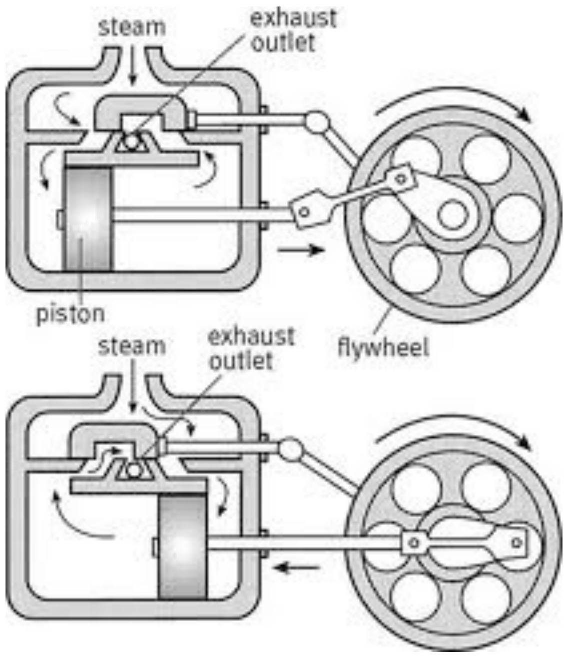
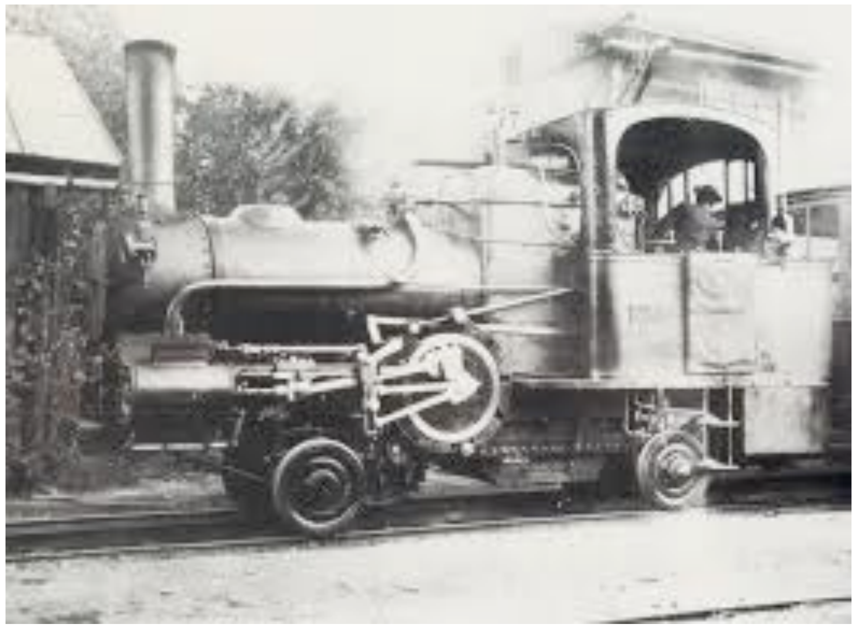
Second Law of Thermo.

Ken Intriligator's week 6 lectures, Nov. 4, 2013

Engine / refrigerator efficiency and

Entropy



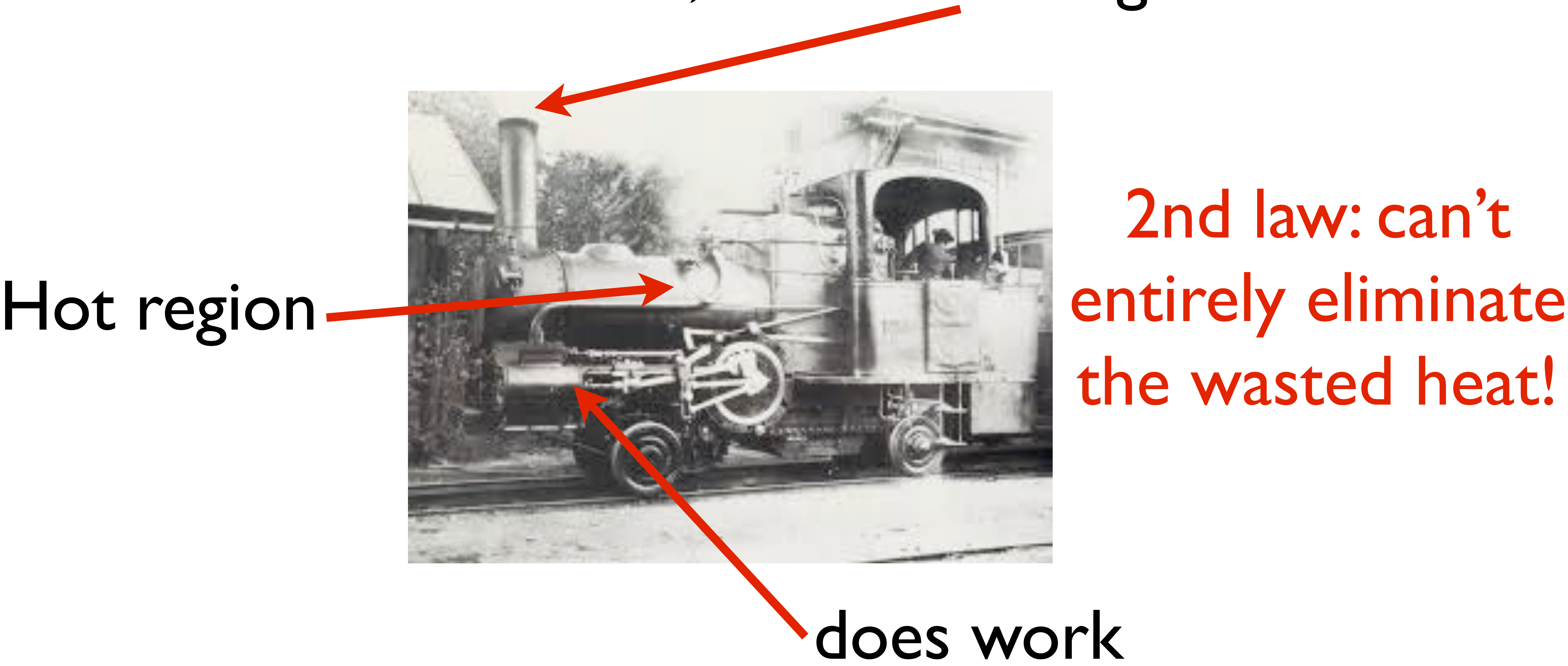


Engine efficiency goal:

- Extract heat, and convert it into work. Want maximal work output per heat input.
- Consider a cyclic engine: same initial and final state, so no change in internal energy. First law: net heat in equals net work out.
- Second law: "Heat can **not** be converted entirely into work, with no other system change!" Related: "Heat can't flow, by itself, from colder to hotter body."

Engines

Take heat out of a hot region, do some work, and waste some heat, into colder region.



Hot region

does work

2nd law: can’t entirely eliminate the wasted heat!

Maximum efficiency:

2nd law: $e \equiv \frac{W}{Q_H} \leq e_R = 1 - \frac{T_C}{T_H}$

We'll explain it on the chalkboard shortly.

Here W is the work done, which we want to be as big as possible, per "what we pay for," which is the heat appearing in the denominator.

Efficiency e = output work done per heat coming in, from the hot region. As we'll discuss, the 2nd law tells us what the maximum efficiency is.

Related

“Heat always flows from hotter object into colder, not vice versa.” For example, heat flows out from the warm kids out into the cold ocean. Why? Note that the ocean is huge, and contains much more thermal energy than the little kids. As we’ll discuss, this is an equivalent statement of the 2nd law of thermodynamics to the statement about maximal engine efficiency.

Entropy S

A **state variable**, determined entirely by the state of the system, not by the history (path) of how the system got in that state. Like energy E. Recall that heat Q and work W are **NOT** state variables, they depend on the path. Entropy is a number (with units of Boltzmann's constant k) which measures the **disorder** of the system. If w is the number of microscopic states with the same macroscopic state variables (e.g. pressure and temperature), then

$$S = k_B \ln w$$

Entropy, qualitatively

Smaller # for S,
more ordered.

Larger # for S,
more disordered.

Irreversible: $S_{before} < S_{after}$

Arrow of time

Newton's law, F=ma, is symmetric if we change t to -t. Microscopic collisions look the same if we film them and then play the movie backwards (aside from some subtle, tiny effects at the subatomic level). But if you watch a film of scrambling an egg, it'd be easy to tell if it's being played forwards or backwards! Why? Large numbers (like Avogadro's) of particles are much more likely to be in disorganized vs organized states, because there are so many more possible disorganized ones. More scrambled vs unscrambled states. This is the...

Second law of thermo:

$$S_{after}(universe) \geq S_{before}(universe)$$

With the equal sign if, and only if the process is **Reversible.** The egg scramble is an example of an irreversible process. A reversible one is where the system undergoes tiny changes, which could have gone either way by slightly adjusting the conditions. Maximal engine or refrigerator efficiency is achieved only when every process is reversible. An idealization. The above inequality gives the arrow of time: "after" is different from "before" because the entropy is bigger.

First law, more precise

$\not{d}W \leq pdV$ Equality iff process is reversible.

$\not{d}Q \leq TdS$ Equality iff process is reversible.

$$dE = \not{d}Q - \not{d}W = TdS - pdV$$

These equalities are whether or not it's reversible.

Entropy change

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} \geq 0$$

$$\Delta S = S_f - S_i = \int dS = \int_{reversible} \frac{\not{d}Q_R}{T}$$

Since entropy, S, is a state variable, this is independent of the path. Can pick any reversible path one likes. Sometimes, computationally, some paths are more convenient than others. So pick a convenient one.

Examples (more, soon)

Reversible adiabatic process: $\Delta S = \int \frac{đQ}{T} = 0.$

Reversible isotherm process: $\Delta S = \int \frac{đQ}{T} = \frac{Q}{T}$

Ideal gas isotherm:

$$\Delta S = \frac{Q}{T} = \frac{W}{T} = \frac{1}{T}\int p dV = Nk \int \frac{dV}{V} = Nk \ln(V_f/V_i)$$

Ideal gas, cont.

$$dE = TdS - pdV = \frac{1}{2}fNkdT$$

so $$dS = \frac{1}{2}fNk\frac{dT}{T} + Nk\frac{dV}{V}$$

so $$S_2 - S_1 = \frac{1}{2}fNk\ln(\frac{T_2}{T_1}) + Nk\ln(\frac{V_2}{V_1})$$

Now, move to chalkboard for further discussion and examples.

Cyclic and/or reversible

Cyclic process (same initial and final states)

$$\Delta S_{system} = 0, \;\; \Delta S_{universe} \geq 0.$$

Reversible process: $\Delta S_{universe} = 0.$

Cyclic and Reversible process:

$$\Delta S_{system} = \Delta S_{universe} = 0.$$

This is the case with maximal efficiency.

Carnot engine

Maximal efficiency if every step is reversible.
The Carnot engine has 4 reversible stages:

$$A \rightarrow B : \text{isotherm expansion at } T_H$$

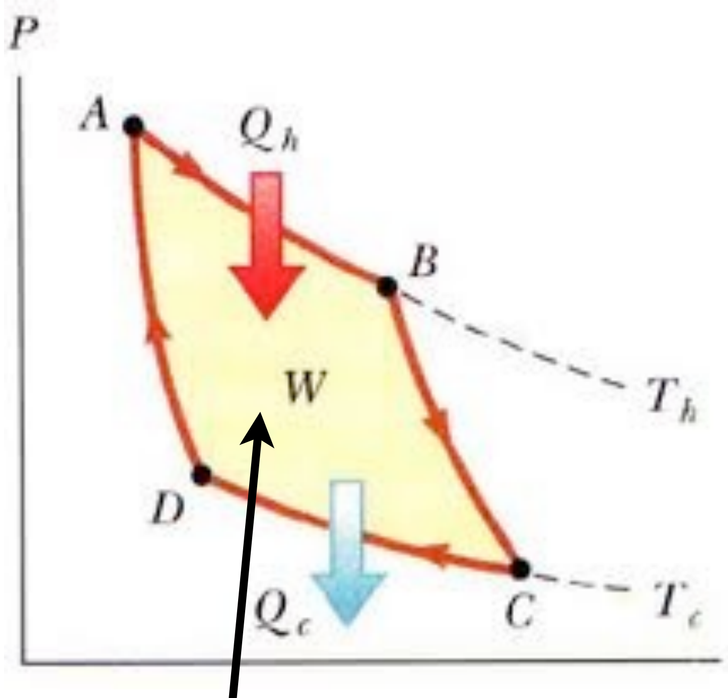
$$B \rightarrow C : \text{adiabatic expansion from } T_H \rightarrow T_C$$

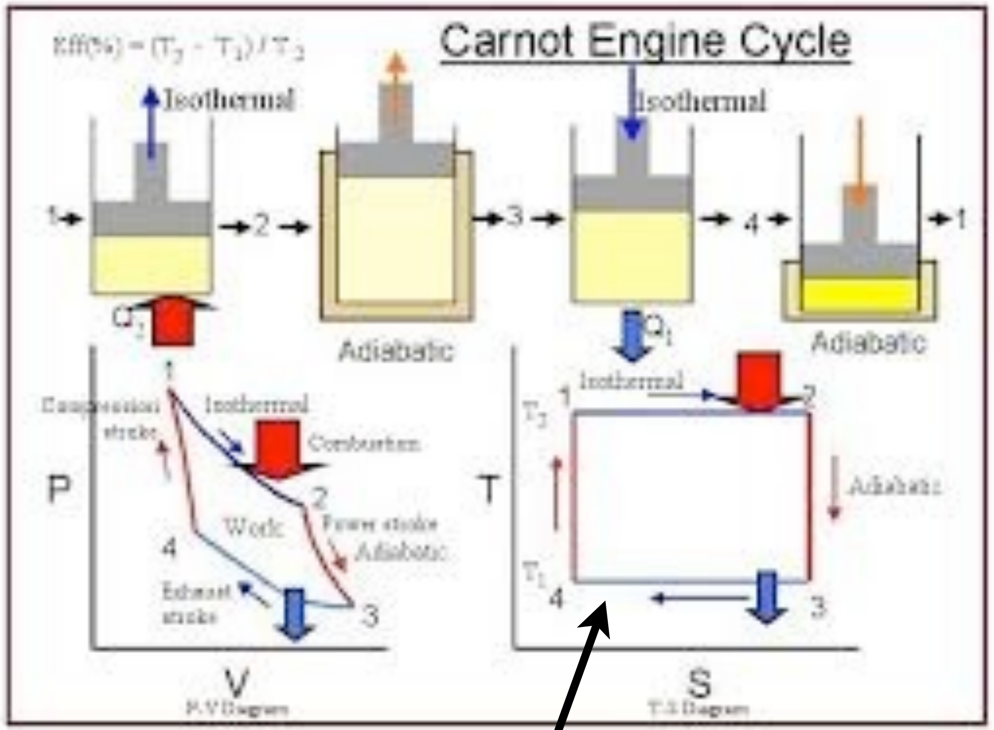
$$C \rightarrow D : \text{isotherm compression at } \ T_C$$

$$D \rightarrow A : \text{adiabatic compression from } T_C \rightarrow T_H$$

Cyclic total process, so state variables E and S have no net change after full cycle.

Carnot engine,cont.





$$W = \oint p\,dV$$

$$W = Q = \oint T\,dS$$

cyclic!

Carnot engine, cont

Will show (on chalkboard) that:

$$W_{total} = Nk_B(T_H - T_C)\ln(V_B/V_A)$$

$$Q_H \equiv Q_{A\to B} = Nk_BT_H\ln(V_B/V_A)$$

$$e \equiv \frac{W}{Q_H} = 1 - \frac{T_C}{T_H} = 1 - \frac{Q_C}{Q_H}$$

Boltzmann formula

$$S = k_B \ln w$$

E.g. ideal gas with N molecules in volume V:

$w \sim V^N$ $S \sim N k_B \ln V$

E.g. free expansion of ideal gas:

$\Delta S = N k_B \ln(V_f / V_i)$ as seen earlier.