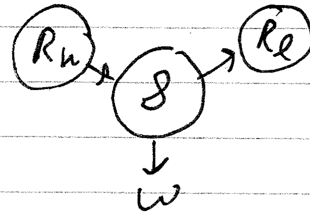
8. Heat and Work

Now we'll study one of the classical topics in thermodynamics: the theory of heat engines



These are systems that move heat from a hot reservoir to a cold reservoir, producing work in the process.

Applications include steam engines, internal combustion engines, electrical generators, etc.—

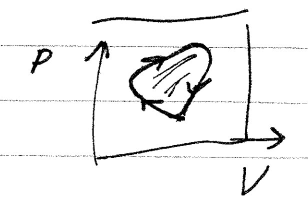
We analyze heat engines using the first law of thermodynamics, written

$$dU = \bar{d}W + \bar{d}Q$$

We write $\bar{d}W$ and $\bar{d}Q$ to emphasize that W and Q are not functions of the state of the system

One can <u>have</u> energy, but one <u>does</u> work.

For example, we may write $\bar{d}W = p\,dV$, where p and V <u>are</u> functions. If we consider a closed <u>cycle</u> in the p, V plane,



then $\oint dV = 0$ but $\oint p\,dV \neq 0$

It is possible to do net work even if the system returns to its initial state

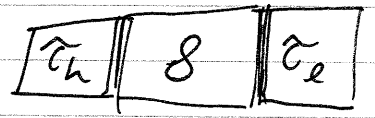
Similarly

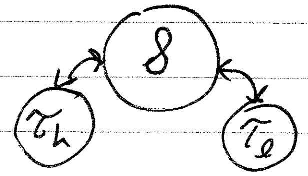
$$\bar{d}Q = \tau\, d\sigma,$$ where τ and σ are functions but Q is not

Thermodynamics examines the fundamental limitations on how much of the heat added to a system can be converted to useful work — arising because $\bar{d}Q$ involves entropy flow, and entropy <u>cannot</u> <u>decrease</u>

It is fun to see how very simple mathematical reasoning can lead to deep and useful physical conclusions

Ideal heat engine:





system can exchange heat w/ either of two reservoirs

① Operates between two reservoirs, one at a higher temperature τ_h, the other at a lower temp. τ_ℓ

② It executes a cycle, with $\mathcal{S}$ returning to initial configuration, which can be executed repeatedly

③ The ideal engine operates reversibly: it removes as much entropy from the τ_h reservoir as it expels at τ_ℓ

We have $Q_h = \tau_h \Delta\sigma$ — the amount of heat withdrawn at τ_h

$Q_\ell = \tau_\ell \Delta\sigma$ — the amount of heat expelled at τ_ℓ

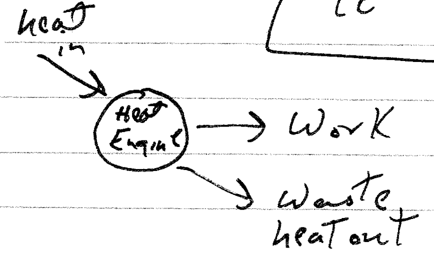
In one cycle $\Delta U = 0$ so

$$W = Q_h - Q_\ell = \left(1 - \frac{\tau_\ell}{\tau_h}\right) Q_h = \frac{\tau_h - \tau_\ell}{\tau_h} Q_h = \eta_c Q_h$$

where the efficiency of the conversion of heat to work is defined as $\eta = W/Q_h$; here it is

$$\boxed{\eta_c = \frac{\tau_h - \tau_\ell}{\tau_h}}$$

which is called the "carnot efficiency". It is the best possible, and applies for $\Delta\sigma = 0$ in a closed cycle.

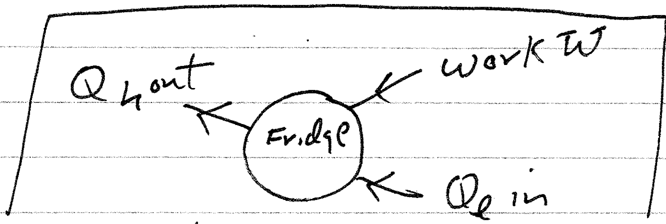


In general $\Delta\sigma \geq 0$, and if > 0, then more heat is wasted.

Note that $\eta_C < 1$ unless $\tau_\ell = 0$; the engine necessarily wastes some of the heat it takes in.

The Carnot efficiency is achievable in principle, but in practice even more heat is wasted for practical reasons: there is friction, irreversible expansion, etc..

<u>Refrigerator:</u>



A refrigerator is a heat engine run backwards: instead of using the flow of heat from hot to cold to do work, it uses work to pump heat from a cold place to a hot place. Its performance is measured by $\gamma = Q_\ell / W$ – the heat removed per unit of work

The best possible refrigerator operates reversibly, so that $W = Q_h - Q_\ell = \left(\frac{\tau_h}{\tau_\ell} - 1\right) Q_\ell$, and so

$$\gamma_C = \frac{Q_\ell}{(\tau_h/\tau_\ell - 1)\, Q_\ell} = \frac{\tau_\ell}{\tau_h - \tau_\ell} \qquad \text{(Carnot)}$$

<u>Heat Pump</u>: A heat pump heats a room by refrigerating the outdoors. From the point of view of thermodynamic efficiency, this is better than direct heating because we take advantage of the heat available in the low temperature reservoir

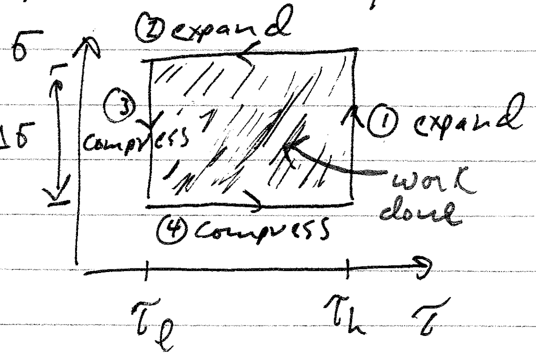
$$\frac{Q_h}{W} = \frac{Q_h}{(1 - \tau_\ell/\tau_h)\, Q_h} = \frac{\tau_h}{\tau_h - \tau_\ell}$$

compared to $Q_h = W$ if we heat directly (e.g. w/ electricity).

(However, a heat pump is expensive...)

Carnot Cycle:

We use (classical) ideal gas in a piston as an ideal heat engine. The engine's reversible cycle consists of 4 "strokes" — two are isothermal (in contact with the reservoirs at τ_h, τ_ℓ) and two are isentropic (the system is isolated, and its temperature changes from τ_h to τ_ℓ or from τ_ℓ to τ_h).



How much work is done in one complete cycle?

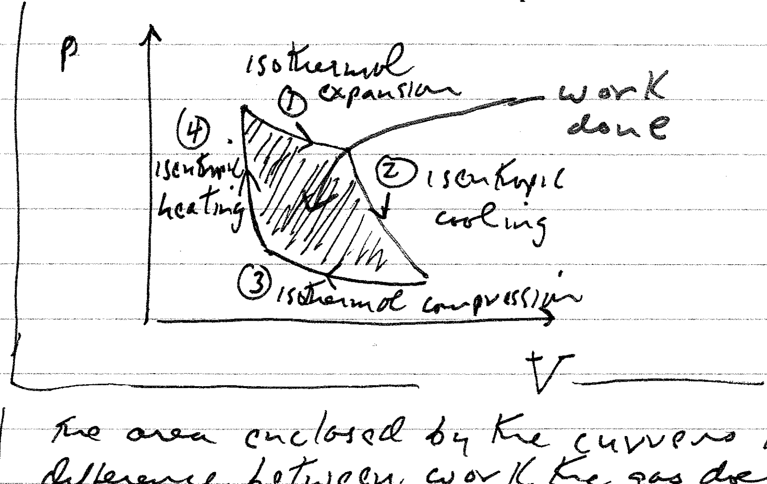
$$0 = \oint dU = \oint \tau\, d\sigma - \oint p\, dV$$

Therefore, the work done by the system is:

$$W = \oint p\, dV = \oint \tau\, d\sigma = \tau_h \Delta\sigma - \tau_\ell \Delta\sigma = (\tau_h - \tau_\ell)\Delta\sigma$$

$$= \text{Area enclosed in } \tau\text{-}\sigma \text{ plane}$$

It is instructive to study the details of each stroke, using properties of the classical ideal gas that we have derived.



Recall that $pV = N\tau$

① Isothermal expansion

$p_f/p_i = V_i/V_f$ and

work done is

$$W = \int p\, dV = N\tau \int \frac{dV}{V}$$

$$= N\tau \ln(V_f/V_i)$$

The area enclosed by the curves is the difference between work the gas does during expansion, and work we do during compression.

(2) Isentropic expansion.
Since $U = \frac{3}{2}N\tau$, and there is no heat flow during the isentropic stroke

$$W = \tfrac{3}{2}N(\tau_i - \tau_f) = \tfrac{3}{2}N(\tau_h - \tau_\ell)$$

— Note that this work is equal and opposite to W during the isentropic compression (since there τ increases from τ_ℓ to τ_h).

To determine the curve in p-V plane, recall

$$\sigma = N\left[\ln\left(\frac{n_Q}{n}\right) + \tfrac{5}{2}\right] = \text{const} \Rightarrow V\tau^{3/2} = \text{const}$$

(monatomic gas) $\Rightarrow V^{5/2}p^{3/2} = \text{const}$ or $p \propto V^{-5/3}$

(and $V_f/V_i = (\tau_i/\tau_f)^{3/2}$)   In particular $p_f/p_i = (V_i/V_f)^{5/3}$

The net work done in the cycle is the difference of work in the two isothermal steps

$$W = (\tau_h - \tau_\ell)N\ln(V_f/V_i)$$

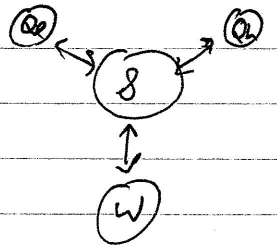
— which we can compare to the heat taken in during the isothermal stroke at τ_h: $Q_h = \tau_h N\ln(V_f/V_i)$

Hence the efficiency is $\eta = \dfrac{W}{Q_h} = \dfrac{\tau_h - \tau_\ell}{\tau_h} = \eta_c$

This had to work because the entropy change $|\Delta\sigma| = N|\ln(V_f/V_i)|$ is the same in both isothermal strokes

(Therefore, the process is reversible.)

Last time: the theory of heat engines



Work $Q_h - Q_l$ is done by reversible engine. Q_h withdrawn from hot reservoir, Q_l expelled to cool reservoir

Efficiency $\eta = \frac{W}{Q_h} = \frac{\tau_h - \tau_l}{\tau_h} = \eta_C < 1$ for $\tau_l > 0$

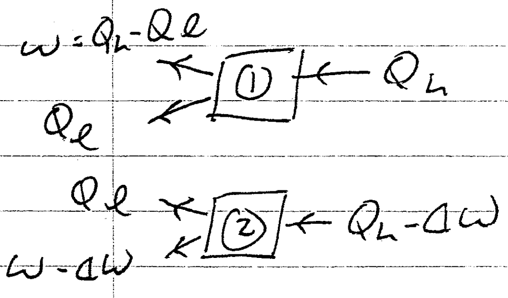
Efficiency is limited because entropy cannot decrease. This can be formulated as:

2nd Law: It is not possible to extract heat Q from a reservoir and convert it to work without producing any waste heat (unless a $\tau = 0$ reservoir is available)

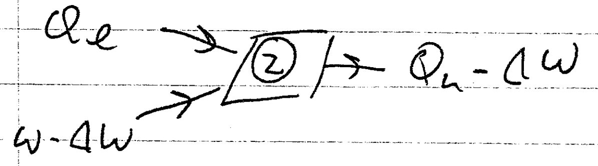
It follows that: All reversible engines operating between reservoirs at temperatures τ_h and τ_l have the same efficiency $\eta = (Q_h/W)^{-1}$

("Reversible" means it is possible in principle to run the engine backwards)

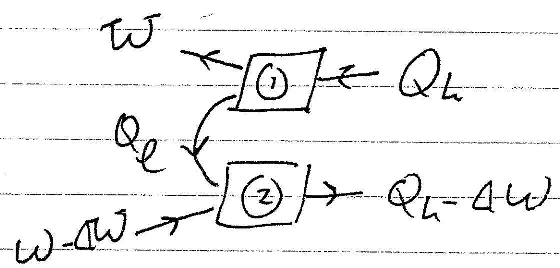
The idea is that, if one heat engine has lower efficiency than the other, then the lower efficiency engine is a more efficient refrigerator. We can run the two in series, the less efficient one in reverse, and violate second law



Here both ① and ② produce the same amount of waste heat, and ② is less efficient because it does less work ($\Delta W > 0$)



But as a refrigerator, (2) is more efficient, because it removes Q_ℓ from cold reservoir, doing less work



Now use the refrigerator to pump waste heat back to the hot reservoir.

All together, we have removed $Q = \Delta W$ from hot reservoir, and converted it all to work, violating the 2nd law.

As applied to engines, the pessimist's version of the laws of Thermo are

1. You can't win (Conservation of energy: useful work $\leq$ heat used)
2. You can't break even, except at absolute zero (efficiency < 1, so we always waste heat)
3. You can't make it to absolute zero

A little bit of history
(e.g. Statistical Physics and the Atomic Theory of Matter, by Stephen Brush)
~~Also: MacMillan Encyc of Physics~~

Sadi Carnot was a brilliant engineer, who published one scientific paper in his life
"Reflections on the Motive Power of Fire" 1824
He was born 1796 and died of cholera in 1832, at 36
His work was unrecognized until 1848, when publicized by William Thompson (Lord Kelvin)

His paper was an analysis of the efficiency of heat engines — but mechanical equivalent of heat (conservation of energy) had not yet been discovered! Yet Carnot understood a lot

- "The falling of caloric from high Temp to low Temp produces work"
- He knew an engine must eject heat
- He insisted on a closed cycle for calculating work done
- He proved that the Carnot cycle is the most efficient possible. (How?)
- He spoke of irreversibility. Carnot knew that uncontrolled flow of heat from hot to cold is wasteful
- But he did not state that some heat must be consumed to produce work ($W = Q_h - Q_c$)
- Claimed: Carnot's notes, discovered in 1878 long after his death show that he had understood $W = Q_h - Q_c$ ("mechanical equivalent of heat") by the time of his death.

In 1840's, Joule and Helmholtz formulated the 1st law and the mechanical equivalent of heat.
1848: Kelvin introduced absolute temperature scale (degrees Kelvin) and wrote

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

Rudolf Clausius (born 1822) pioneered the modern formulation of thermodynamics

1850: statement of 2nd Law: you can't make heat flow from cold to hot without "compensation"

1854: Proposes $\frac{dQ}{T}$ as a measure, and writes

$$\frac{\Delta Q_1}{T_1} + \frac{\Delta Q_2}{T_2} \geq 0$$

1857: First systematic treatment of kinetic theory: "the kind of motion we call heat"

1865: Defines entropy $\Delta S = \frac{dQ}{T}$ and states $\Delta S \geq 0$

[1916: Nernst "New heat thm" $C_V \to 0$ as $T \to 0$ introduces the Third Law

Why does that mean $T=0$ is unattainable?

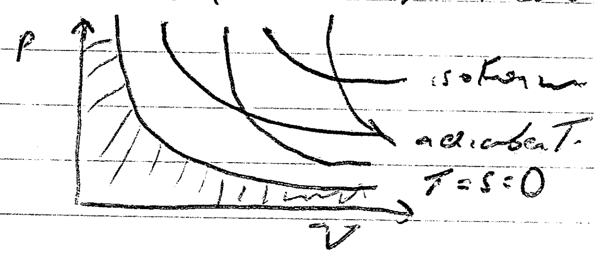
was reformulated by Planck as $S \to 0$ as $T \to 0$

$$C_V = T\frac{dS}{dT} \Rightarrow S = \int \frac{dT}{T} C_V \quad \text{so } C_V \to 0 \text{ needed for convergence}$$

Callen, page 188

Nernst means that isotherm $T=0$ and "adiabat" $S=0$ coincide

In an adiabatic process then, since adiabats cannot intersect, we can't reach $T=0$



And an adiabatic process seemed to be our best hope... contact with a $T>0$ reservoir will only make things more difficult