Physics 161: Thermodynamics

Lecture #7

A heat engine extracts heat from a hot reservoir, preforms work on the surroundings, and dumps heat into a cold reservoir. It can also be run backwards; Work can be performed on the engine for the purpose of extracting heat from a cold reservoir and dumping it into a hot reservoir. This is known as a heat pump, common examples of which are the refrigerator and the air conditioner.

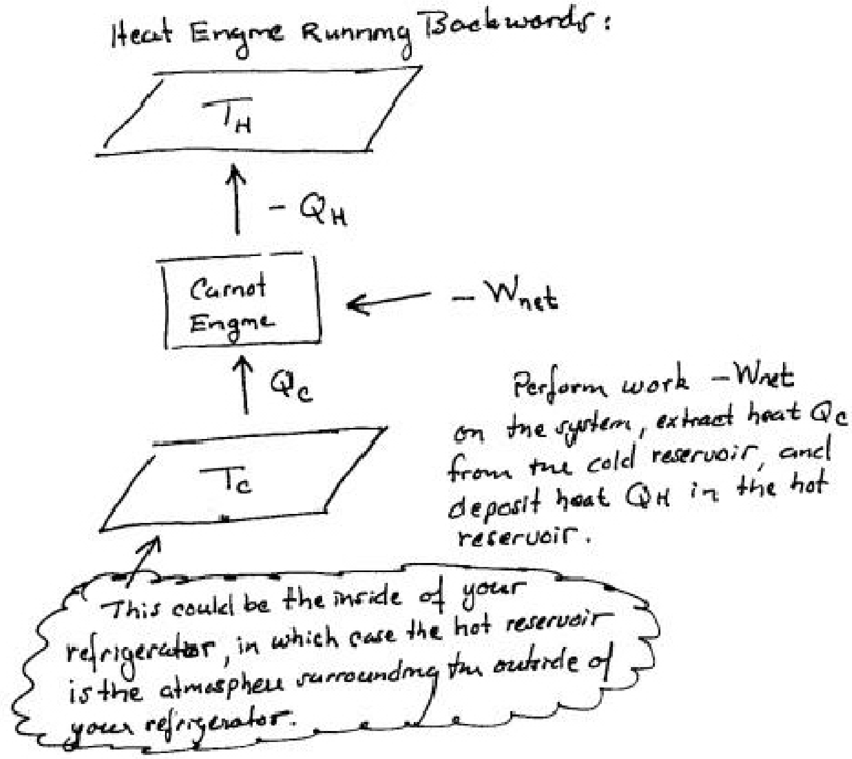
When a Carnot engine is run forwards, it extracts an amount of heat Q_H, and performs an amount of work $W_{\rm net}$ in each cycle, such that the ratio which gives the efficiency,

$$\frac{W_{\rm net}}{Q_H} = \varepsilon = \frac{T_H - T_C}{T_H}$$

As we have seen, for the case that the working fluid is an ideal gas, this ratio only depends on the ratio of the temperature of the hot reservoir to the temperature of the cold reservoir. In each cycle it delivers heat

$$\begin{aligned} Q_C &= W_{\rm net} - Q_H \\ &= -Q_H \frac{T_C}{T_H} \end{aligned}$$

to the cold reservoir. Because the Carnot cycle engine is reversible, the relations between heat and work remain the same when it is run backwards as a heat pump.



Example 1:

Suppose that the outdoors temperature is -5 C, and the temperature inside your house is 25 C. How much electrical work would be required to supply 1000 kJ of heat to the inside of a house using a Carnot heat pump (operating with an ideal gas)?

The coefficient of performance of a heat pump

$$K = \frac{(-Q_H)}{(-W_{\rm net})}$$

is the ratio of the output energy to the energy you must input to run the machine. In this case, the output energy is the heat delivered to the building by the system, $-Q_H$, and the input energy is the work which must be performed *on* the system, $-W_{\rm net}$. This ratio is just the reciprocal of the efficiency of the

Carnot cycle,

$$\frac{Q_H}{W_{\rm net}} = \frac{1}{\varepsilon}.$$

Therefore, for the case in which the ideal gas is the working fluid, we have

$$\begin{aligned} K &= \frac{T_H}{T_H - T_C} \\ &= \frac{298 \text{ K}}{298 \text{ K-}268 \text{ K}} \\ &= 9.93 \end{aligned}$$

Consequently,

$$\begin{aligned} (-W_{\rm net}) &= \frac{(-Q_H)}{9.93} \\ &= \frac{1000 \text{ kJ}}{9.93} \\ &= 101 \text{ kJ} \end{aligned}$$

Only 100 kJ of work is required to deliver 1000 kJ of heat to the inside of the house! You can see by inspection that the ratio of the heat delivered to the work performed becomes better as the difference $T_H - T_C$ becomes smaller. Heat pumps are cost efficient in southern regions of the US, where the winter temperatures do not fall too much below the desired indoor temperature. They are rather common in homes Pheonix, for example, with an estimated savings on winter heating costs of approximately 30% over heating by burning natural gas*. Moreover, in the summer months, the same unit running backwards becomes the air conditioner - so the same piece of equipment is used for both heating and cooling. In contrast, the vast majority of homes in Albuquerque burn natural gas for winter heat, and we use a separate AC unit, or a swamp cooler for the summer months. Indeed, heat pumps are surprisingly rare in Albuquerque - sold as novelty items for those who can afford to "go green". There is a simple explanation for this; the price of natural gas in Albuquerque is 30% lower than the price in Phoenix, while electrical rates for the two cities are about the same - 11 cents/kWh. The 30% discrepancy in natural gas prices has been consistent for at least the past two decades.

*https://swenergy.org/pubs/benefits-of-heat-pumps-for-homes-in-the-southwest—full-report

The Second Law of Thermodynamics

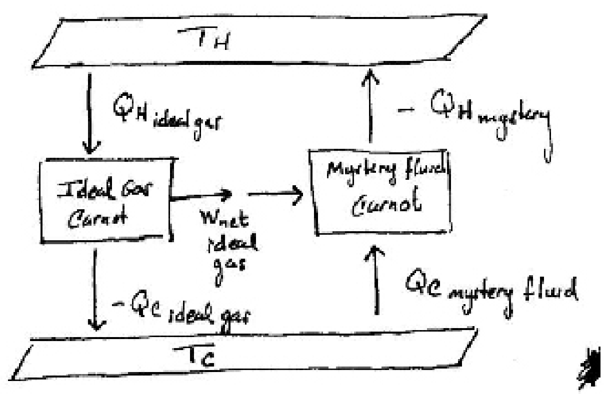
> There is no process possible whose sole result is to transfer heat from a cold body to a hot body- Rudolph Clausius (1850)

The second law is an assertion of the fact of experience that heat flows spontaneously from a hot body to a cold body, but it does not flow spontaneously from a cold body to a hot body. It has implications for the Carnot cycle:

1) "All Carnot engines have the same efficiency, regardless of the working fluid."

$$\varepsilon = \frac{T_H - T_C}{T_H}\text{; any fluid, Carnot cycle}$$

To prove this, we imagine a composite engine where we use the ideal gas Carnot engine to drive a second Carnot engine backwards. The second Carnot engine uses some non-ideal gas, a *mystery fluid.* The engines operate between the same two reservoirs.



The work delivered by the ideal gas Carnot engine to the mystery fluid Carnot heat pump is

$$W_{\text{net (ideal gas)}} = \varepsilon_{\text{ideal gas}} \times Q_{H\text{ (ideal gas)}}$$

The heat delivered by the mystery fluid Carnot heat pump to the hot reservoir is

$$-Q_{H\text{ (mystery)}} = W_{\text{net (ideal gas)}} \times \frac{1}{\varepsilon_{\text{mystery}}}$$

Combining these two equations, we have

$$-Q_{H\text{ (mystery)}} = \frac{\varepsilon_{\text{ideal gas}}}{\varepsilon_{\text{mystery}}} \times Q_{H\text{ (ideal gas)}}$$

If $\varepsilon_{\text{mystery}} < \varepsilon_{\text{ideal gas}}$, then the composite engine dumps more heat into the hot reservoir than it takes out.

$$\begin{aligned} -Q_{H\text{ (net)}} &= -Q_{H\text{ (mystery)}} - Q_{H\text{ (ideal gas)}} \\ &= \left(\frac{\varepsilon_{\text{ideal gas}}}{\varepsilon_{\text{mystery}}} - 1\right) Q_{H\text{ (ideal gas)}} \\ &> 0 \end{aligned}$$

In such a case, the sole effect of the composite engine is to transfer heat from the cold reservoir to the hot reservoir, which violates the second law.

On the other hand, suppose that $\varepsilon_{\text{mystery}} > \varepsilon_{\text{ideal gas}}$. In such a case, by running the mystery engine forward and the ideal gas engine backward, we again come to the conclusion that the second law is violated; Heat is transferred from the cold reservoir to the hot reservoir, and no external work need be performed.

2) "All reversible engines have the same efficiency as a Carnot engine."

Notice that, in our proof of (1) above, we never demanded that our engines be Carnot engines. All that we required is that they be reversible, in the sense that the ratio of heat to work remains the same whether they be run forward or backwards. It follows that

$$\varepsilon = \frac{T_H - T_C}{T_H}$$

for *all* reversible heat engines operating between two reservoirs.

At first glance, a Carnot cycle is the only cycle we can imagine that will allow an engine to operate between two reservoirs reversibly. But there are some clever mechanisms for allowing other cycles to approach the reversible limit. For example, for the Stirling cycle, one can attach a *heat recuperator* which takes the heat given off in the isochoric cooling stage and transfers it to the isochoric heating stage. In such a case, the only heat exchanged with the reservoirs takes place during the isothermal expansion and compression stages. If carried out reversibly, the Stirling cycle efficiency with heat recuperators must then be the same as the Carnot cycle efficiency.

3) "No heat engine is more efficient than a reversible heat engine" - Carnot's theorem.

What this means is that an engine operating irreversibly cannot have a higher efficiency than an engine operating reversibly. This is easy to understand. If an irreversible engine had a higher efficiency than a reversible engine, it would be possible to use the irreversible engine to drive the reversible engine backwards, such that the effect of the composite engine is to transfer heat to the hot reservoir from the cold reservoir spontaneously. According to the analysis from (1) above, we would have

$$\begin{aligned} -Q_{H\text{ (net)}} &= -Q_{H\text{ (reversible)}} - Q_{H\text{ (irreversible)}} \\ &= \left(\frac{\varepsilon_{\text{irreversible}}}{\varepsilon_{\text{reversible}}} - 1\right) Q_{H\text{ (irreversible)}} \\ &> 0 \end{aligned}$$

which would violate the second law.

Consequently, we may conclude that

$$\varepsilon_{\text{irreversible}} \leq \varepsilon_{\text{reversible}}. \tag{1}$$

If the reversible engine is used to drive the irreversible engine backwards, then, following the same analysis, we find

$$\begin{aligned} -Q_{H\ (\text{net})} &= -Q_{H\ (\text{irreversible})} - Q_{H\ (\text{reversible})} \\ &= \left(\varepsilon_{\text{reversible}} K_{\text{irreversible}} - 1\right) Q_{H\ (\text{reversible})}. \end{aligned}$$

Here we have to be careful to write the coefficient of performance $K_{\text{irreversible}}$ as though it were a separate variable (not necessarily equal to $\varepsilon^{-1}_{\text{irreversible}}$) since, for an irreversible cycle, the ratio of heat to work need not be the same when the engine is driven forward as it is when it is driven backwards. In order to satisfy the second law, we require that $Q_{H\ (\text{net})}$ be positive, and since $Q_{H\ (\text{reversible})}$ is positive this means that

$$\varepsilon_{\text{reversible}} K_{\text{irreversible}} - 1 \leq 0.$$

Rearranging terms, we have

$$\begin{aligned} K_{\text{irreversible}} &\leq \frac{1}{\varepsilon_{\text{reversible}}} \\ K_{\text{irreversible}} &\leq K_{\text{reversible}} \end{aligned}$$

In going from the next to the last line to the last line we have substituted $K_{\text{reversible}} = \varepsilon^{-1}_{\text{reversible}}$ on the right hand side of the inequality.

In summary, we have proved two inequalities for irreversible engines:

$$\begin{aligned} \varepsilon_{\text{irreversible}} &\leq \varepsilon_{\text{reversible}} \\ K_{\text{irreversible}} &\leq K_{\text{reversible}} \end{aligned}$$

We can combine these as a chain of inequalities,

$$\frac{1}{\varepsilon_{\text{irreversible}}} \geq \frac{1}{\varepsilon_{\text{reversible}}} \geq K_{\text{irreversible}}.$$

In summary, based on Clausius's statement of the second law, we can prove that an irreversible heat engine will have an efficiency that is less than or equal to the efficiency of a reversible heat engine, and we can prove that an irreversible heat pump will have a coefficient of performance that is less than or equal to the coefficient of performance of a reversible heat pump.

Thermodynamic Temperature Scale

We can use the universal efficiency of a reversible cycle to establish the definition of absolute temperature without having to make reference to the pressure-volume relation of an ideal gas. Since

$$\varepsilon = 1 - \frac{T_C}{T_H} = 1 + \frac{Q_C}{Q_H}$$

it follows that

$$\frac{Q_C}{Q_H} = -\frac{T_C}{T_H}$$

The ratio of the heats in the Carnot cycle is the same as the ratio of the temperatures in Kelvin. Thus, if we choose a reference temperature for a particular reservoir, say 273.16 K = T for H_2O at the triple point, then the temperature of all other reservoirs can be found by operating a Carnot engine between them and our triple point reservoir. In this way we give a meaning to absolute temperature that does not require the existence of an ideal gas (remember that the second law requres that a Carnot engine has the same efficiency regardless of the working fluid).

A New State Function: Entropy (S)

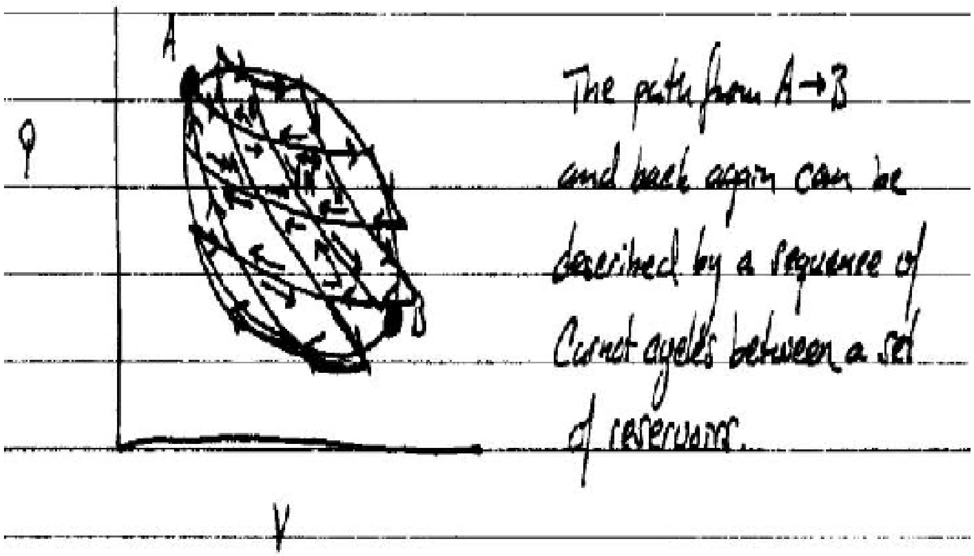
Note that the relation

$$1 - \frac{T_C}{T_H} = 1 + \frac{Q_C}{Q_H}$$

implies that

$$\frac{Q_C}{T_C} + \frac{Q_H}{T_H} = 0; \text{ two reservoirs, reversible cycle}$$

There are many reversible cycles (closed paths on a PV diagram) that can not be described in terms of a heat engine operating between just two heat reservoirs. Nevertheless, their efficiency can be calculated by considering an infinite sequence of reversible isotherms and reversible adiabats, where along each isotherm the system is in contact with a different heat reservoir.



To calculate the work, we would need to calculate the area inside the closed loop connecting A and B on the PV diagram. If we connect the sequence of isotherms and adiabats that follow the loop by an imaginary mesh of isotherms and adiabats which fill the area inside the loop, then we can describe the total work as the sum of the total work associated with an infinite number of Carnot engines, each connected between their respective reservoirs at T_{H_i} and T_{C_i}, each taking in an amount of heat δQ_{H_i} from the high temperature reservoir, and dumping heat δQ_{C_i} in the cold reservoir.

For each infinitesimal Carnot loop in the diagram, we can write

$$\frac{\delta Q_{C_i}}{T_{C_i}} + \frac{\delta Q_{H_i}}{T_{H_i}} = 0$$

If we were to sum over all loops, we would therefore have the sum of a lot of zeros,

$$\sum_i \left(\frac{\delta Q_{C_i}}{T_{C_i}} + \frac{\delta Q_{H_i}}{T_{H_i}} \right) = 0$$

The interior paths for adjacent loops cancel out, leaving the result that the sum must be zero if we consider only the exterior paths;

$$\sum_{i \text{ exterior}} \frac{\delta Q_i}{T_i} = 0.$$

In the limit, we could write an integral for the closed loop

$$\oint \frac{\delta Q_{\text{reversible}}}{T} = 0; \text{any reversible cycle}$$

But we can always break this up as

$$\int_A^B \frac{\delta Q_{\text{reversible}}}{T} + \int_B^A \frac{\delta Q_{\text{reversible}}}{T} = \oint \frac{\delta Q_{\text{reversible}}}{T} = 0.$$

Therefore it follows that the integral between any two points doesn't depend on the path taken;

$$\int_A^B \frac{\delta Q_{\text{reversible}}}{T}_{\text{path 1}} = \int_A^B \frac{\delta Q_{\text{reversible}}}{T}_{\text{path 2}}$$

It must therefore depend only on the initial and final system states. Let us denote this functional dependence by introducing a function S called entropy;

$$\int_A^B \frac{\delta Q_{\text{reversible}}}{T} \equiv S(B) - S(A) = \Delta S$$

The entropy is obviously a state function. The change in entropy of the system

$$dS = \frac{\delta Q_{\text{reversible}}}{T}$$

is related to the heat *when the heat is taken on reversibly.*