_1 - Q_2) - W$$ **Note the signs!**

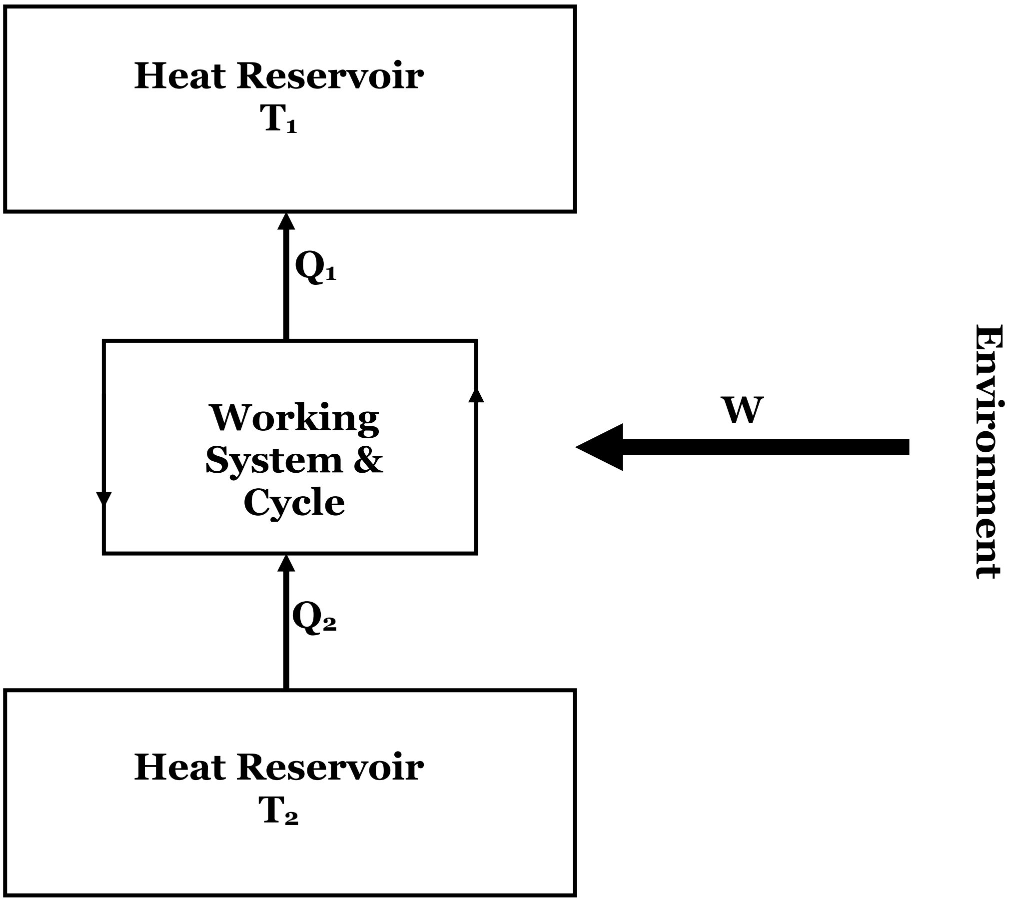
or

$$W = Q_1 - Q_2$$

And therefore

$$\eta_E = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1}$$

Refrigerators and Heat Pumps



Refrigerators are simply heat engines cycled in the opposite direction, work in takes heat out as shown in the above schematic where work, W, is done on the working system and heat, Q_2 is extracted from the cold reservoir at the end of a cycle.

The heat pump is identical in operation to the refrigerator except that the focus is on delivering heat Q_1 to the hot reservoir. We may write the figures of merit for the refrigerator or heat pump with the same considerations used for the engine

$$\eta = efficiency = figure \quad of \quad merit = \frac{What \;\; we \;\; get \;\; out}{What \;\; we \;\; put \;\; in}$$

For a <u>refrigerator</u> this is

$$\eta_R = \frac{Q_2}{W}$$

And using the first law

$$W = W_{in} = Q_{Out} = Q_1 - Q_2$$

it may be written as

$$\eta_R = \frac{Q_2}{Q_1 - Q2} = \frac{1}{\frac{Q_1}{Q_2} - 1}$$

For a <u>heat pump</u> this is

$$\eta_{HP} = \frac{Q_1}{W}$$

And using the first law

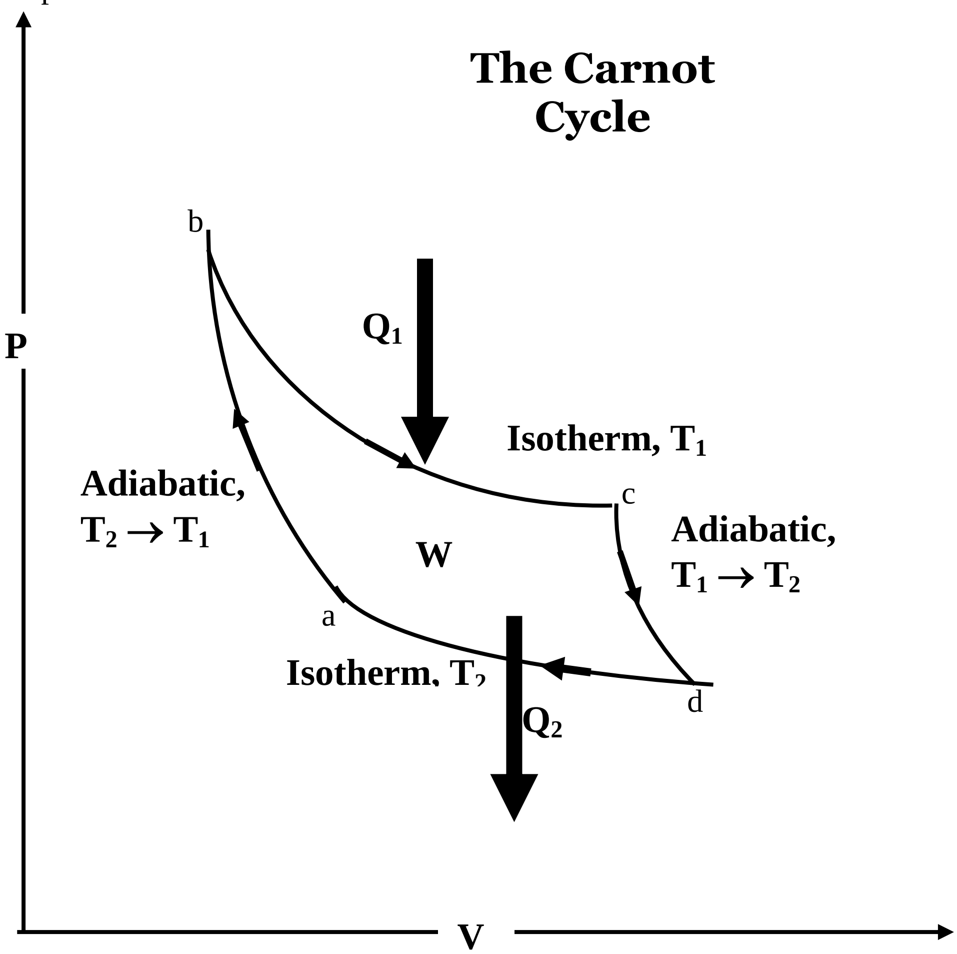
$$W = W_{in} = Q_{Out} = Q_1 - Q_2$$

it may be written as

$$\eta_{HP} = \frac{Q_1}{Q_1 - Q2} = \frac{1}{1 - \frac{Q_2}{Q_1}} = \frac{1}{\eta_E}$$

Ideal (Carnot) Engine

What form of engine will give the greatest efficiency? Looking at the efficiency of an engine $\eta_E = 1 - \frac{Q_2}{Q_1}$ we need a cycle that will minimise the heat rejected to the low temperature reservoir, Q_2 and to maximise the heat into the system as extracted from the hot reservoir, Q_1 .The question was first answered by Sadi Carnot who, it is worth recalling, began his seminal work whilst it was still believed that heat was a substance, namely caloric that couldn't be created or destroyed. He looked at what was required of an efficient cycle and came to the conclusion that what was required was a reversible cycle. This would be a cycle in which any heat flows should take place with little or no temperature differences. To achieve this he proposed a cycle composed of an isothermal expansion of the system at the temperature of the hot reservoir T_1 with heat transfer to the system from the reservoir with no temperature difference and an isothermal compression of this system at the temperature of the cold reservoir with heat transfer to that reservoir from the system at T_2. The two isotherms are joined by two adiabatic processes (no heat flow) taking the expanded substance from the high to the low temperature and taking the compressed substance from the low temperature to the high temperature.



The Carnot cycle is shown in the diagram above.

The four reversible processes associated with the Carnot cycle may be summarised;

(i) **b ⇒ c Reversible addition of heat at constant temperature T_1**

(ii) **c ⇒ d Reversible adiabatic expansion to temperature T_2**

(iii) **d ⇒ a Reversible rejection of heat at constant temperature T_2**

(iv) **a ⇒ b Reversible adiabatic compression back to temperature T_1**

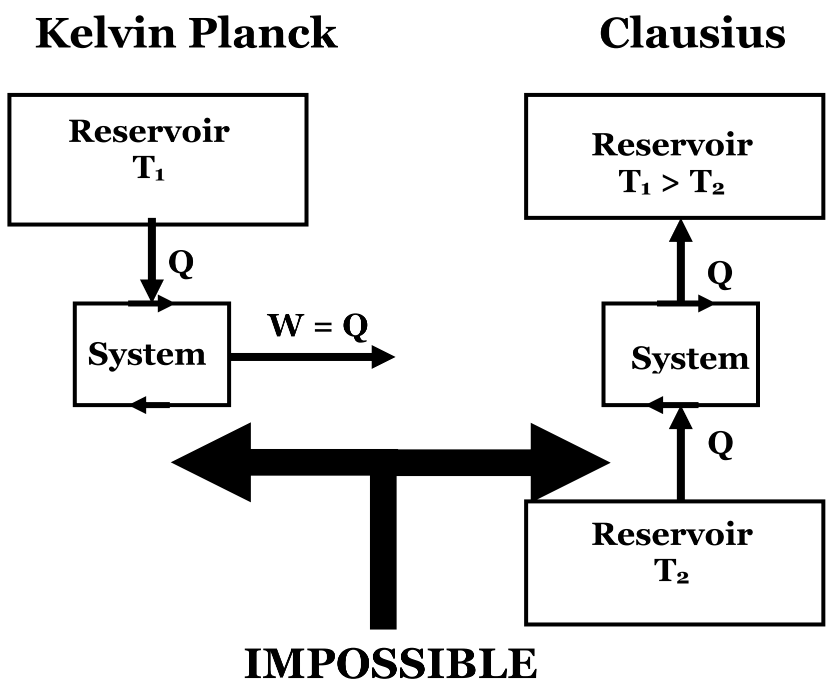
Before we continue and find the optimal efficiency attainable with a heat engine, one running on the Carnot cycle, a brief interlude is needed to look at;

The Second Law of Thermodynamics

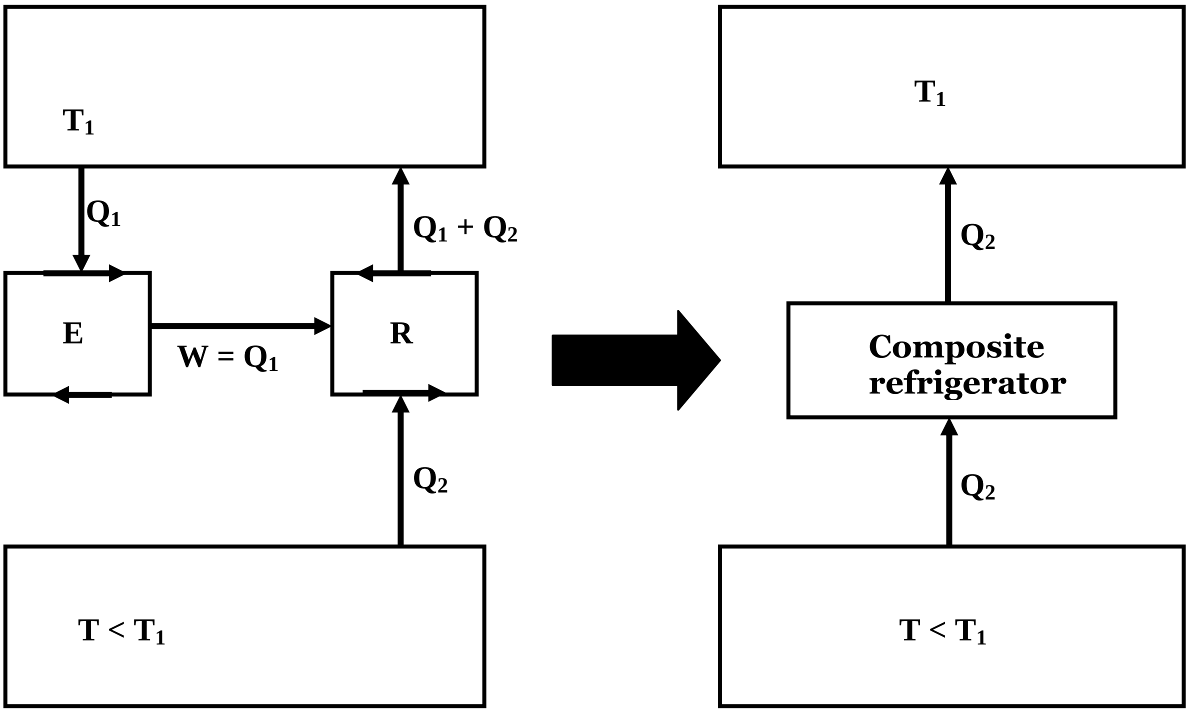
The second law originated as an empirical statement about the limitations of heat engines. There are two early statements of the second law made after empirical observation of how the real world behaved;

(i) **The Kelvin-Planck Statement:** ***It is impossible to devise a device that , operating in a cycle, produces no other effect than the extraction of heat from a single body (a reservoir) with the production of an equivalent amount of work.***

(ii) **The Clausius Statement:** ***It is impossible to devise a device that , operating in a cycle, produces no other effect than the transfer of heat from a cooler to a hotter body (reservoir).***

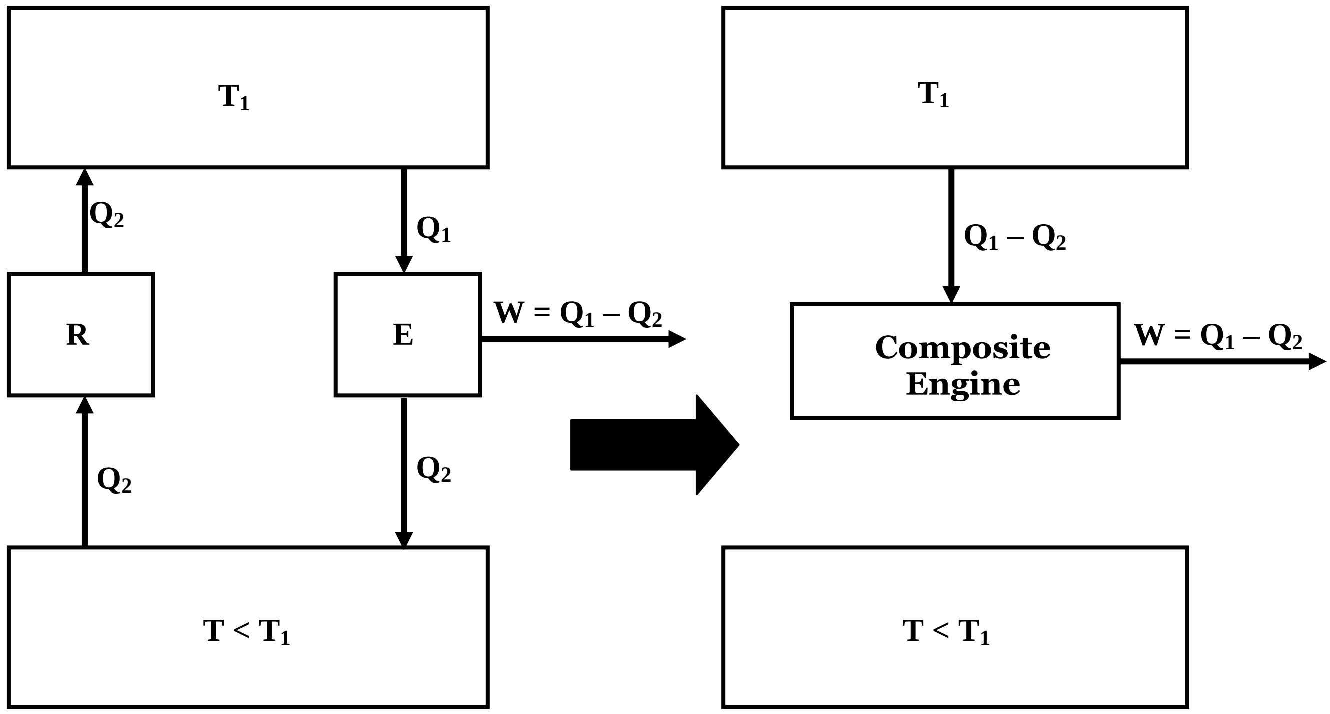


Both statements, while seemingly addressing different aspects of the question of heat, **are in fact equivalent.** They are shown schematically in the two diagrams above and the equivalence of the two statements is demonstrated by considering the composite heat engines shown in the diagrams below.



IMPOSSIBLE

The diagram on the left above shows an engine and a refrigerator running between the hot and the cold reservoir with the engine with its cycle adjusted to provide the work that runs the refrigerator. Only if the Kelvin statement was incorrect could the engine E in principle be made to work. If it worked then it could be used to run the refrigerator between the hot and cold reservoir. The refrigerator itself obeys the first law that is to say heat out equals heat plus work in. However the engine plus refrigerator can be considered a composite unit and the composite unit is equivalent to a composite refrigerator **extracting heat from the low temperature reservoir and delivering it to the high temperature reservoir, heat flowing from cold to hot with no input of work**, a violation of the Clausius statement.



IMPOSSIBLE

The diagram above left shows a refrigerator taking heat from a low temperature reservoir and delivering it to a high temperature reservoir with no input of work, in contravention of the Clausius statement, and an engine, both operating between the same two reservoirs with the engine delivering work and waste heat, Q_2 to the cold reservoir. The engine is obeying the first law. The left hand diagram can be deconstructed into the right hand diagram. This shows an amount of heat extracted from a hot reservoir with the delivery of an equivalent amount of work, a violation of the Clausius statement.

The two statements, which otherwise appear to be addressing very different questions are thus shown to be logically equivalent.

Carnot's Theorem

Carnot's theorem simply states that

<u>no heat engine operating between two given heat reservoirs can be more efficient than a Carnot engine operating between those same two reservoirs</u>

A Carnot engine as briefly mentioned earlier is;

(i) A reversible engine

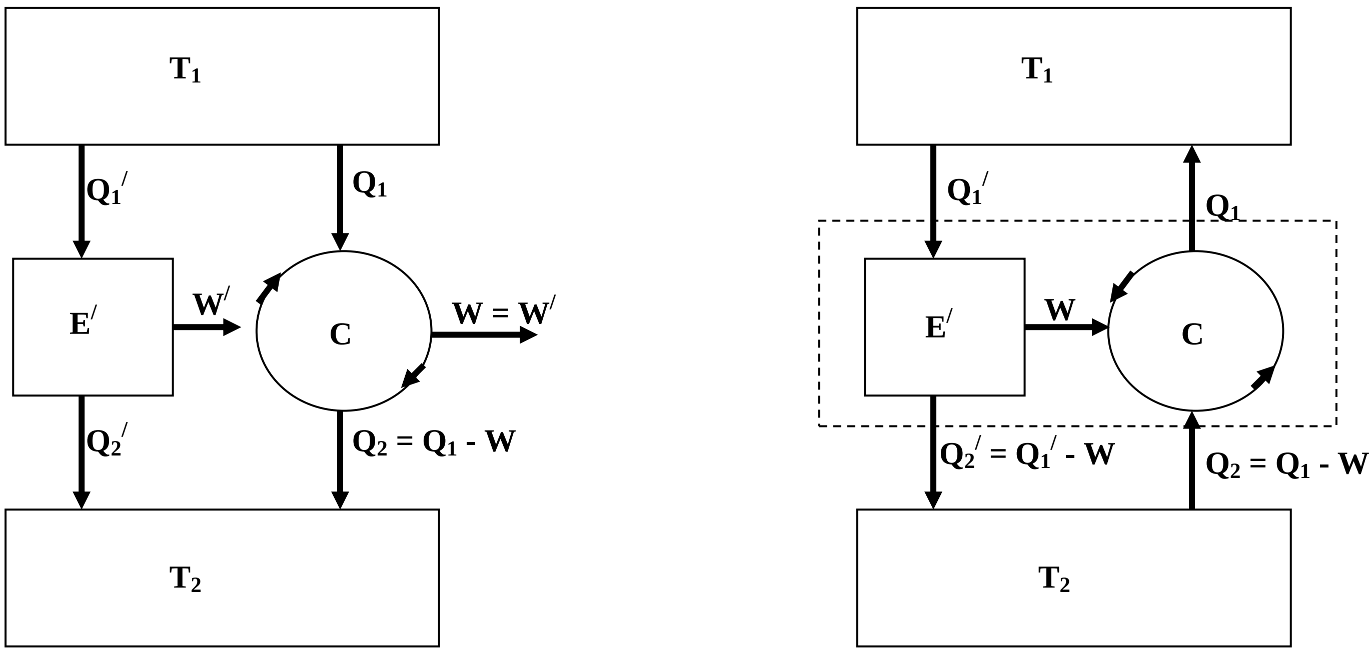
(ii) An engine operating between two heat reservoirs.

To achieve this heat is transferred reversibly (that is at zero temperature difference) to and from the system on a cycle of two isotherms at the high and the low temperature linked in a cycle by two adiabatic curves. This is a reversible engine with heat transfer taking place at constant system temperature ie. isothermally.

Proof.

Suppose such an engine, $E^{/}$, with $\eta_{E^{/}} > \eta_C$ did exist and did an amount of work, $W^{/}$.

Choose a Carnot engine that does the same work. If we reverse the Carnot engine it acts as a refrigerator. We can represent this on diagrams as shown below.



Looking at the upper left hand diagram, the efficiency of the engine $E^{/}$ is

$$\eta^{/} = \frac{W^{/}}{Q_1^{/}} > \eta_C = \frac{W}{Q_1} = \frac{W^{/}}{Q_1} \quad \Rightarrow \qquad Q_1 > Q_1^{/}$$

It therefore follows

$$Q_2 = Q_1 - W > Q_1^{/} - W = Q_2^{/} \Rightarrow \qquad Q_2 > Q_2^{/}$$

Now turn attention to the upper right hand diagram. Within the dashed box the Carnot engine is being run in reverse and acting as a refrigerator. The composite system extracts positive heat $Q_2 - Q_2^{/}$ from the cold reservoir and delivers an amount of heat to the hot reservoir $Q_1 - Q_1^{/}$. But we have

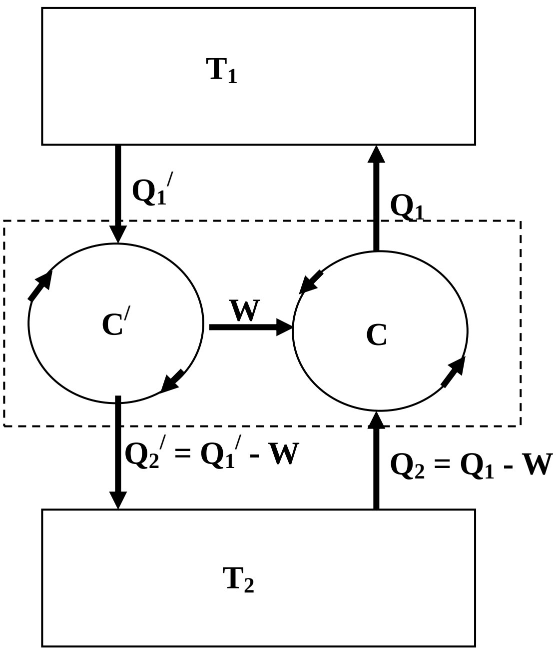
$$Q_1 - Q_1^{/} = (Q_2 + W) - \left(Q_2^{/} + W\right) = Q_2 - Q_2^{/}$$

The composite system is then in disaccord with the Clausius statement and our premise that $\eta_{E^{/}} > \eta_C$ cannot be correct. On the other hand, if $\eta_{E^{/}} = \eta_C$ then $Q_1 = Q_1^{/}$ and no net heat is delivered. This is allowed so we have proven ***reductio ad absurdum*** that

$$\eta_E \le \eta_C$$

thus proving the Carnot theorem. This proof is valid for any truly reversible engine as that was the only property that the proof relied upon, the details of the cycle not being mentioned.

A corollary to this theorem is that ***all Carnot engines running between the same two temperatures have the same efficiency***. To demonstrate this



We imagine two Carnot engines running between the same reservoirs with their cycles adjusted to deliver the same amount of work. Now reverse one and use the other to run it as a refrigerator. We have just seen that to avoid a contradiction with the Clausius statement we must have $\eta_C \leq \eta_{C'}$. We can now reverse the roles of the two Carnot engines and find $\eta_{C'} \leq \eta_C$.

The conclusion, **reductio ad absurdum,** is then, that $\eta_{C'} = \eta_C$.

NB, ***The efficiency of a Carnot engine is independent of the working substance and can depend only on the equilibrium properties of the reservoirs. This is a non-trivial remark!!***

It was understood by Kelvin that this provided a method of establishing an **absolute temperature scale.** He realised that if we have a Carnot engine its efficiency is

$$\eta_C = 1 - \frac{Q_2}{Q_1}$$

Independent of the material of the system and <u>dependent only upon the temperatures</u> of the two reservoirs.

With this observation he claimed that we could define **thermodynamic temperatures**, ***θ***, for the reservoirs by

$$\frac{\theta_2}{\theta_1} = \frac{Q_2}{Q_1} = 1 - \eta_C$$

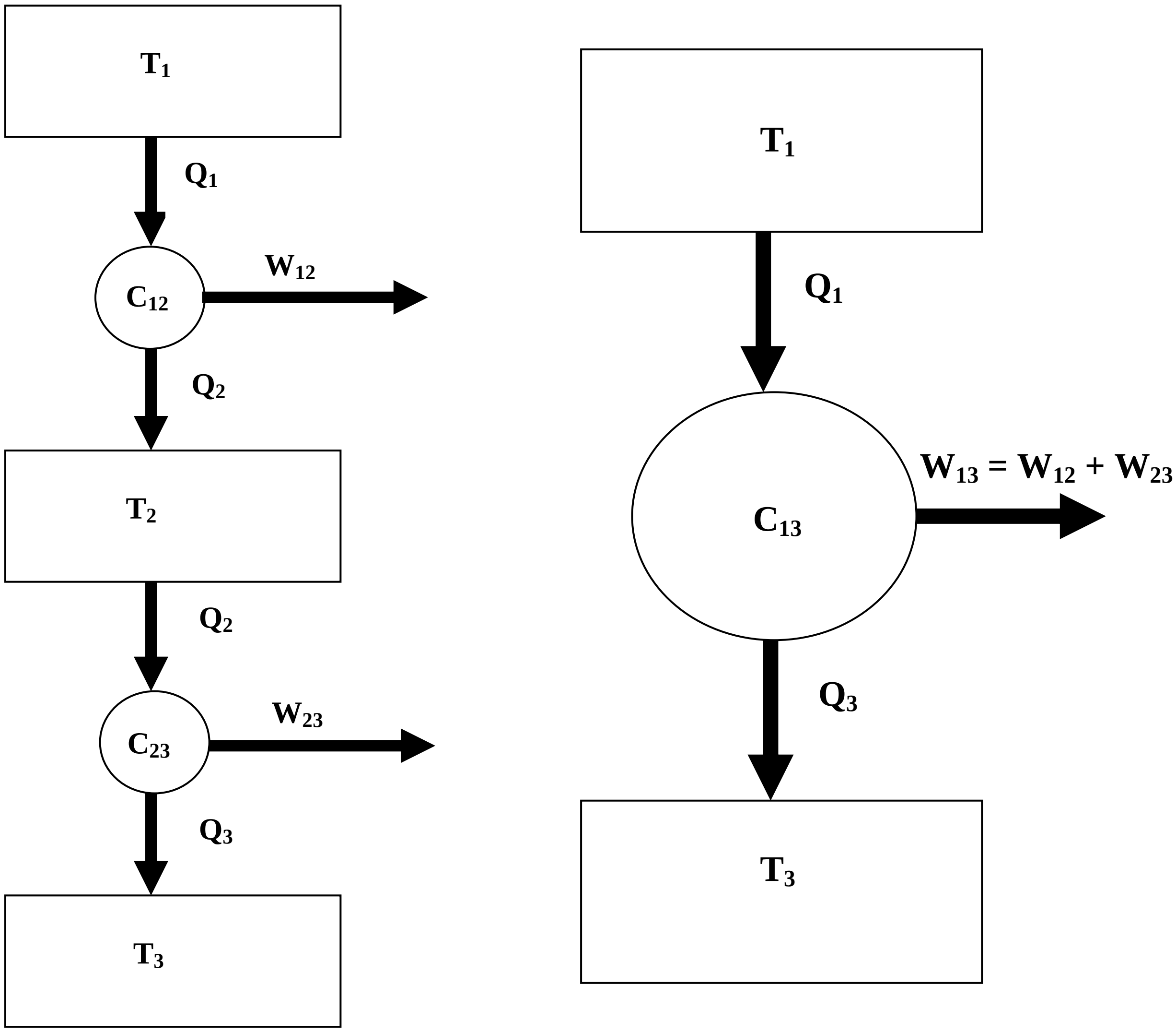
We fix the scale factor by defining $\theta_{Triple\ Point} = 273.16$ and θ is then an

Absolute Thermodynamic Temperature

found for example by measuring the efficiency of a Carnot engine between a reservoir at the unknown temperature and a second at the triple point of water. The temperature so found is

<u>independent of any particular material</u>.

This proposition is demonstrated by consideration of two Carnot engines running in series as shown below where the heat rejected by the first engine is equal to the heat taken in by the second engine



The two engines on the left operate such as to leave the reservoir at T_2 unchanged with engine C_{12} adjusted to deposit the same amount of heat into T_2 as is taken by engine C_{23}. By Kelvin's definition of a thermodynamic temperature scale we have

$$\frac{\theta_2}{\theta_1} = \frac{Q_2}{Q_1}$$

and

$$\frac{\theta_3}{\theta_2} = \frac{Q_3}{Q_2}$$

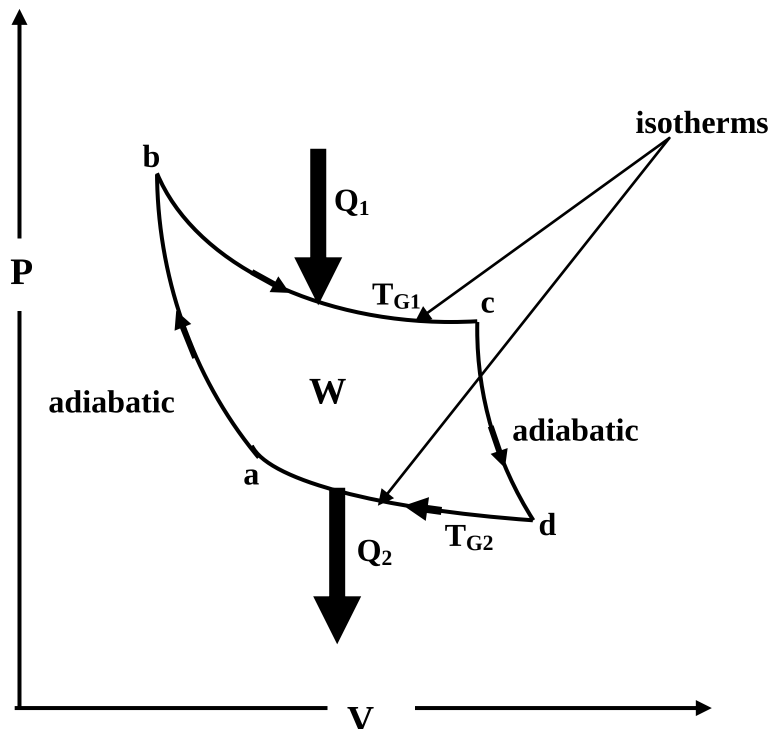
It follows by dividing the first by the second that

$$\frac{\theta_3}{\theta_1} = \frac{Q_3}{Q_1}$$

Thus, using a range of Carnot engines a complete temperature scale may be defined.

It might be supposed (hoped!), that **the absolute temperature, θ, is identical to the ideal gas temperature, T_G** and we proceed to prove this by analysis of the Carnot cycle

Proof.



The diagram shows the Carnot cycle with an ideal gas as working substance. To remind ourselves that we are comparing the thermodynamic temperature θ with the ideal gas temperature I include a subscript G with the gas temperatures, T_G.

For the isotherm, b $\rightarrow$ c , $T_G = T_{G1}$ and $PV = nRT_{G1}$

$$\Delta U_{b\rightarrow c} = 0 \quad \text{(isotherm)} \qquad \Rightarrow \qquad 1^{st} \text{ Law gives} \qquad 0 = \Delta Q + \Delta W$$

$$\Delta Q = Q_1 = -\Delta W = \int_{V_b}^{V_c} PdV = nRT_{G_1} \int_{V_b}^{V_c} \frac{dV}{V} = nRT_{G_1}\, ln\frac{V_c}{V_b}$$

Similarly for the isotherm, d $\rightarrow$ a, $T_G = T_{G2}$ and $PV = nRT_{G2}$

$$\Delta U_{d\rightarrow a} = 0 \quad \text{(isotherm)} \qquad \Rightarrow \qquad 1^{st} \text{ Law gives} \qquad 0 = \Delta Q + \Delta W$$

$$\Delta Q = -Q_2 = -\Delta W = \int_{V_d}^{V_a} PdV = nRT_{G_2} \int_{V_d}^{V_a} \frac{dV}{V} = nRT_{G_2}\, ln\frac{V_a}{V_d}$$

$$Q_2 = nRT_{G_2}\, ln\frac{V_d}{V_a}$$

$$\frac{Q_2}{Q_1} = \frac{\theta_2}{\theta_1} = \frac{nRT_{G_2}\, ln\frac{V_d}{V_a}}{nRT_{G_1}\, ln\frac{V_c}{V_b}} = \frac{T_{G_2}}{T_{G_1}} \frac{ln\frac{V_d}{V_a}}{ln\frac{V_c}{V_b}}$$

Now we look at the adiabatics where

$$\left.\begin{array}{ll} c \rightarrow d & T_{G_2}V_d^{\gamma-1} = T_{G_1}V_c^{\gamma-1} \\ \text{and} & \\ a \rightarrow b & T_{G_2}V_a^{\gamma-1} = T_{G_1}V_b^{\gamma-1} \end{array}\right\} \qquad \left(\frac{V_d}{V_a}\right)^{\gamma-1} = \left(\frac{V_c}{V_b}\right)^{\gamma-1}$$

therefore we find that

$$\frac{V_d}{V_a} = \frac{V_c}{V_b}$$

We use this in the earlier equation proving that

$$\frac{\theta_2}{\theta_1} = \frac{T_{G_2}}{T_{G_1}}$$

and that with

$$\theta_{TP} = T_{TP} = 273.16$$

it is the case that

$$\boldsymbol{\theta = T_{\mathrm{G}} \; (= T_{\mathrm{Kinetic}} = T)}$$

Returning to the efficiency of the Carnot cycle,

$$\boxed{\eta_C = 1 - \frac{Q_2}{Q_1} = 1 - \frac{\theta_2}{\theta_1} = 1 - \frac{T_2}{T_1}}$$

And this is the MAXIMUM THEORETICAL EFFICIENCY of any engine.

<u>We note that $\eta_{\mathrm{C}} = 1$ only if $T_2 = 0$!</u>

If we run the Carnot engine in reverse we have a refrigerator. The efficiency of a Carnot refrigerator is

$$\eta_R(Carnot) = \frac{Q_2}{Q_1 - Q2} = \frac{1}{\frac{Q_1}{Q_2} - 1} = \frac{1}{\frac{T_1}{T_2} - 1}$$

We can also operate it as a heat pump with efficiency

$$\eta_{HP}(Carnot) = \frac{Q_1}{Q_1 - Q2} = \frac{1}{1 - \frac{Q_2}{Q_1}} = \frac{1}{1 - \frac{T_2}{T_1}} = \frac{1}{\eta_C}$$

Just a quick observation,

If the reservoir temperatures are very close then the heat pump and refrigerator efficiencies become very large, in fact much greater than 1 but the engine efficiency becomes very small approaching zero. **The same is true of non-Carnot systems.** Thinking about this it is clear that a refrigerator required to keep its contents at a temperature only slightly cooler than the ambient temperature will not be required to work very hard, W will be small and $\eta_R = \frac{Q_2}{W}$ will be very large.

Example.

A Carnot heat pump is designed to operate between T_2 = 283K and T_1 = 300K

The efficiency is

$$\eta_{HP}(Carnot) = \frac{1}{1-\frac{T_2}{T_1}} = \frac{1}{1-\frac{283}{300}} = \frac{300}{17} = 17.6 = \frac{1}{\eta_C}$$

$$\eta_R(Carnot) = \frac{1}{\frac{300}{283}-1} = \frac{283}{17} = 16.6$$

$$\eta_C = 1-\frac{283}{300} = \frac{17}{300} = 0.057$$

Example.

A steam engine operating with superheated steam at 200^0C and exhaust at 10^0C.

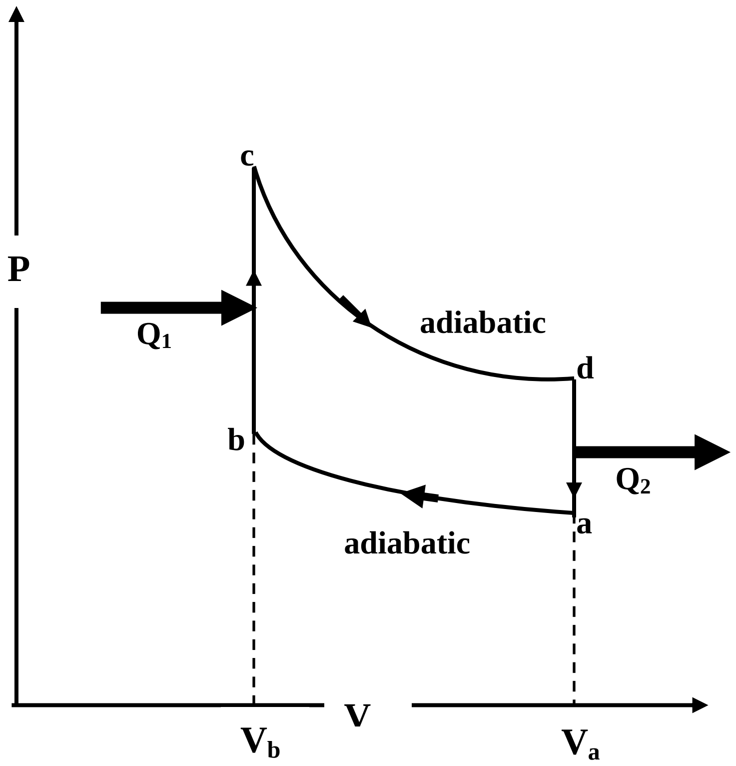
We can give an upper limit of the Carnot efficiency.

T_1 = 473.16K, and T_2 = 283.16K

$$\eta_E \le \eta_C = 1-\frac{283.16}{473.16} = 0.40$$

Real Engines.

1. The Otto Cycle.



The Otto cycle is a reasonable approximation to the petrol engine but with two strokes, expansion followed by compression. It is depicted above with the expansion and compression undergone adiabatically (no heat input from external sources). Joining these two adiabatic curves are isochores, (no change in volume). This is a readily analysed engine cycle as we have the tools developed and to hand.

analysis

a → b is an adiabatic compression where work is done on the gas and the usual equation holds,

$$T_a V_a^{\gamma-1} = T_b V_b^{\gamma-1}$$

c → d is an adiabatic expansion where work is done by the gas

$$T_d V_a^{\gamma-1} = T_c V_b^{\gamma-1}$$

b → c is an isochore and no work is done as dV = 0. The heat can be calculated from the first law

$$\Delta U = U_c - U_b = \frac{3}{2} nR(T_c - T_b) = \Delta Q = Q_1$$

We can see that Q_1 is positive as $T_c > T_b$ and it is therefore a flow of heat into the gas.

d $\rightarrow$ a is also an isochore and again no work is done as $dV = 0$. The heat can be calculated from the first law

$$\Delta U = U_a - U_d = \frac{3}{2} nR(T_a - T_d) = \Delta Q = -Q_2$$

We can see that Q_2 is negative as $T_a < T_d$ and it is therefore a flow of heat from the gas.

The efficiency is

$$\eta_E = 1 - \frac{Q_2}{Q_1} = 1 - \frac{C_V(T_d - T_a)}{C_V(T_c - T_b)}$$

$$\eta_E = 1 - \left(\frac{V_b}{V_a}\right)^{\gamma - 1}$$

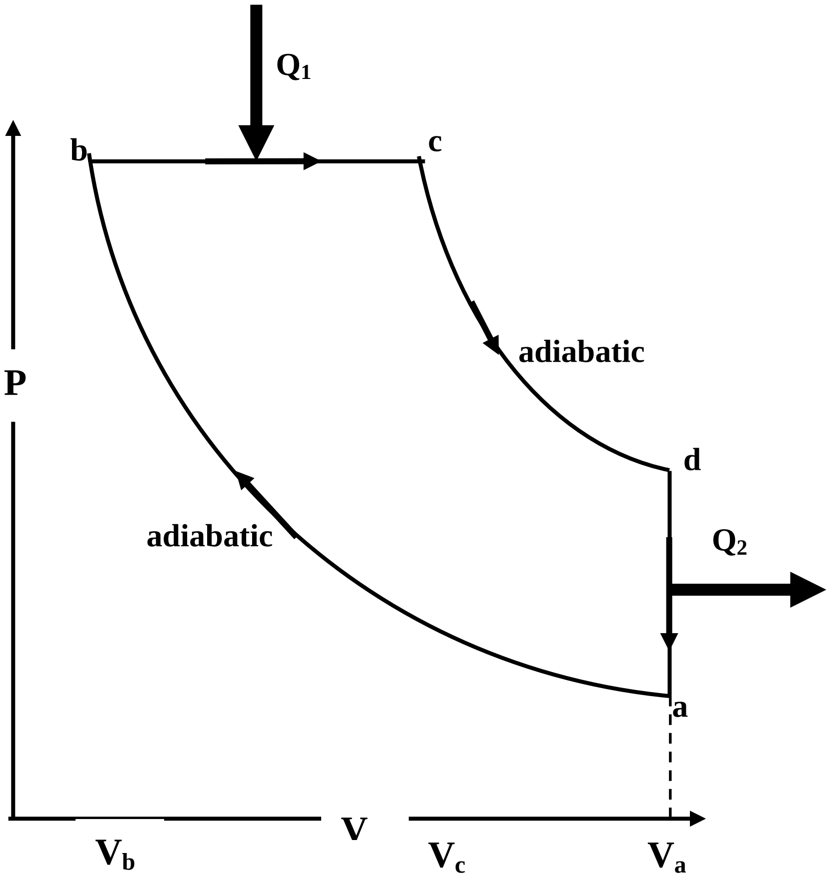
Defining **the compression ratio** $r_C = \frac{V_a}{V_b}$

$$\eta_E = 1 - \frac{1}{r_C^{\gamma - 1}}$$

For a compression ratio of 8 and $\gamma = \frac{7}{5} = 1.4$ for a rigid diatomic gas.

$$\eta_E = 0.54$$

2. The Diesel Cycle.



The diesel engine cycle is shown above

We analyse as usual to find Q_1 and Q_2 and thus the efficiency

analysis

b → c is an isobaric process joining two adiabats from T_b to T_c ($T_c > T_b$)

P is constant so $dQ = C_P dT$

$$Q_1 = \int dQ = \int_{T_b}^{T_c} C_P dT = C_P(T_c - T_b)$$

d → a is an isochoric process, $\Delta V = 0$ so $\Delta W = 0$

From the first law

$$\Delta U = U_a - U_d = \frac{3}{2} nR(T_a - T_d) = C_V(T_a - T_d) = \Delta Q = -Q_2$$

Is a heat flow out as we go from a higher to lower temperature and the sign is negative. We must therefore take the absolute value of ΔQ for Q_2 when used in the efficiency equations.

$$\eta_E = 1 - \frac{Q_2}{Q_1} = 1 - \frac{C_V(T_d - T_a)}{C_P(T_c - T_b)}$$

$$\eta_E = 1 - \frac{1}{\gamma}\frac{T_d - T_a}{T_c - T_b}$$

Now analyse the adiabats

c $\rightarrow$ d is an adiabatic process thus

$$T_c V_c^{\gamma-1} = T_d V_d^{\gamma-1} \quad \Rightarrow \quad T_d = T_c\left(\frac{V_c}{V_d}\right)^{\gamma-1}$$

a $\rightarrow$ b is also an adiabatic process and similarly

$$T_a V_a^{\gamma-1} = T_b V_b^{\gamma-1} \quad \Rightarrow \quad T_a = T_b\left(\frac{V_b}{V_a}\right)^{\gamma-1}$$

We also know that

$P_b V_b = nRT_b$ $\qquad$ $P_c V_c = nRT_c$ $\qquad$ and $\qquad$ $P_b = P_c$

$$\frac{V_b}{V_c} = \frac{T_b}{T_c} \quad \Rightarrow \quad T_c = T_b\frac{V_c}{V_b}$$

We now have the ingredients to conclude the analysis

$$T_d - T_a = T_c\left(\frac{V_c}{V_a}\right)^{\gamma-1} - T_b\left(\frac{V_b}{V_a}\right)^{\gamma-1}$$

$$T_d - T_a = T_b\left(\frac{V_c}{V_b}\right)\left(\frac{V_c}{V_a}\right)^{\gamma-1} - T_b\left(\frac{V_b}{V_a}\right)^{\gamma-1} = \frac{T_b V_a}{V_b}\left[\left(\frac{V_c}{V_a}\right)^{\gamma} - \left(\frac{V_b}{V_a}\right)^{\gamma}\right]$$

And similarly

$$T_c - T_b = T_b\left(\frac{V_c}{V_b}\right) - T_b = \frac{T_b V_a}{V_b}\left[\left(\frac{V_c}{V_a}\right) - \left(\frac{V_b}{V_a}\right)\right]$$

$$\eta_E = 1 - \frac{1}{\gamma}\frac{T_d - T_a}{T_c - T_b} = 1 - \frac{1}{\gamma}\frac{\left[\left(\frac{V_a}{V_c}\right)^{-\gamma} - \left(\frac{V_a}{V_b}\right)^{-\gamma}\right]}{\left(\frac{V_a}{V_c}\right)^{-1} - \left(\frac{V_a}{V_b}\right)^{-1}} = 1 - \frac{1}{\gamma}\left[\frac{r_E^{-\gamma} - r_C^{-\gamma}}{r_E^{-1} - r_C^{-1}}\right]$$

$r_E = \dfrac{V_a}{V_c}$ is the expansion ratio

$r_C = \dfrac{V_a}{V_b}$ is the compression ratio

Example; $r_E = 5$, $r_C = 15$, $\gamma = 1.4$

$$\eta_E = 0.56$$

3. The Stirling Cycle.

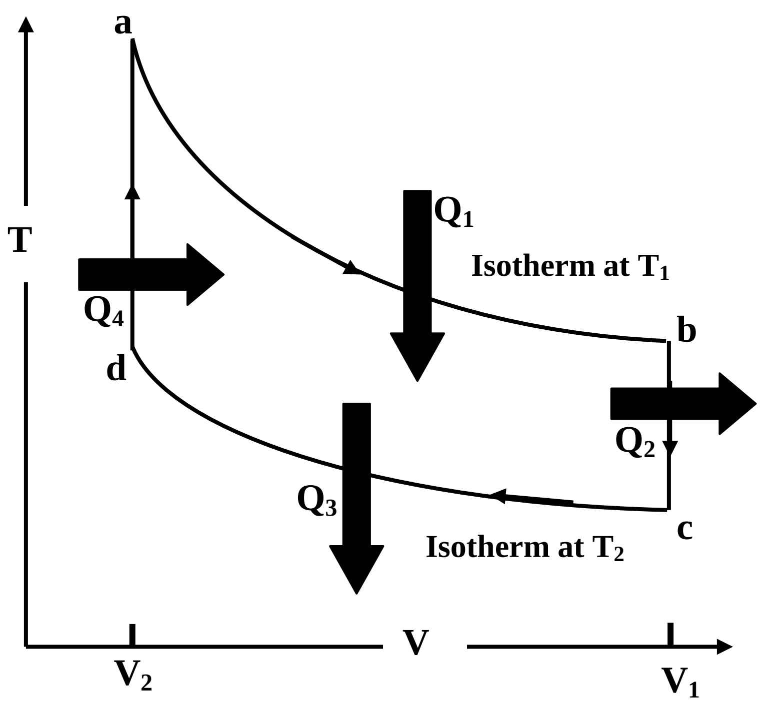
The Stirling cycle is an example of another engine **cycle**. The Stirling engine operates on a closed system and offers a quiet performance with potentially high efficiencies. It's action may be described as follows

(i) **a ⇒ b Reversible addition of heat and expansion at constant temperature T_1**

(ii) **b ⇒ c Heat rejection and cooling at constant volume V_1 from T_1 to T_2**

(iii) **c ⇒ d Reversible rejection of heat and compression at constant temperature T_2**

(iv) **d ⇒ a Addition of heat at constant volume V_2 back from T_2 to temperature T_1**



We note, already that as opposed to the Carnot cycle, here as well as the heat flow isothermally there is also heat added and rejected during the isochoric processes and as heat is added with no work done this should reduce the efficiency of the Stirling cycle when compared with the Carnot cycle. Further, that heat is added or extracted irreversibly and the cycle is therefore irreversible.

To obtain the efficiency of the Stirling heat engine we need to find W, Q_{added} and $Q_{rejected}$ on each part of the cycle.

Work is only performed on or by the system during the isothermal expansion **a ⇒ b** and the isothermal compression **c ⇒ d** no work being performed on the isochores.

$$\left.\begin{aligned} W_{a\to b} &= nRT_1\, ln\left(\frac{V_1}{V_2}\right) \\ W_{c\to d} &= nRT_2\, ln\left(\frac{V_2}{V_1}\right) \\ W &= nR(T_1 - T_2)ln\left(\frac{V_1}{V_2}\right) \end{aligned}\right\}$$

NB. The signs reflect the work done BY the system

The heat **added to the system** occurs both during the isothermal expansion **a ⇒ b** and the isochoric temperature rise, process **d ⇒ a**

$$Q_{in} = C_V(T_1 - T_2) + nRT_1\, ln\left(\frac{V_1}{V_2}\right)$$

Putting this together for the efficiency we have

$$\eta_S = \frac{W}{Q_{in}} = \frac{nR(T_1 - T_2)ln\left(\frac{V_1}{V_2}\right)}{C_V(T_1 - T_2) + nRT_1\, ln\left(\frac{V_1}{V_2}\right)}$$

Divide top and bottom by $nR\, ln\left(\frac{V_1}{V_2}\right)$

$$\eta_S = \frac{T_1 - T_2}{\dfrac{C_V(T_1 - T_2)}{nR\, ln\, V_1/V_2} + T_1}$$

And then divide top and bottom by T_1

$$\eta_S = \frac{1 - T_2/T_1}{1 + \frac{C_V(T_1 - T_2)}{nRT_1 \ln V_1/V_2}}$$

This gives us the Stirling efficiency in terms of the Carnot efficiency;

$$\eta_S = \frac{1 - T_2/T_1}{1 + \frac{C_V}{nR \ln V_1/V_2}\left(1 - T_2/T_1\right)} = \frac{\eta_C}{1 + \frac{C_V}{nR \ln V_1/V_2}\eta_C}$$

From this result we can immediately see that **the efficiency of a Stirling engine is lower than the efficiency of a Carnot engine running between the same two reservoirs.**

Further, if we recall that for an ideal gas $C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{s}{2}nR$ where s is the number of degrees of freedom (3 for a monatomic gas, 5 or 7 for a diatomic molecule depending on whether it is rigid or vibrates respectively)

$$\eta_S = \frac{\eta_C}{1 + \frac{s}{2 \ln V_1/V_2}\eta_C}$$

The Stirling engine will perform better for a monatomic gas.

The real world.

It is time to signal a note of caution after the foregoing analysis. We have looked at four cycles, the ideal Carnot cycle, the Otto, Diesel and Stirling cycle suggesting that the latter three are more like real engines. In many ways of course they are except for one big difference. Any real engine operates with losses or dissipation not included here in our analysis, sometimes between more than two heat reservoirs, with leaky valves and with friction in the moving parts and the Otto, Diesel and Stirling cycles as analysed here were themselves idealisations, that is, as approximations to real cycles. Clearly the analysis of a real engine through thermodynamics is a difficult and involved task. What has been presented here is a way of approaching the tasks by breaking the job down into manageable pieces. It has also been very useful practice at thermodynamic analysis.

Real refrigerators, again operate on irreversible cycles and are difficult to analyse theoretically. They use a working substance, the refrigerant, that must be a vapour at the operating temperature of the cold reservoir otherwise the operating medium would condense. This is the reason for many of the exotic refrigerants that have been used over the years.

Refrigerant	Chemical	BP ^{0}F	BP ^{0}C
Ammonia	NH_3		-33.35
Freon `12	CCl_2F_2	-21.6	-29.8
DichloroDiFluoroMethane	$C_2Cl_2F_4$	38	3.3
	CCl_3F	75.3	24.1
	$C_2Cl_3F_3$	118	47.8

Chlorofluoro carbons, CFCs have dominated but are now recognised as environmentally unacceptable. In the 19th century ammonia was the refrigerant of choice allowing perishables such as fish to be transported around the world.

Refrigeration is usually achieved by expansion of the saturated liquid through a valve, the temperature and pressure being both lowered significantly in the process, with up to 10 atm drop in pressure producing a mix of liquid and vapour in co-existence. For this to work using the Joule Kelvin effect a positive Joule Kelvin coefficient is necessary it is to be recalled that there is an inversion temperature below which the coefficient will be negative and an expansion will cause a rise in temperature. Clearly the gas cannot be used in such a refrigeration cycle below the inversion temperature.