Modern
Day 21

<u>Today</u>

I Last time

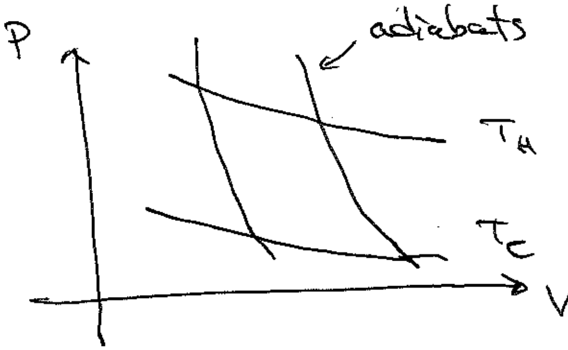
II Entropy

• There is no more efficient engine that operates btwn T_H & T_c.

This is a consequence of the 2nd law of thermodynamics

So, today we move towards formulating the 2nd law and a notion of entropy.

I. Studied Carnot's engine



$$\epsilon = 1 - \left(\frac{\Delta Q_{out}}{\Delta Q_{in}}\right) \overset{\text{proved}}{=} 1 - \frac{T_C}{T_H}$$

II (1) <u>The 2nd law of thermodynamics:</u>
Heat flows spontaneously from hot to cold.

Again $\frac{\Delta W}{\Delta Q_{in}} = 1 - \frac{T_c}{T_H}$ for Carnot.

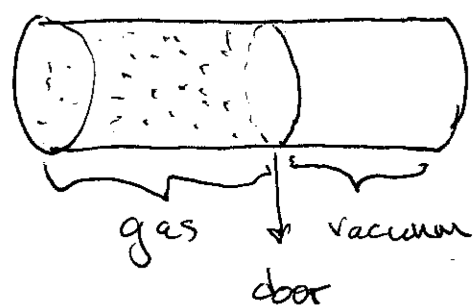
Every irreversible heat engine is worse.

(2) <u>Reversible & Irreversible Processes:</u>

<u>Reversible</u>: Can run backwards — at any moment can change your

mind and retrace your steps:

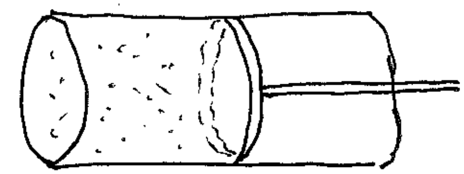
Ex.: "Free expansion" of a gas



→ irreversible process

Most real life processes are to some degree irreversible

Contrast "controlled" expansion



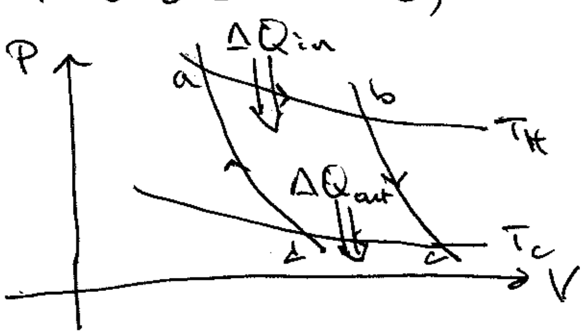
reversible

Essence of a reversible process: Proceeds by a succession of equilibrium states.

During an irreversible process Thermodynamic variables lose their meaning. (P, V, T not well defined)

(3) <u>Entropy</u>

<u>Step 1</u> Carnot Cycle (two isotherms & two adiabats)



$$\Delta Q_{in} = \Delta W_{ab} = \int P\,dV = nRT_H \ln\left(\frac{V_b}{V_a}\right)$$

$$\Delta Q_{out} = nRT_C \ln\left(\frac{V_c}{V_d}\right)$$

$$\frac{\Delta Q_{in}}{\Delta Q_{out}} = \frac{T_H \ln\left(\frac{V_b}{V_a}\right)}{T_C \ln\left(\frac{V_c}{V_d}\right)} = \frac{T_H}{T_C}$$

But then

$$\frac{\Delta Q_{in}}{T_H} = \frac{\Delta Q_{out}}{T_C}$$

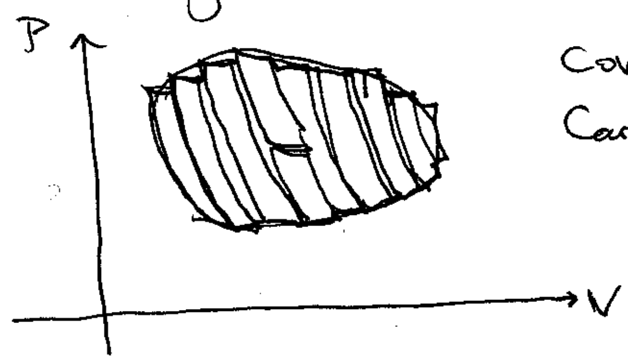
and if we revert to usual convention with

ΔQ_{in} positive

ΔQ_{out} negative

$$\boxed{\frac{\Delta Q_{in}}{T_H} + \frac{\Delta Q_{out}}{T_C} = 0}$$

<u>Step 2</u>: Any reversible process

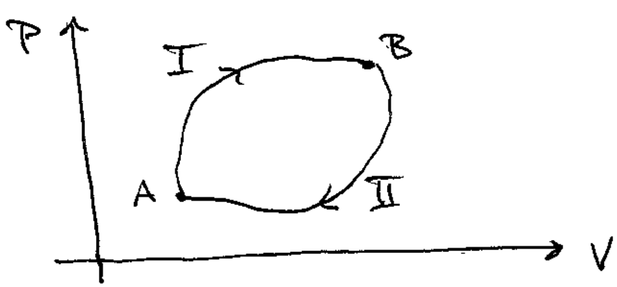


Cover it with Carnot cycles

$$\sum_{\text{edges } i} \frac{\text{đ}Q_i}{T_i} = 0 \quad \text{(over all Carnot cycles)}$$

But, all internal lines cancel in pairs

$$\sum_{\text{sawtooth bndry}} \frac{\text{đ}Q_i}{T_i} = 0$$



$$0 = \oint \frac{\text{đ}Q}{T} = \int_{I\,A}^{B} \frac{\text{đ}Q}{T} + \int_{B\,II}^{A} \frac{\text{đ}Q}{T}$$

$$= \int_{I\,A}^{B} \frac{\text{đ}Q}{T} - \int_{II\,A}^{B} \frac{\text{đ}Q}{T}$$

$$\Rightarrow \boxed{\int_{I\,A}^{B} \frac{\text{đ}Q}{T} = \int_{II\,A}^{B} \frac{\text{đ}Q}{T}}$$

Let # of long skinny Carnot cycles $\longrightarrow \infty$ and you get a perfect fit of the sawtooth to original cycle for any reversible cycle:

$$\oint \frac{\text{đ}Q}{T} = 0$$

<u>Step 3</u>: We can now show that $\int_A^B \frac{\text{đ}Q}{T}$ is independent of path taken from A to B.

The paths I and II are arbitrary and so we learn that the integral is completely independent of any choice of path.

Hence $\frac{\text{đ}Q}{T}$ is <u>exact</u> and we can introduce a state function S such that

$$dS = \frac{\text{đ}Q}{T}$$

The value of S only depends on where in state space you are, e.g. at A or at B.