Lecture 11

The second law of thermodynamics

The microscopic laws of physics are time reversible. If you look at a film of atoms and molecules interacting with each other and run it backwards, there is no way of telling which one is actually forward. Yet, in macroscopic world, time seems to follow a particular trajectory. Broken eggs do not rebuild themselves, or melted ice ~~of~~ cubes do not solidify spontaneously. This arrow of time, is intimately connected to the second law of thermodynamics. In these few lectures we are going to tackle the essential ~~ingd~~ ingredients of the second law of thermodynamics, and connect it to entropy.

The practical impetus for the developement of the science of thermodynamics was the advent of heat engines. The increasing reliance on machines to do work during the industrial revolution required better understanding of the principles underlying conversion ~~to~~ of heat to work. It is interesting to see how such practical considera-tion like efficiency of engines gave the abstract ideas like the entropy.

An idealized "heat engine" works by taking a certain heat Q_H from a heat source (for example a coal fire), converting a portion of it to work W, and dumping the remaining heat Q_c into a heat sink (for example, atmosphere). The efficiency of the engine is calculated as –

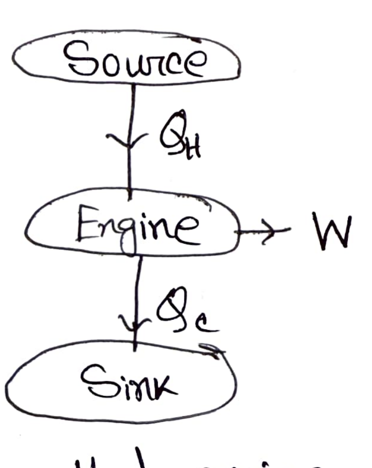
$$\eta = \frac{W}{Q_H} = \frac{Q_H - Q_c}{Q_H}$$

$$= 1 - \frac{Q_c}{Q_H} \leq 1$$

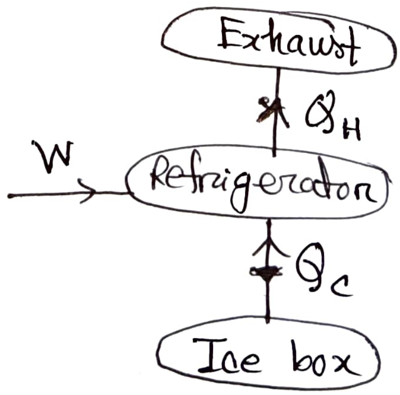
An idealized refrigerator is like an engine running backward, that is, using work W to extract heat Q_c from a cold system, and dumping Q_H to a higher temperature reservoir. We can define a similar figure of merit for the performance of a refrigerator as –

$$\omega = \frac{Q_c}{W} = \frac{Q_c}{Q_H - Q_c}$$

ω can be less than or greater than 1.



Heat engine



Refrigerator

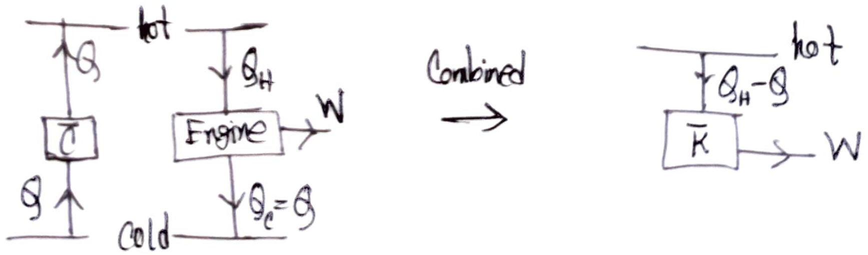
The first law rules out so called "perpetual motion machines of first kind", that is engines that produce works without consuming any energy (heat). However the conservation of energy won't be violated if some engine spontaneously produces work by converting water into ice, that is taking heat from a colder body. Such a "perpetual motion machine of second kind" would solve the energy crisis of the world for sure. But, sadly, these types of machines is ruled out by second law. The observation that the natural direction for the flow of heat is from hotter to colder object is the essence of the second law of thermodynamics. There are few different statements of the second law. We will state two such statements now.

1. Kelvin's statement: No process is possible whose sole result is complete conversion of heat into work.

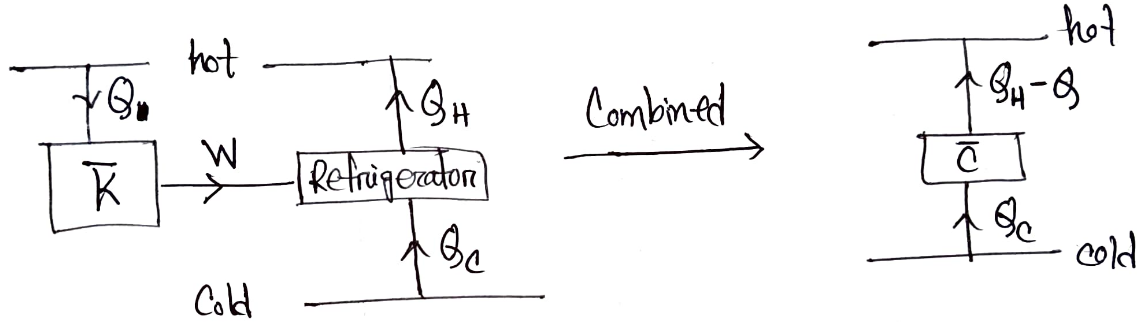
2. Clausius's statement: No process is possible whose sole result is the transfer of heat from a colder to a hotter body.

A perfect engine is ruled out by Kelvin's statement, and a perfect refrigerator is ruled out by Clausius's statement. These two statements are actually equivalent. The equivalance is shown by the fact that, if one ~~engine~~ statement is violated, so is the other.

(a) Let's assume that there is a machine that violates Clausius's statement by taking heat Q from a cooler region to hotter one. Now, consider an engine working between these two regions, that take Q_H heat from the hotter body and dumps Q_c to the cooler one. The combined system then takes $Q_H - Q$ heat from the source, produces a work $Q_H - Q_c$ and dumps $Q_c - Q$ at the cold sink (cooler body). If the engine's output is $Q_c = Q$, then the net result is a 100% efficient engine, which violates Kelvin's statement.



(b) Alternatively, consider a machine violates Kelvin's statement. So, it takes Q heat from hot object and converts the whole to work. This work output can be given to a refridgerator, which can transfer heat from colder to hotter body. The combined system then violates ~~ct~~ Clausius's statement by transferring heat from hotter to colder body.



The work done must be, for Kelvin violator, $W = Q$

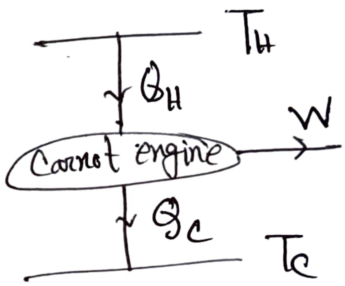
For the refrigerator, $W = Q_H - Q_C$

$$\therefore \; Q_H = W + Q_C = Q + Q_C$$

So, the heat dumped in hot reservoir is $Q_H - Q$ $= Q + Q_C - Q = Q_C$. So, the combined system basically takes Q_C heat from the cold region and dump it to the hot region, meaning violating Clausius's statement.

The Carnot engine

The Carnot engine is a system operating in a reversible cyclic process, that converts heat into work, with its heat exchange taking place at a source temperature T_H and a sink temperature T_C. It has to be cyclic so that it can ~~co~~ be continuously operated, producing a steady power.



A reversible process here simply states that the process can be run backward in time by simply reversing the inputs and outputs. It is thermodynamic equivalent of ~~first~~ frictionless motion in mechanics. Since reversibility implies equilibrium, the process must be quasi-static.

An engine that runs in a cycle returns to its original internal state at the end of the process. We can find two isotherms at temperatures T_H and T_C for the heat exchanges with the reservoir. To complete the cycle, we have to connect these isotherms by reversible adiabats. Although, since heat is not a state function, we do not know how to construct such path in general.

But we do have enough information to construct a Carnot's engine using ideal gas as working substance. For example, consider the substance is monoatomic ideal gas with internal energy, $U = \frac{3}{2} N k_B T = \frac{3}{2} PV$

Now, $đQ = dU + đW = d\left(\frac{3}{2}PV\right) + PdV$

$$= \frac{3}{2} PdV + \frac{3}{2} VdP + PdV$$

$$\Rightarrow đQ = \frac{5}{2} PdV + \frac{3}{2} VdP$$

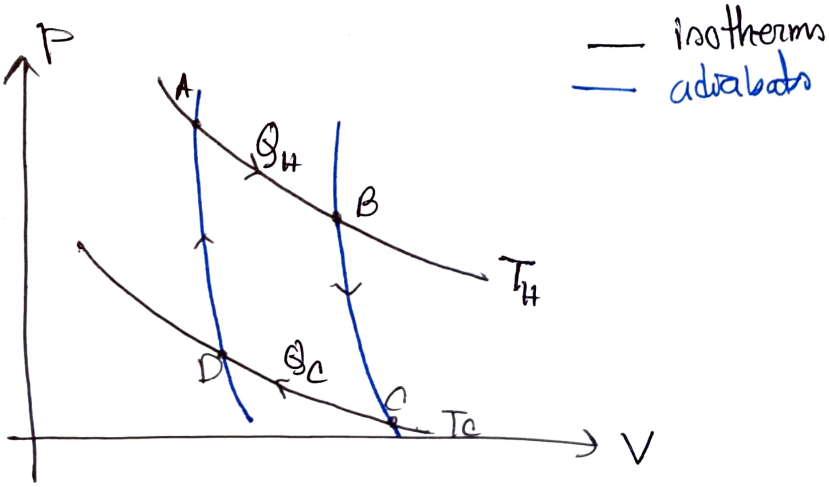
But in adiabatic expansion, $đQ = 0$

$$\therefore \frac{5}{2} PdV = -\frac{3}{2} VdP$$

$$\therefore \frac{dP}{P} + \frac{5}{3}\frac{dV}{V} = 0$$

$$\Rightarrow PV^{5/3} = \text{constant}$$

Any curve corresponding to $PV^{5/3}$ = constant will be an adiabat. In general, adiabats are curves where PV^{γ} = constant, whereas in isotherms PV = constant.



Heat enters or leaves during reversible isotherms. Heat Q_H enters during the expansion $A \to B$ and heat Q_C leaves during the compression $C \to D$. Since, the change in internal energy is a state function, the change in internal energy when the engine returns to A is zero.

$$\therefore W = Q_H - Q_C$$

Carnot's theorem

No engine operating between two reservoirs (T_H and T_C) is more efficient than a Carnot engine operating between them.

Imagine a non-Carnot ~~engine~~ engine. Since a Carnot engine is reversible, We can run this engine backwards, as a refrigerator. The heats of non-Carnot are denoted by Q_H and Q_C. Similarly, a Carnot engine working between same temperatures which is operated as a refrigerator has heats Q'_H and Q'_C. If we combine the two engines, then the combined system takes $-Q'_H + Q_H$ heat and dumps $-Q'_C + Q_C$ heat. If we imagine the non-Carnot engine is more efficient, then,

$$\eta_{n.c.} > \eta_C$$

$$\Rightarrow \frac{W}{Q_H} > \frac{W}{Q'_H}$$

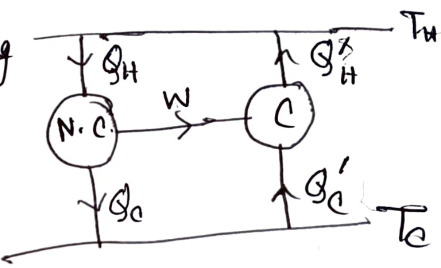
$$\therefore Q'_H > Q_H$$

with $W = Q'_H - Q'_c = Q_H - Q_c$

$$\therefore Q'_H - Q_H = Q'_c - Q_c$$

Since, $Q'_H - Q_H$ is positive, so is $Q'_c - Q_c$.

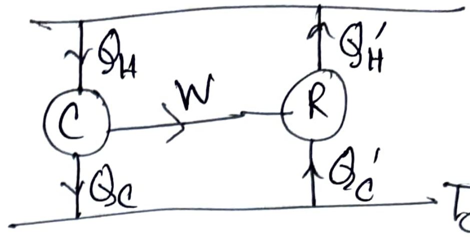
So, the combined system dumps $|Q_H - Q'_H|$ amount of heat in the hot reservoir and takes $|Q_c - Q'_c|$ from the cold reservoir. So, the combined system is violating Clausius's statement. So, no such engine is possible for which $\eta_{n.c} > \eta_c$.



<u>Corollary</u>: All reversible engines working between two temperatures have the same efficiency η_{Carnot}.

~~Consider two Carnot engines in series, one between~~

Imagine another engine R, which has an efficiency $\eta_R \leq \eta_{Carnot}$ by Carnot's theorem. We run it in reverse and connect it to a Carnot engine going forward. This combined system will take $Q_H - Q_H'$ heat from hot reservoir and

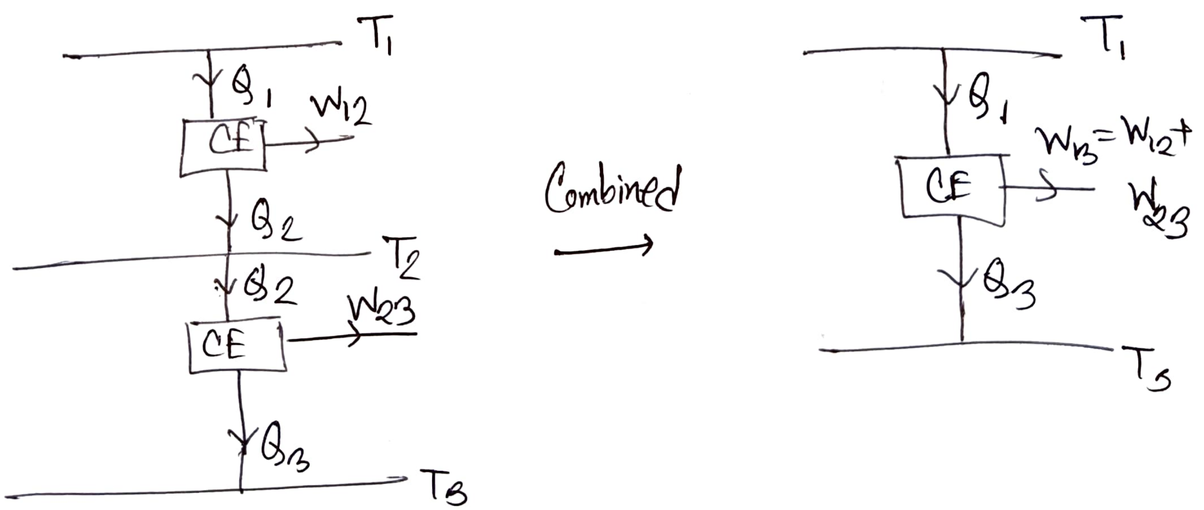


dump $Q_C - Q_C'$ heat to cold reservoir. The combined system will violate Clausius's statement if $\eta_R < \eta_{Carnot}$

Since, then, $\frac{W}{Q_H'} < \frac{W}{Q_H} \Rightarrow Q_H' > Q_H$. So, for Clausius's statement not to be violated,

$$\eta_R = \eta_{Carnot}.$$

Now, consider two Carnot engine in series, one working between T_1 and T_2, another between T_2 and T_3. $(T_1 > T_2 > T_3)$. Note that, the heat dumped



by the first engine is taken by the second.

The combined system is another Carnot engine with Q_1, Q_3 and work output $W_{13} = W_{12} + W_{23}$.

Now, $W_{12} = Q_1 - Q_2$

$\Rightarrow Q_2 = Q_1 - W_{12} = Q_1 - Q_1 \eta(T_1, T_2)$

$\therefore Q_2 = Q_1 [1 - \eta(T_1, T_2)]$

$$\eta(T_1, T_2) = \frac{Q_1 - Q_2}{Q_1} = \frac{W_{12}}{Q_1}$$

Similarly, $Q_3 = Q_2 - W_{23} = Q_2 [1 - \eta(T_2, T_3)]$ — (i)

and combined, $Q_3 = Q_1 - W_{13} = Q_1 [1 - \eta(T_1, T_3)]$ — (ii)

From (i) ~~and (ii)~~ $\rightarrow$ $Q_3 = Q_2 [1 - \eta(T_2, T_3)]$

$\therefore Q_3 = Q_1 [1 - \eta(T_1, T_2)] [1 - \eta(T_2, T_3)]$ — (iii)

Comparing (ii) and (iii) we get,

$$[1 - \eta(T_1, T_3)] = [1 - \eta(T_1, T_2)] [1 - \eta(T_2, T_3)]$$

$$\therefore f(T_1, T_3) = f(T_1, T_2) f(T_2, T_3) \text{ — (iv)}$$

where we ~~redefin~~ redefined $f(T_1, T_2) = 1 - \eta(T_1, T_2)$

Now, equation (iv) implies that, the ~~right~~ left hand side is a function of T_1 and T_3, and so should be right hand side. So,

$f(T_1, T_2)$ must be of the form $\dfrac{\phi(T_2)}{\phi(T_1)}$

so that the cancellation can take place.

$$\therefore \quad f(T_1, T_2) = \frac{\phi(T_2)}{\phi(T_1)}$$

$$\therefore \quad 1 - \eta(T_1, T_2) = \frac{\phi(T_2)}{\phi(T_1)}$$

Since the L.H.S. is dimensionless, so should the R.H.S. be. So, the powers of numerator and denominator of R.H.S. of T_2 and T_1 must be same, and by convension we write (and define) $\phi(T) = T$ to be the thermodynamic temperature.

$$\therefore \quad 1 - \eta(T_1, T_2) = \frac{T_2}{T_1}$$

$$\boxed{\therefore \quad \frac{Q_2}{Q_1} = \frac{T_2}{T_1}} \quad \text{———} \circledast$$

$$\boxed{\therefore \quad \eta(T_H, T_C) = 1 - \frac{T_C}{T_H} = \frac{T_H - T_C}{T_H}}$$

Equation $\circledast$ determines the absolute temperature scale (since it's not dependent on properties of any particular substance, but only on a general property of Carnot cycle) except for an arbitrary constant of proportionality. The reference point is now accepted as $T_{\text{triple point}} = 273.16\,\text{K}$. If anyone gives you a bath of unknown temperature, you can formulate an engine by operating it between $T_{\text{tripple point}}$ and T_{unknown}, calculate the efficiency of the engine and finally find T_{unknown}. For example, the melting point of ice is considered to have a temperature of 273.15 K. This can also be used for the reference point.