Lecture 23 – 2nd law implications

Purdue ME 200, Thermodynamics I

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Outline

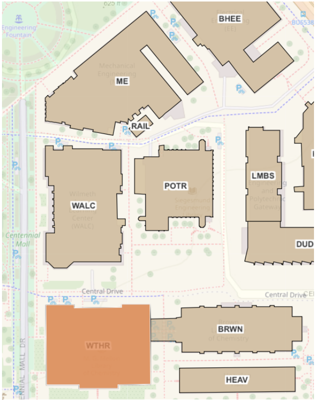
Exam 2 reminders

Thermodynamic temperature scales

Proof of the Clausius inequality

When and where is exam #2?

- 6:30-7:30 PM in Wetherill 200 this Thursday, March 9



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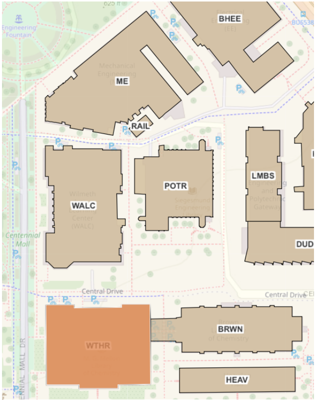

- no class Friday, March 11
- homework 22–24 due 11:59 PM Monday, March 20

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- but mostly lectures 13-19 and homework 14-21

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- closed book, closed notes
- we'll provide equation sheet and any necessary tables
- don't interpolate tables; just use closet data point

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  - ◇ Casio: fx-115 or fx-991

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- exams 1, 2 and 3 are each 20% of course grade
- final exam is 25%

Outline

Motivations

- early temperature scale definitions were a bit arbitrary
  - ⋄ 0 °C at p_{atm} water freeze, 100 °C at p_{atm} water boil
  - ⋄ ∼0 °F for cold winter air, ∼100 °F for bodies

Motivations

- early temperature scale definitions were a bit arbitrary
  - $0\ ^\circ$C at p_{atm} water freeze, $100\ ^\circ$C at p_{atm} water boil
  - $\sim 0\ ^\circ$F for cold winter air, $\sim 100\ ^\circ$F for bodies
- Kelvin and others found this unsatisfying
- how to define a temperature scale that's "universal"?

Connections to reversible cycles

- for all reversible cycles between reservoirs at T_h and T_c,

$$\text{power: } \eta = 1 - \frac{Q_c}{Q_h} = 1 - \frac{T_c}{T_h}$$

$$\text{refrigeration: } \beta = \frac{Q_c/Q_h}{1 - Q_c/Q_h} = \frac{T_c/T_h}{1 - T_c/T_h}$$

$$\text{heat pump: } \gamma = \frac{1}{1 - Q_c/Q_h} = \frac{1}{1 - T_c/T_h}$$

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- not all temperature scales work in these formulas
- ones that do are called **thermodynamic** temperature scales
- for all reversible cycles between T_h and T_c, these scales have

$$\frac{T_c}{T_h} = \frac{Q_c}{Q_h}$$

The thermodynamic thermometer

- pick a temperature T_0 at some fixed, reproducible conditions
- to measure the temperature T of any arbitrary reservoir,
  - ◇ run a reversible cycle between it and a reservoir at T_0
  - ◇ measure Q and Q_0
  - ◇ report $T = T_0 Q/Q_0$

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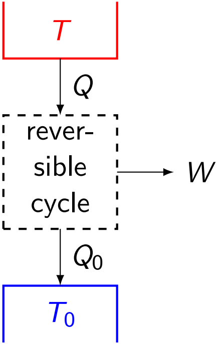

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  1. a reservoir at T_0
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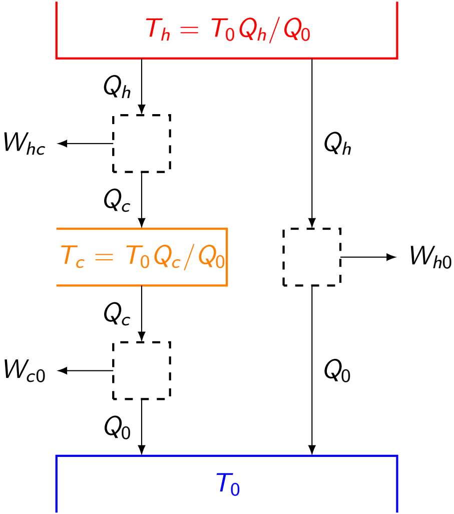
- so it's in some sense "universal"
- it's also consistent with the 2nd law performance limits

Consistency with 2nd law performance limits



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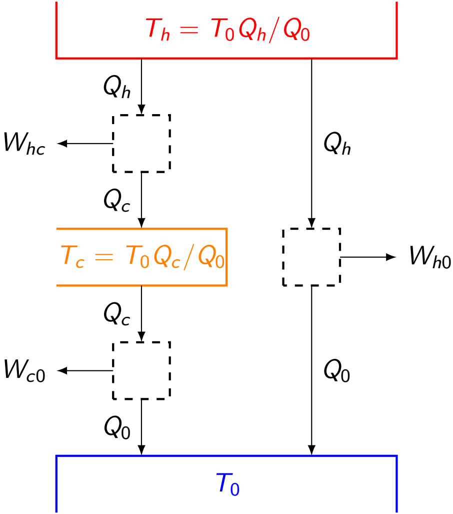

$$\frac{T_c}{T_h} = \frac{T_c}{T_0}\frac{T_0}{T_h} = \frac{Q_c}{Q_0}\frac{Q_0}{Q_h} = \frac{Q_c}{Q_h}$$

Defining the base temperature T_0

- thermodynamic temperature scales must specify T_0
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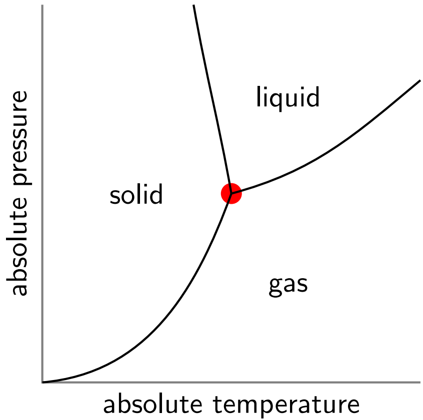

(so maybe the Kelvin scale is not quite "universal")

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Exam 2 reminders

Thermodynamic temperature scales

Proof of the Clausius inequality

Reminder: Entropy statement of 2nd law

- there is an extensive property called **entropy**, S (kJ/K)
- heat transfer δQ into system at boundary temperature T_b
- and entropy generation $\delta\sigma$ (always ≥ 0) within system
- cause change in system entropy

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- for any isolated system,
  - ◇ $\mathrm{d}S = 0$ in reversible processes
  - ◇ $\mathrm{d}S > 0$ in irreversible processes

Reminder: The Clausius inequality

- consider any cycle where the system
  - absorbs Q_{in} from a reservoir whose temperature is T_{in}
  - emits Q_{out} to a reservoir whose temperature is T_{out}
- the entropy statement of the 2nd law implies that

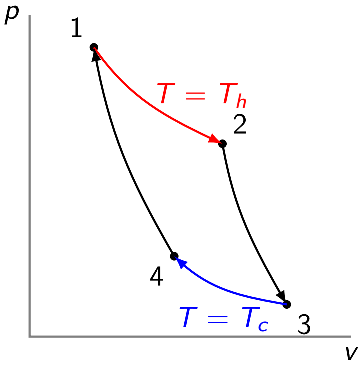
$$\frac{Q_{\text{in}}}{T_{\text{in}}} \leq \frac{Q_{\text{out}}}{T_{\text{out}}}$$

- this is called the **Clausius inequality**
- it holds with equality if and only if the cycle is reversible

Notation: cyclic integral $\oint$

- a **cyclic integral** is a path integral over a closed path
- for example, the net work in a piston-cylinder Carnot cycle is

$$\oint \delta W = W_{12} + W_{23} + W_{34} + W_{41}$$



Proof of Clausius inequality

- system entropy change over cycle is

$$\oint \mathsf{d}S = \oint \frac{\delta Q_{\mathsf{in}}}{T_b} - \oint \frac{\delta Q_{\mathsf{out}}}{T_b} + \oint \delta\sigma$$

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- $T_b \leq T_{\text{in}}$ during heat transfer with input reservoir, so

$$\oint \frac{\delta Q_{\text{in}}}{T_b} \geq \oint \frac{\delta Q_{\text{in}}}{T_{\text{in}}}$$

- $T_b \geq T_{\text{out}}$ during heat transfer with output reservoir, so

$$\oint \frac{\delta Q_{\text{out}}}{T_b} \leq \oint \frac{\delta Q_{\text{out}}}{T_{\text{out}}} \quad \text{or equivalently} \quad -\oint \frac{\delta Q_{\text{out}}}{T_b} \geq -\oint \frac{\delta Q_{\text{out}}}{T_{\text{out}}}$$

Proof of Clausius inequality (continued)

- if $x \geq a$, $y \geq b$ and $z \geq c$, then $x + y + z \geq a + b + c$, so

$$\oint \mathrm{d}S = \oint \frac{\delta Q_{\text{in}}}{T_b} - \oint \frac{\delta Q_{\text{out}}}{T_b} + \oint \delta\sigma \geq \oint \frac{\delta Q_{\text{in}}}{T_{\text{in}}} - \oint \frac{\delta Q_{\text{out}}}{T_{\text{out}}} + 0$$

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- but S is a property ($\oint \mathrm{d}S = 0$), so $0 \geq \oint \frac{\delta Q_{\mathrm{in}}}{T_{\mathrm{in}}} - \oint \frac{\delta Q_{\mathrm{out}}}{T_{\mathrm{out}}}$
- reservoir temperatures T_{in} and T_{out} are constant, so

$$\oint \frac{\delta Q_{\mathrm{in}}}{T_{\mathrm{in}}} - \oint \frac{\delta Q_{\mathrm{out}}}{T_{\mathrm{out}}} = \frac{1}{T_{\mathrm{in}}} \oint \delta Q_{\mathrm{in}} - \frac{1}{T_{\mathrm{out}}} \oint \delta Q_{\mathrm{out}}$$

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- $\oint \delta Q_{\mathrm{in}} = Q_{\mathrm{in}}$ and $\oint \delta Q_{\mathrm{out}} = Q_{\mathrm{out}}$, so

$$0 \geq \frac{Q_{\mathrm{in}}}{T_{\mathrm{in}}} - \frac{Q_{\mathrm{out}}}{T_{\mathrm{out}}} \quad \text{or equivalently} \quad \frac{Q_{\mathrm{in}}}{T_{\mathrm{in}}} \leq \frac{Q_{\mathrm{out}}}{T_{\mathrm{out}}}$$

Proof of reversibility condition

- if and only if cycle is reversible, we can run it in reverse:
  - absorb Q_{out} from reservoir at T_{out}
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- $x \geq y$ and $x \leq y$ if and only if $x = y$
- so $Q_{\text{in}}/T_{\text{in}} = Q_{\text{out}}/T_{\text{out}}$ if and only if the cycle is reversible

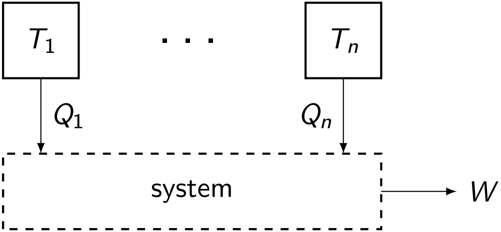
Generalization to n reservoirs

- if system interacts with reservoirs at $T_1, \ldots, T_n$ over a cycle
- and exchanges heat Q_i (possibly < 0) with reservoir at T_i
- then similar arguments show that

$$\sum_{i=1}^{n} \frac{Q_i}{T_i} \leq 0$$

- equality holds if and only if the cycle is reversible

Alternative proof from Kelvin-Planck statement



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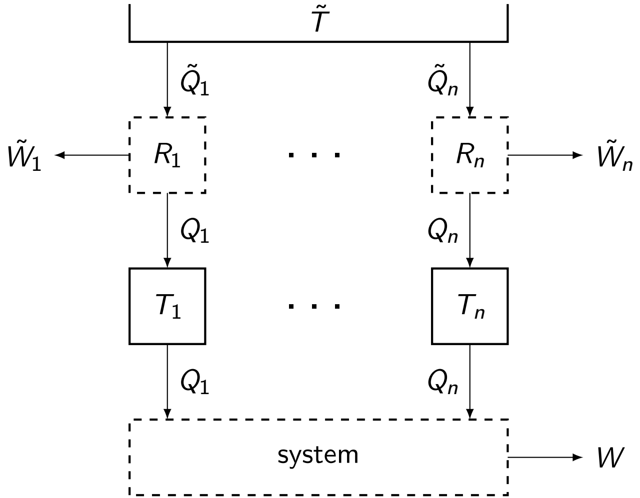

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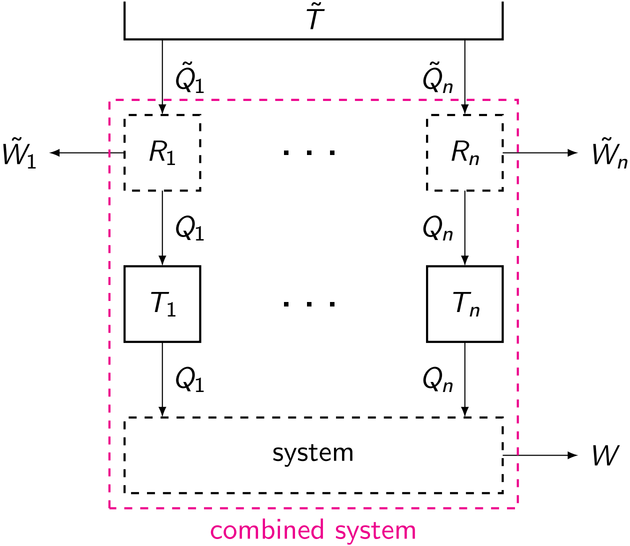

Alternative proof from Kelvin-Plank statement (continued)

- because cycles R_1, ..., R_n are reversible,

$$\frac{T_i}{\tilde{T}} = \frac{Q_i}{\tilde{Q}_i} \quad \text{or equivalently} \quad \tilde{Q}_i = \tilde{T}\frac{Q_i}{T_i}$$

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$$W_{\text{net}} = \tilde{Q}$$

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$$W_{\text{net}} = \tilde{Q}$$

- but $W_{\text{net}} \leq 0$ by the KP statement of the 2nd law, so

$$\tilde{Q} = \tilde{T}\sum_{i=1}^{n} \frac{Q_i}{T_i} \leq 0 \quad \text{or equivalently} \quad \sum_{i=1}^{n} \frac{Q_i}{T_i} \leq 0$$