Lecture 20 – 2nd law introduction

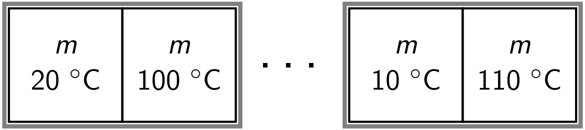
Purdue ME 200, Thermodynamics I

Kevin J. Kircher, kircher@purdue.edu

Outline

Example

Identical incompressible blocks, initially at $T_1^a = 20\ ^\circ\text{C}$ and $T_1^b = 100\ ^\circ\text{C}$, come into contact inside a closed rigid insulated stationary box. Some time later, $T_2^a = 10\ ^\circ\text{C}$ and $T_2^b = 110\ ^\circ\text{C}$. Show that this process violates conservation of mass, the 1st law, or both.



Solution

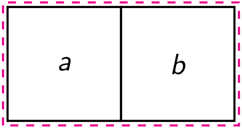
- conservation of mass holds since there are no mass flows
- we can look for 1st law violations in energy balances on
  - ◇ block *a*
  - ◇ block *b*
  - ◇ combined system

Solution (continued)

- block a and b energy balances: $\Delta U_a = -Q$ and $\Delta U_b = Q$
- blocks are identical and incompressible, so
  - ◇ $\Delta U_a = mc\Delta T_a = mc(10^\circ\text{C} - 20^\circ\text{C}) = mc(-10^\circ\text{C})$
  - ◇ $\Delta U_b = mc\Delta T_b = mc(110^\circ\text{C} - 100^\circ\text{C}) = mc(10^\circ\text{C})$

$\Longrightarrow$ $\Delta U_a = -\Delta U_b$, as block energy balances require

Solution (continued)



- combined system energy balance: $\Delta U = 0$
- but $\Delta U = \Delta U_a + \Delta U_b$ and $\Delta U_a = -\Delta U_b$

$\implies$ $\Delta U = 0$, as combined system energy balance requires

Something is missing…

- spontaneous heat flow from cold to hot is unphysical
- but it satisfies conservation of mass and the 1st law
- many other spontaneous processes tell similar stories
    - ◇ cold drinks in warm rooms don't spontaneously get colder
    - ◇ balloons in atmosphere don't spontaneously inflate
    - ◇ heating up a resistor doesn't make current flow
    - ◇ but the 'wrong' directions all satisfy CoM and the 1st law

What the 2nd law of thermodynamics does

- the 2nd law provides a way to rule out unphysical processes
- it also provides
  - ◇ fundamental limits on cycle efficiencies and COPs
  - ◇ ways to identify and quantify inefficiencies
  - ◇ a logical foundation for absolute temperature scales
  - ◇ a bunch of other cool ideas and tools

Outline

Thermal reservoirs

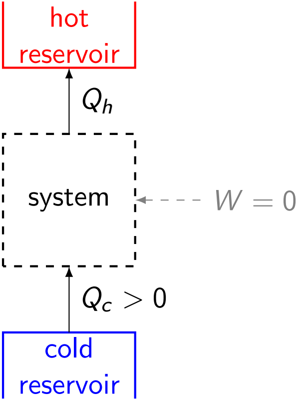
- a **reservoir** is a system with constant T despite heat transfer
- examples:
  - saturated liquid-vapor mixtures with $0 < x < 1$
  - really big things (lakes, the atmosphere, huge hunks of metal)

Clausius statement

No cycle can have the sole effect of heat transfer from a colder reservoir to a warmer one.

Clausius statement (loosely rephrased)

- refrigeration cycles require work
- so this cycle (with $W = 0$) is impossible:

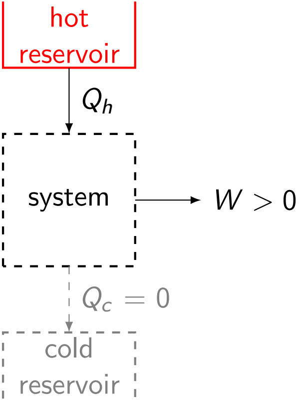


Kelvin-Planck statement

No cycle can receive energy via heat transfer from a single reservoir and produce net work.

Kelvin-Planck statement (loosely rephrased)

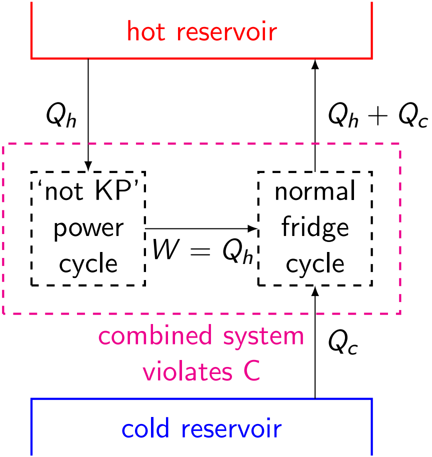
- power cycles must produce waste heat
- so this cycle (with $Q_c = 0$) is impossible:



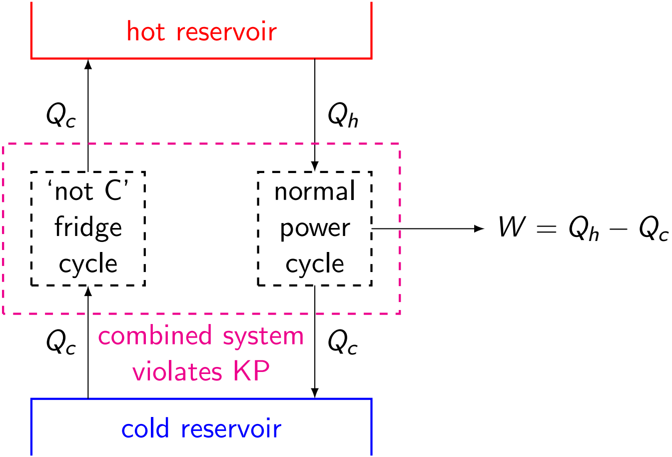
Equivalence of Clausius and Kelvin-Planck statements

- they sound different, but C and KP are equivalent
- to show that C $\iff$ KP, we'll show
  - ◇ C $\implies$ KP
  - ◇ KP $\implies$ C
- both arguments use the contrapositive:
  - ◇ the logical proposition A $\implies$ B
  - ◇ is equivalent to 'not B' $\implies$ 'not A'

Clausius implies Kelvin-Planck (‘not KP’ $\implies$ ‘not C’)



Kelvin-Planck implies Clausius (‘not C’ $\implies$ ‘not KP’)



Outline

Reversibility

- a **reversible** process
  - lets system and surroundings return to their exact initial states
  - is an idealization, like a frictionless plane or point mass
  - is a limit that real processes can approach but never attain
- all real processes have **irreversibilities** such as
  - friction
  - electric resistance
  - unrestrained expansion of a fluid to lower pressure
  - substances with different states or compositions mixing
  - heat transfer driven by nonzero temperature differences

Reminder: 1st law for closed stationary systems

- there is an extensive property called **internal energy**, U (kJ)
- heat transfer δQ into system
- and work δW done by system
- change system internal energy by

$$\mathrm{d}U = \delta Q - \delta W$$

Entropy statement of 2nd law for closed systems

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

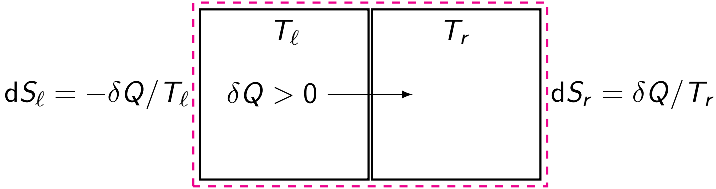
$$\mathrm{d}S = \frac{\delta Q}{T_b} + \delta\sigma$$

- for any isolated system undergoing any process,
  - ◇ $\mathrm{d}S \geq 0$ always
  - ◇ $\mathrm{d}S = 0$ only if the process is reversible

Internal entropy generation is always nonnegative

- suppose entropy is generated within system over some process
- isolate the system and rerun the same internal activities
- then by the 2nd law,
  - $\mathrm{d}S = \cancel{\delta Q}/T_b + \delta\sigma = \delta\sigma$
  - $\delta\sigma \geq 0$ always
  - $\delta\sigma = 0$ only if the process is reversible
- we call a process or system with $\delta\sigma = 0$ **internally reversible**
- standing assumption: reservoirs are internally reversible

Entropy changes in heat transfer



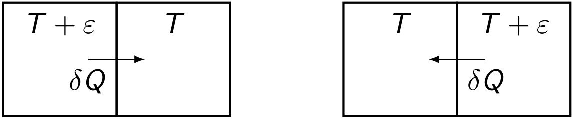
- consider two reservoirs at temperatures T_ℓ and T_r
- combined system entropy change is

$$dS = dS_\ell + dS_r = \delta Q \left(\frac{1}{T_r} - \frac{1}{T_\ell} \right)$$

- combined system is isolated, so $dS \geq 0$ (2nd law)
- since $\delta Q > 0$, we get $T_\ell \geq T_r$ (heat flows from hot to cold)
- heat transfer is reversible only if $dS = 0$, meaning $T_\ell = T_r$

(Approximately) reversible heat transfer

- real (irreversible) heat transfer is always driven by a nonzero ΔT
- but heat transfer approaches reversibility as $\Delta T \to 0$
- systems at T_ℓ and T_r exchange heat ~reversibly if $T_\ell \approx T_r$



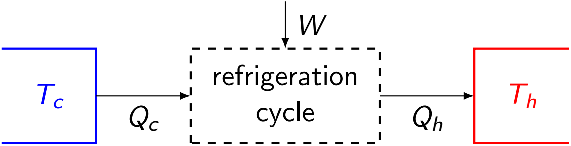
Clausius inequality

- 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

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

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

Entropy statement of 2nd law implies Clausius statement



- Clausius statement: $W > 0$ in any refrigeration cycle
- 1st law for cycles: $W + Q_c = Q_h$, so $W > 0$ if $Q_h/Q_c > 1$
- Clausius inequality (a consequence of the entropy statement):

$$\frac{Q_\mathrm{c}}{T_\mathrm{c}} \leq \frac{Q_\mathrm{h}}{T_\mathrm{h}} \quad \text{or equivalently} \quad \frac{Q_\mathrm{h}}{Q_\mathrm{c}} \geq \frac{T_\mathrm{h}}{T_\mathrm{c}}$$

- but $T_h > T_c$, so $T_h/T_c > 1$
- therefore $Q_h/Q_c > 1$, and $W > 0$

Summary

- the C, KP and E statements of 2nd law all sound different
- but we've shown that E $\implies$ C and C $\iff$ KP
- it's also possible to show that KP $\implies$ E (or C $\implies$ E)
- this closes the circle: all 3 statements are equivalent
- C and KP are more intuitive, but E is more useful

Outline

Motivations

Clausius and Kelvin-Planck statements

Entropy statement

Completely optional: Proof of the Clausius inequality

Individual inequalities

- system entropy change over cycle is

$$\oint \mathrm{d}S = \oint \frac{\delta Q_{\text{in}}}{T} - \oint \frac{\delta Q_{\text{out}}}{T} + \oint \delta\sigma$$

- $\oint \delta\sigma \geq 0$ since $\delta\sigma \geq 0$
- $T \leq T_{\text{in}}$ during heat transfer with input reservoir, so

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

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

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

Combined inequality

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

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

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

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

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

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

Reversibility condition (continued)

- if cycle is reversible, then
  - $\delta\sigma = 0$ throughout the cycle
  - $T = T_{\text{in}}$ during input heat transfer
  - $T = T_{\text{out}}$ during output heat transfer
- in this case,

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

- but $\oint \mathrm{d}S = 0$, so $Q_{\text{in}}/T_{\text{in}} = Q_{\text{out}}/T_{\text{out}}$

$\implies$ Clausius inequality holds with equality for reversible cycles

Reversibility condition (continued)

- if cycle is irreversible, then one of the following must be true:
  - $\delta\sigma > 0$ at some point in the cycle
  - $T < T_{\text{in}}$ at some point during input heat transfer
  - $T > T_{\text{out}}$ at some point during output heat transfer
- any of these imply that the Clausius inequality is strict ($<$)
- so it holds with equality only if cycle is reversible