General Physics I

Lect19. The Laws of Thermodynamics

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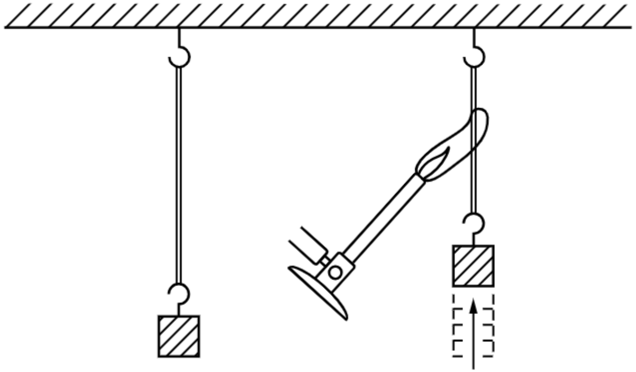
Thermodynamics

- The determination of the relationships among the various properties of materials (heat, mechanical work, etc.), without knowing their internal structure, is the subject of **thermodynamics**.

- If we pull a rubber band, it gets warm; relaxing the rubber band will get it cooler. In fact, if we apply a gas flame to a rubber band holding a weight, we will see that the band contracts abruptly.

- The detailed mechanism is complicated and beyond simple kinetic theory, but still work our the relation between work and heat, and use these principle to design “heat engine”!



Rubber band can pull the weight up when heated.

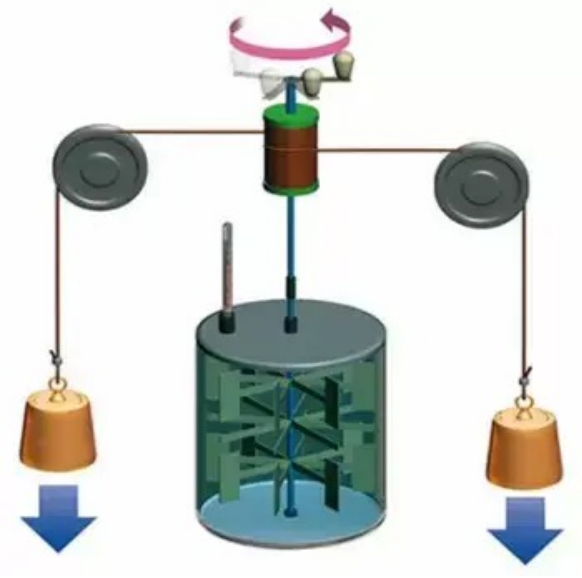
Conservation of energy– Joule's Experiment

- James Joule proposed a rotary shaft with blades rotating between four sets to stir liquid in free space, connected to masses using pulleys and ropes, and watertight, thick wood walls.

- The walls of the container were watertight and thick to simulate an *adiabatic* wall.

- Such experiment was repeated many times varying:
  The type of mechanical work.
  The type of liquid and, therefore, its properties.

- The results of all experiments showed that the change observed in the system---*temperature*, is always the same.



Joule's setup

The first law—energy conservation

Julius Robert von Mayer (1841), James Prescott Joule (1842) and Hermann Helmholtz (1847) conducted their experiment at similar times leading to the final Energy Conservation Act.

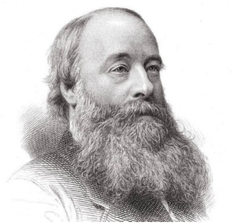
$$\text{Change in } U = Q + W$$

$$\Delta U = \Delta Q + \Delta W$$

- Energy conservation and transfer: if one has a system and puts heat into it, and does work on it, then its internal energy is increased by the heat put in and the work done.

- W>0 environment does work to system
- W<0 environment receives work to system
- Q>0 heat transfer to system
- Q<0 heat transfer from system

Julius Mayer



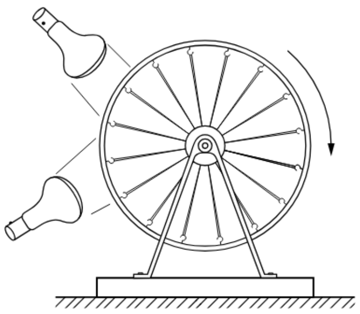
James Joule

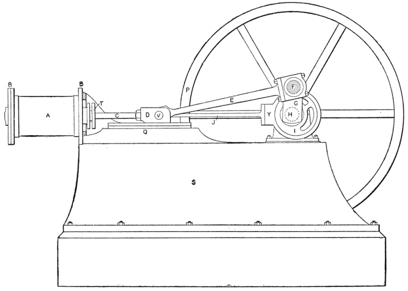
Hermann Helmholtz

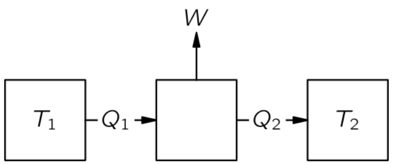
The second law—the direction of thermodynamics

- Thermodynamic processes that occur in nature are all irreversible processes. These are processes that proceed spontaneously in one direction but not the other.
- Heat naturally flow from one hot object to one cooler object, but not the opposite. Also, it's easy to convert mechanical energy completely into heat---e.g. car brakes.
- What about the reverse possibility, i.e., a **heat engine**? What's the limit of those engines? Can all heat be converted back to work? Is it possible to convert the heat back into work at a single temperature?

- A process whose only **net** result is to take heat from a reservoir and convert it to work is impossible. -- *second law of thermodynamics.*


"Rubber band" engine

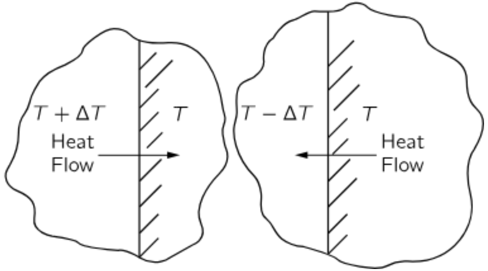

Steam engine



Heat engines convert heat to work

Reversible engines

- In a Gedankenexperiment (German: “thought experiment”), Carnot proposed the “frictionless heat transfer” as an analog of frictionless motion. We set the temperature of the system and the reservoir infinitely close, differed by only ΔT. The heat flow is reversible, with a change of sign for ΔT for infinitesimal temperature difference.



Nicolas Léonard Sadi Carnot
(1796~1832)

- The *ideal* engine is a ***reversible*** one, where every process can be reversed by minor changes. That means no friction, no direct contact with something definitely cooler or warmer.

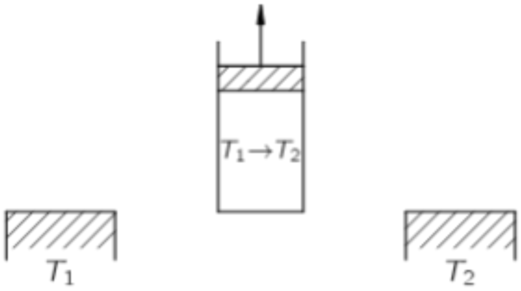
Carnot cycle

Step (1) Isothermal expansion at T_1, absorb heat Q_1

- A perfect gas in a cylinder with a frictionless piston can be heated and expanded while in contact with two heat pads, where $T_1 > T_2$.
- Pulling the piston out slowly ensures the gas's temperature never gets too far from T_1. Pulling it out slowly keeps the gas's temperature constant.
- This ***isothermal expansion*** is a reversible process, governed by the relation

$$PV=Nk_BT$$

Carnot cycle



Step (2) Adiabatic expansion, temperature falls from T_1 to T_2

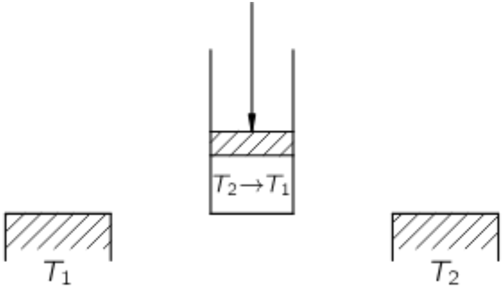
- We now move the box away from the left reservoir and make the entire piston heat resistant.
- The piston continue to move upward and the gas undergo ***adiabatic expansion.***
- Since no heat was pumped in to the system, the pressure and volume follows the relation

$$PV^{\gamma}=\text{const.},$$

and the temperature decreases from T_1 to T_2.

Carnot cycle

Step (3) Isothermal compression at T_2, deliver heat Q_2



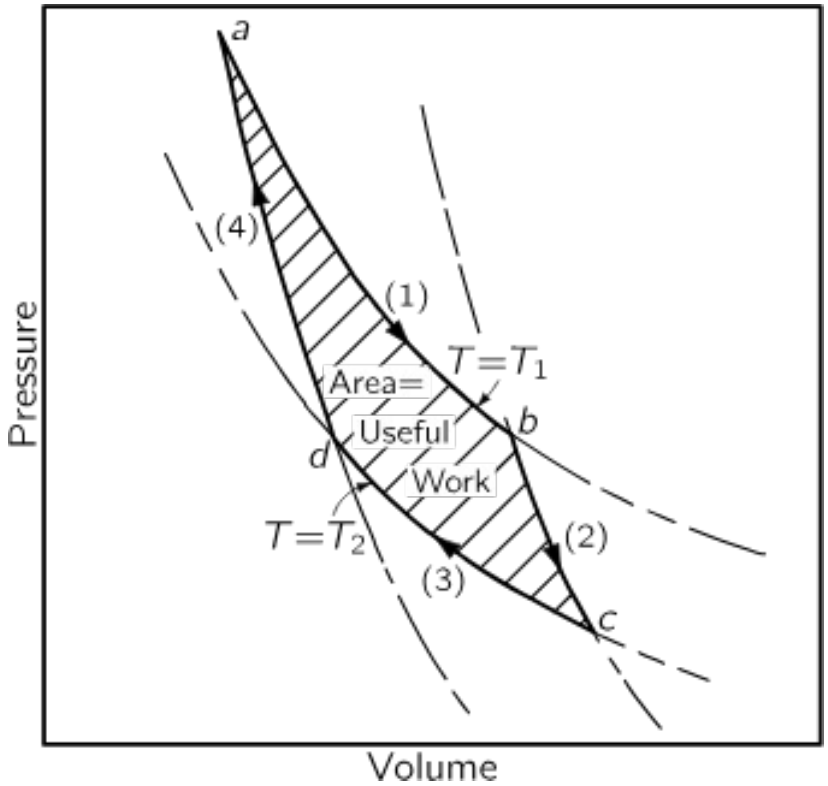
Step (4) Adiabatic compression, temperature rises from T_2 to T_1

- The box is then moved to low-temperature reservoir (at T_2) on the right. The piston is then compressed, again, slowly to keep the temperature stable, i.e., ***isothermal compression***. The volume goes down while the pressure goes up.

- We then remove the right reservoir, and further compress the system with no heat exchange. The gas undergoes the ***adiabatic compression*** process and the temperature will rise back to T_1, the system returns to its initial point. A reversible cycle is completed.

- This is the <u>simplest reversible cycle</u> since only two heat reservoirs are needed.

PV diagram of Carnot cycle



- A Carnot cycle can be expressed in a P(pressure)-V(volume) diagram, which has a clear advantage---we can easily see the ***net work*** done of the cycle, denoted by the shadowed area

- In *isothermal* processes (1) and (3), $P\sim V^{-1}$; in (1) the gas absorb Q_1 heat at T_1, and in (3) the gas release Q_2 heat at T_2

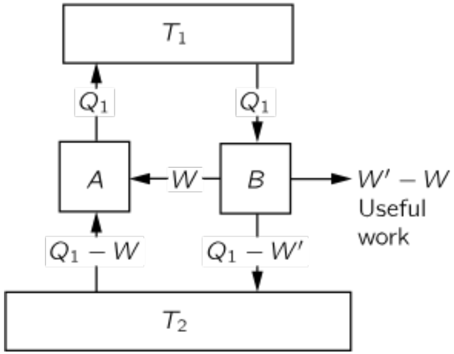
- In *adiabatic* processes (2) and (4), $P\sim V^{-\gamma}$, since $\gamma>1$, the slope is steeper than that of isothermal, while the heat exchange Q=0

Carnot's ideal engine

- If we have another engine B, with its W'>W, we can reverse Carnot's engine A to consume an amount W of work to pump heat from T_2 to T_1, where engine B produce such work. At such, we have a combined machine with a net work of W'-W>0 from a reservoir at a single temperature with no other changes. This violates the 2nd law! Hence engine B does not exist.

- Now let's assume engine B is also reversible, any |W-W'|>0 means that the 2nd law is violated.

- Carnot's conclusion: if an engine is reversible, it makes no difference how it is designed. Reversible engine will always absorbs a given amount of heat at temperature T_1 and delivers heat at some other temperature T_2 . Reversible engine should be **universal**.



The efficiency of an ideal engine

- With ideal engine, let's determine the work W as a function of Q_1, T_1, and T_2.
- In isothermal processes (1), the heat obtained from the reservoir at T_1 is Q_1. Since U is unchanged given constant T and N, the heat equal to the work done

$$W = \int_a^b p\, dV$$

- Given $pV=nkT$, we have

$$Q_1 = \int_a^b p\, dV = \int_a^b NkT_1 \frac{dV}{V}$$

$$Q_1 = NkT_1 \ln \frac{V_b}{V_a}$$

Q is path dependent

- In the same way, the for the (3) isothermal compression, the heat delivered to the reservoir

$$Q_2 = NkT_2 \ln \frac{V_c}{V_d}$$

- Finally, let's use the relation of the adiabatic process, from $pV^\gamma=const$ and $pV=NkT$, we have $TV^{\gamma-1}=const$. Thus from (2) and (4)

$$T_1 V_b^{\gamma-1} = T_2 V_c^{\gamma-1} \text{ and } T_1 V_a^{\gamma-1} = T_2 V_d^{\gamma-1}$$

- Hence $V_b/V_a=V_c/V_d$, substituting back to the log functions,

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$$

- The **efficiency** defined as W/Q_1:

$$\eta = \frac{Q_1 - Q_2}{Q_1} = \frac{T_1 - T_2}{T_1} < 1$$

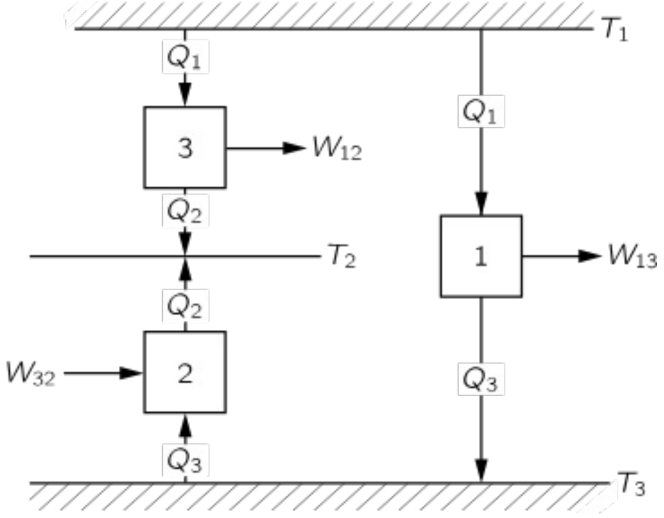
Universal property for reversible engine

- Consider engine 3 takes Q_1 from the reservoir of T_1, and produce W_{12} and Q_2 to reservoir of T_2; and engine 2 runs in reverse, taking Q_3 from reservoir of T_3, consuming W_{32} and put Q_2 to reservoir of T_2. Given the first law of thermodynamics, it can be viewed as a single engine 1, takes Q_1 from T_1, and do work $W_{13}=W_{12}+W_{32}$, and put Q_3 to T_3
- Define a function f_i based on heat ratio

$$f_1(T_1,T_3)=Q_3/Q_1=(Q_3/Q_2)*(Q_2/Q_1)=f_2\ (T_2,T_3)*f_3\ (T_1,T_2)$$

- So for a given amount of heat Q_S delivered at some degree from an engine running at temperature T degrees, the heat Q absorbed must be that amount Q_S times some increasing function of the temperature:

$$Q=Q_sf(T)$$



3 plus 2 is equivalent to 1.