Thermodynamics

PHY 215
Thermodynamics and Modern Physics

Fall 2025
MSU

Outline

- Clausius's Theorem
- Entropy: a new state function
  - Entropy of an Ideal Gas
- Entropy change in reversible and irreversible processes
  - Carnot Cycle
  - Free Expansion
- Entropy form of 2^{nd} law

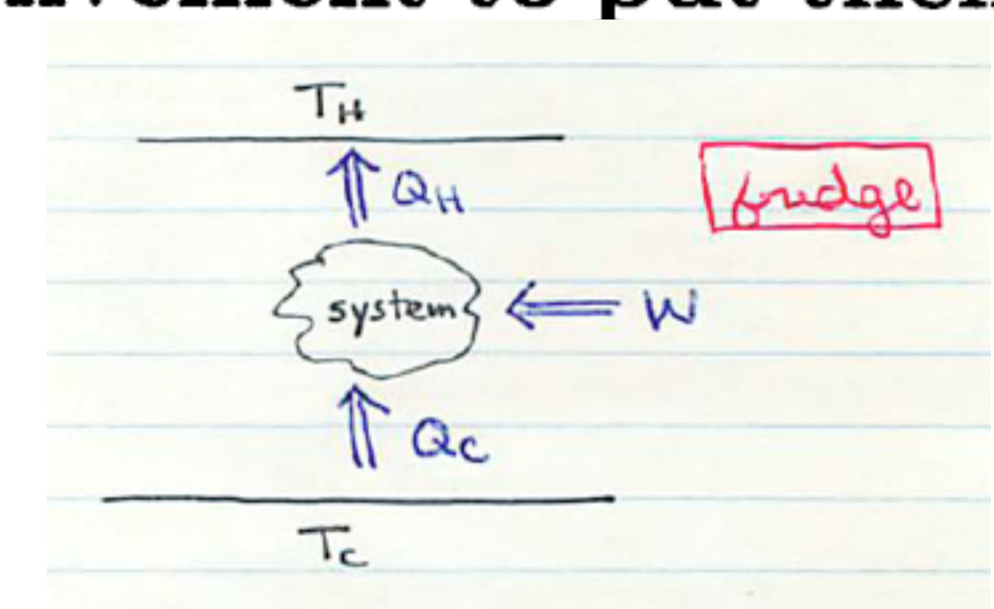
Concept Test

Air conditioners are placed in windows because:

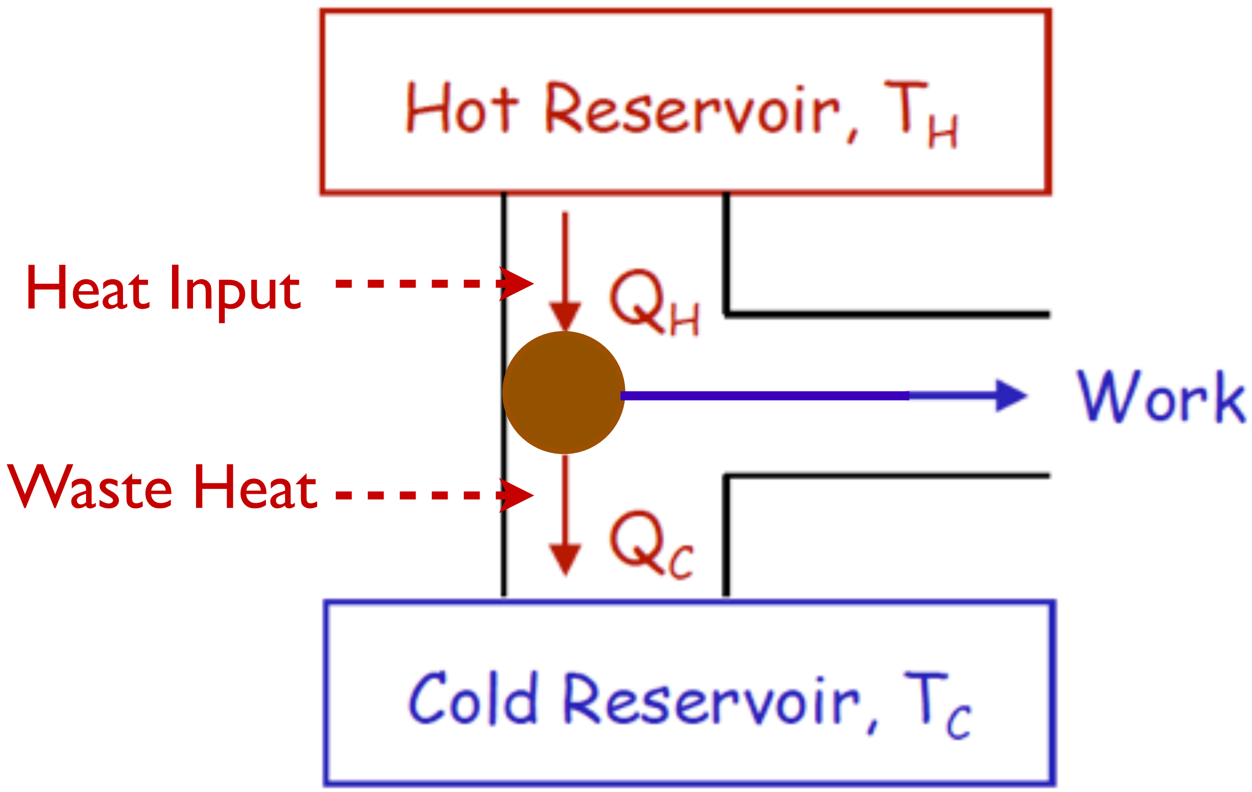
A. It is necessary to have air flowing from the room to the outside while the machine is on.

B. At least two heat reservoirs are needed for a heat engine to work.

C. Their size makes it inconvenient to put them entirely in the house.



Clausius's Theorem I



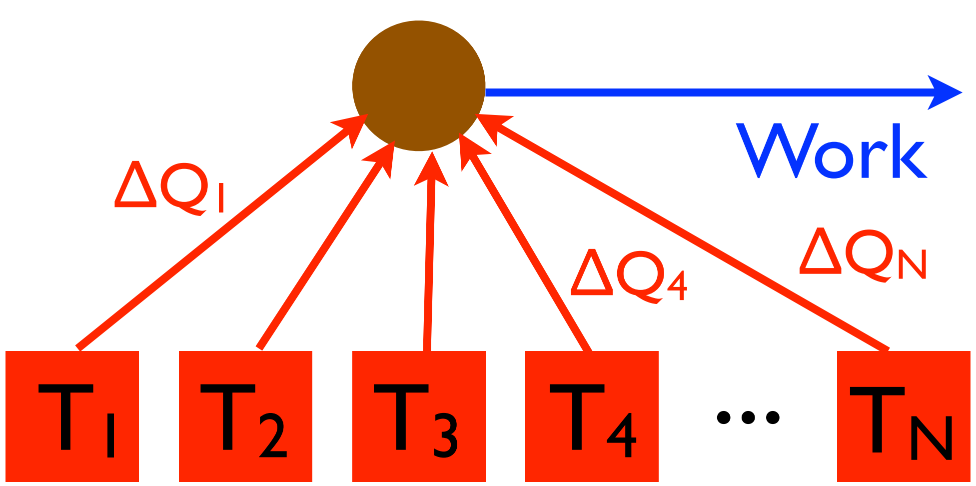
"2-Step" Heat Engine

$$\eta = \frac{W}{Q_H} = \frac{Q_H - Q_C}{Q_H} \leq \eta_{Carnot} = 1 - \frac{T_C}{T_H}$$

$$\frac{Q_H}{T_H} + \frac{-Q_C}{T_C} \leq 0$$

$$\sum_{i=1,2} \frac{\Delta Q_i}{T_i} \leq 0$$, ΔQ_i= "absorbed" heat

"N-Step" Heat Engine:



Compare to "N" Carnot Engines:

"Kelvin" 2nd law ⇒

$$\boxed{\sum_{i=1}^{N} \frac{\Delta Q_i}{T_i} \leq 0}$$

$$\eta \equiv 1 - \frac{Q_c}{Q_H} \leq \eta_{carnot} = 1 - \frac{T_c}{T_H}$$

$$\Rightarrow \quad \frac{Q_c}{Q_H} \geq \frac{T_c}{T_H}$$

$$\Rightarrow \quad \frac{Q_c}{T_c} \geq \frac{Q_H}{T_H}$$

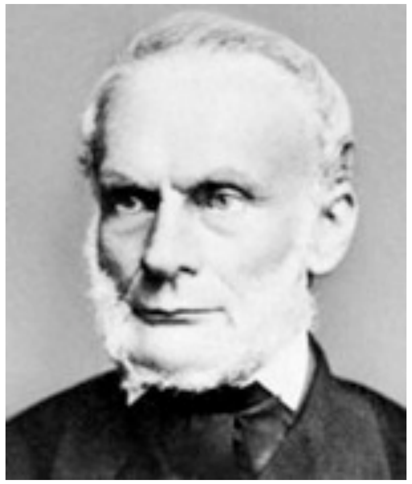
$$\Rightarrow \quad 0 \geq \frac{Q_H}{T_H} - \frac{Q_c}{T_c} = \frac{Q_H}{T_H} + \frac{(-Q_c)}{T_c}$$

$$\Rightarrow \quad 0 \geq \sum_{i=1}^{2} \frac{\Delta Q_i}{T_i}$$

(for the "absorbed" heat ΔQ_i at T_i)

Clausius's Theorem II

<u>Statement of Theorem:</u>

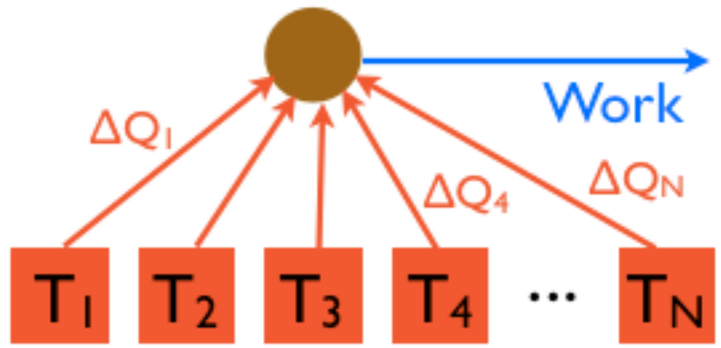


Rudolf Clausius
1822-1888

- For *any* N-step, cyclic, thermodynamic cycle, with reversible or irreversible steps:

$$\boxed{\sum_{i=1}^{N} \frac{\Delta Q_i}{T_i} \leq 0}$$

"N-Step" Heat Engine:

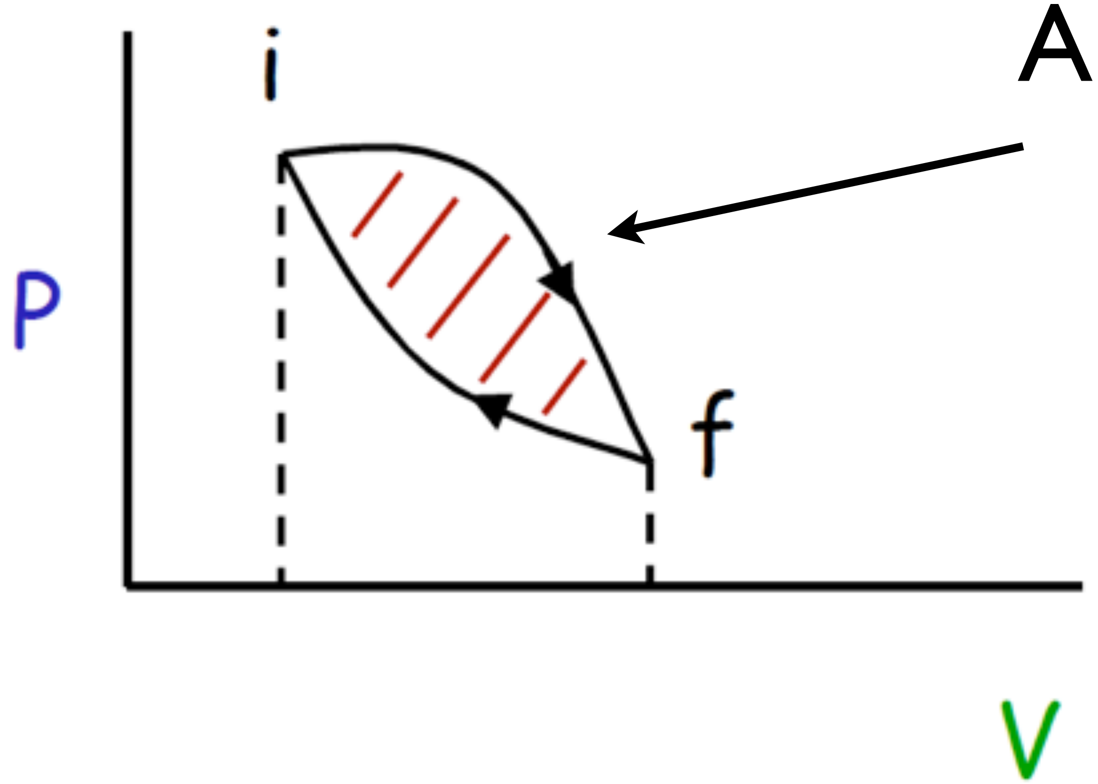


- ΔQ_i heat "absorbed" in i^{th} step
- T_i temperature of i^{th} reservoir
- <u>Equality</u> holds only if all steps reversible!

Follows, logically, from 2^{nd} law of thermodynamics.

Image: http://en.wikipedia.org

Clausius's Theorem III

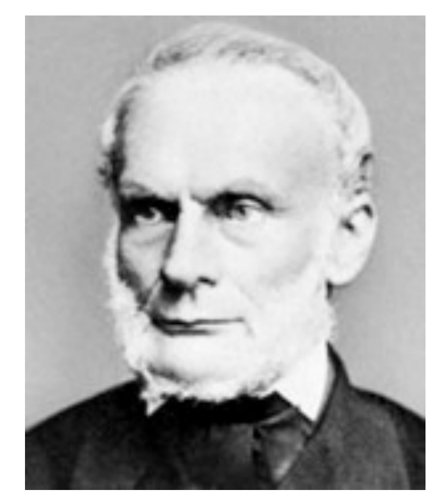


A continuous cycle is an "∞-Step" process!

$$\sum_{i=1}^{N} \frac{\Delta Q_i}{T_i} \rightarrow \oint \frac{dQ}{T} \leq 0$$

For a reversible cycle:

$$\oint \frac{dQ_{rev}}{T} = 0$$



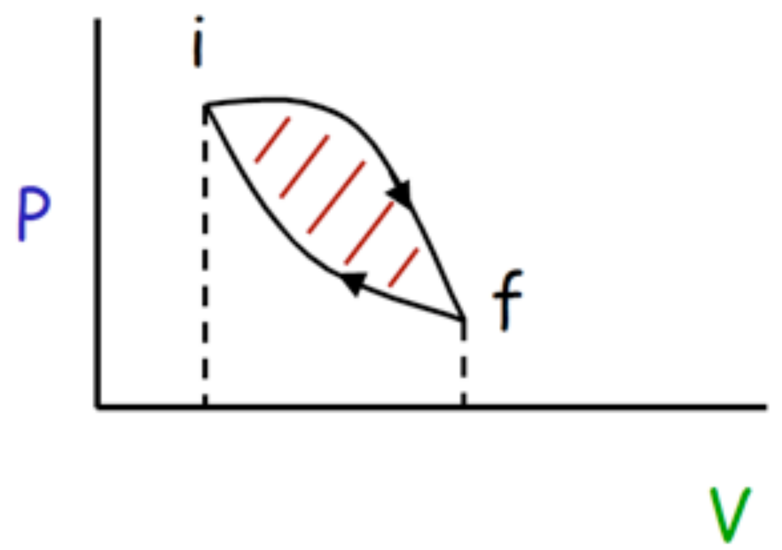
Rudolf Clausius
1822-1888

Image: http://en.wikipedia.org

Clausius Consequences: All Cycles

$$\oint \frac{dQ}{T} \leq 0$$

$\Rightarrow$ dQ_{rev} must have both <u>positive</u> and <u>negative</u> contributions!



The system must both <u>absorb heat</u> from and <u>reject heat</u> to the environment!

Kelvin form of 2^{nd} law.

Recall: "State Functions"

- "State Functions" depend only on the parameters which define an equilibrium state, e.g. p, V, T, n, ...
- Example: U(n,T)=(3/2)nRT, monoatomic gas

$$\int_i^f dU = U_f - U_i \quad \& \quad \oint dU = 0$$

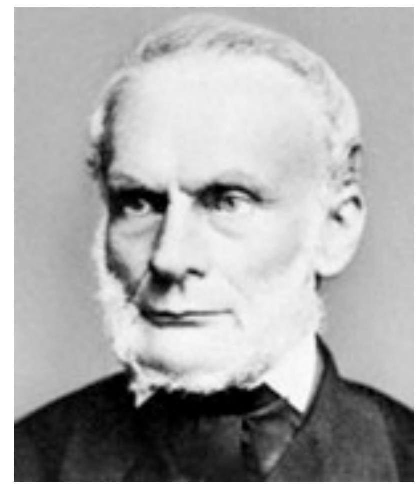
- W and Q are *not* state functions: depend on process which produced state.

$$\oint dW, dQ \neq 0$$

Entropy

For a reversible cycle:

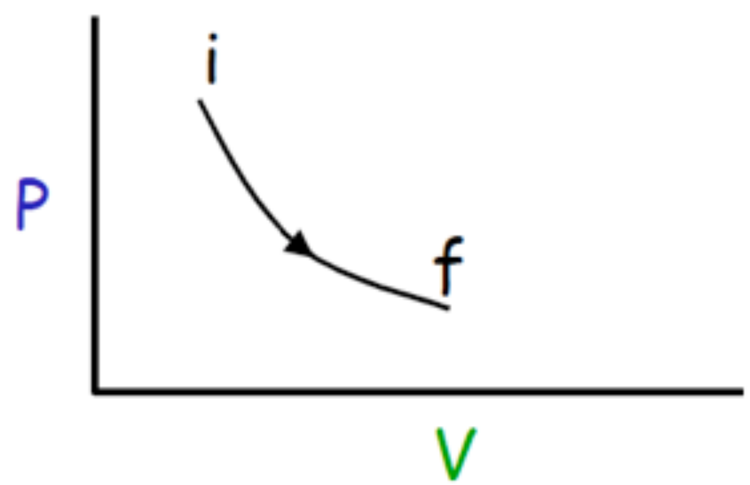
$$\oint \frac{dQ_{rev}}{T} = 0$$



Rudolf Clausius
1822-1888

Define a new state function: Entropy, S

$$dS = \frac{dQ_{rev}}{T}$$



$$S_f - S_i = \int_i^f \frac{dQ_{rev}}{T}$$

Entropy is a "thermodynamic potential": defined up to a constant!

Image: http://en.wikipedia.org

Ideal Gas Entropy I

$$dQ_{rev} = dU + dW = nC_V dT + pdV$$

$$= nC_V dT + nRT\frac{dV}{V}$$

$$\frac{dQ_{rev}}{T} = nC_V\frac{dT}{T} + nR\frac{dV}{V}$$

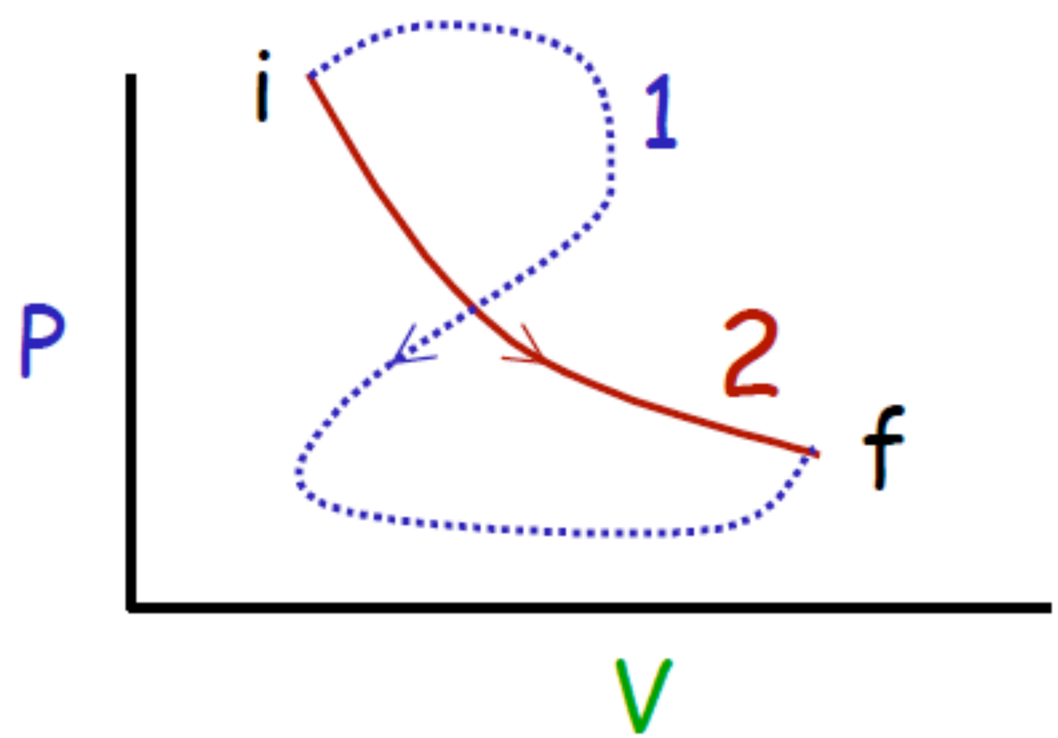
$$= nC_V\, d\log T + nR\, d\log V$$

$$S_f - S_i = \int_i^f \frac{dQ_{rev}}{T}$$

$$= \boxed{nC_V \log\left(\frac{T_f}{T_i}\right) + nR\log\left(\frac{V_f}{V_i}\right)}$$

Ideal Gas Entropy II

$$S_f - S_i = nC_V \log\left(\frac{T_f}{T_i}\right) + nR\log\left(\frac{V_f}{V_i}\right)$$

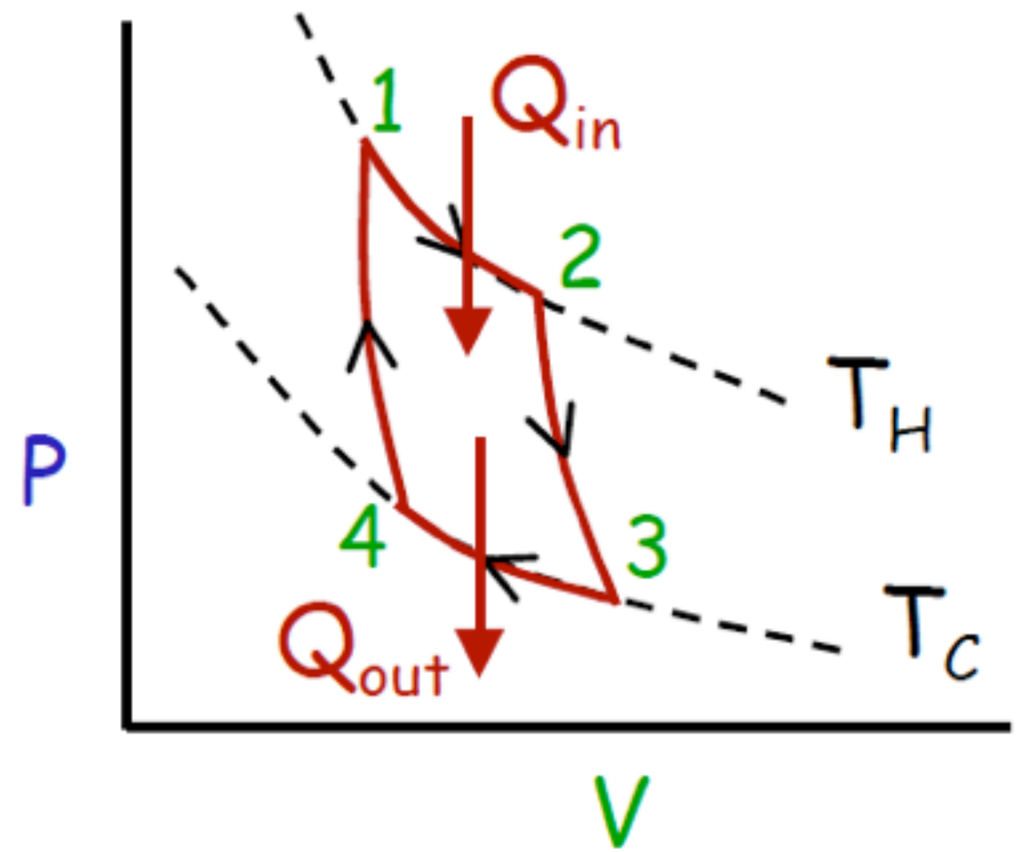


NB: Depends only on initial and final states!

Hence: any path can be used to define ΔS!

Makes sense: S(T,V) a state function ✔

The Carnot Engine



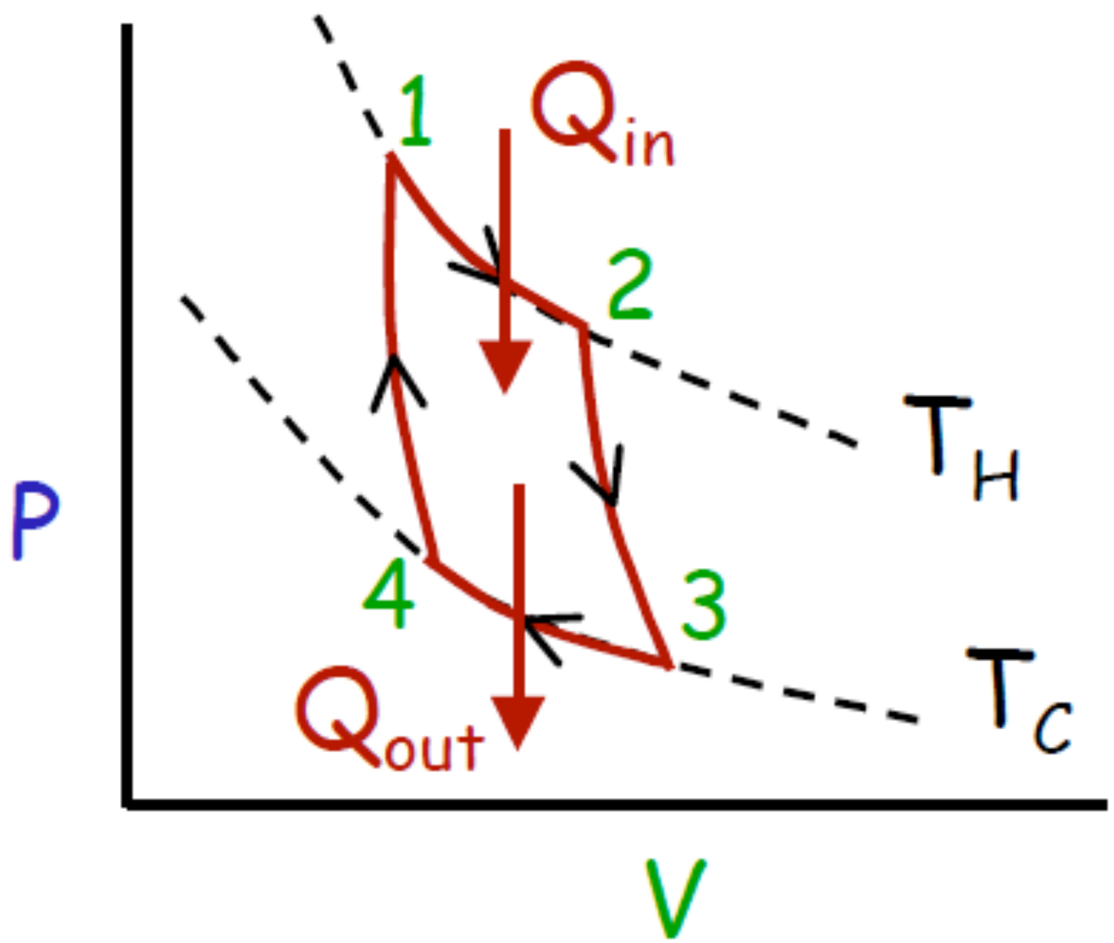
1→2 & 3→4
isothermal

2→3 & 4→1
adiabatic

1. It is reversible: no friction or other dissipative forces.
2. Heat conduction only occurs isothermally at the temperatures of the two reservoirs.

NB: idealized and impractical!

Carnot Cycle



	ΔQ	ΔU	ΔW
1→2	$nRT_H \log \frac{V_2}{V_1}$	0	$nRT_H \log \frac{V_2}{V_1}$
2→3	0	$nC_V \Delta T$	$-nC_V \Delta T$
3→4	$nRT_C \log \frac{V_4}{V_3}$	0	$nRT_C \log \frac{V_4}{V_3}$
4→1	0	$-nC_V \Delta T$	$nC_V \Delta T$
total	?	0	?

Work done during isothermal expansion

$$W = \int_{V_1}^{V_2} (nRT) \frac{dV}{V} = (nRT) \log\left(\frac{V_1}{V_2}\right)$$

Change in internal energy of an ideal gas

$$\Delta U = nC_V \Delta T$$

Carnot Cycle

$$\Delta S \equiv \frac{\Delta Q}{T}$$

	ΔQ	T	ΔS
$1 \to 2$	$nRT_H \ln\left(\frac{V_2}{V_1}\right)$	T_H	$nR \ln\left(\frac{V_2}{V_1}\right)$
$2 \to 3$	0		0
$3 \to 4$	$nRT_c \ln\left(\frac{V_4}{V_3}\right)$		$nR \ln\left(\frac{V_4}{V_3}\right) = -nR \ln\left(\frac{V_2}{V_1}\right)$
$4 \to 1$	0	T_c	0
Total			0

(for $\frac{V_4}{V_3} = \frac{V_1}{V_2}$)

$(\Delta S)_{total} = 0$ for a reversible, cyclic TD process.

Entropy S is a "state function".

Entropy Change: Isothermal Expansion

Isothermal Expansion: $T_f = T_i$, $V_f > V_i$

The amount of heat which leaves the reservoir and enters the gas is

$Q = n R T \ln(V_f/V_i)$.

The entropy change of the gas is

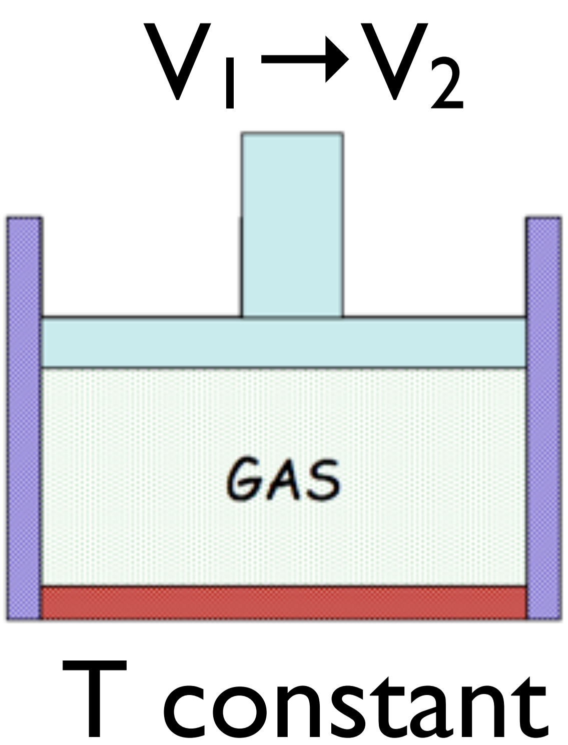
$\Delta S_{gas} = + Q/T = n R \ln(V_f/V_i)$.

The entropy change of the reservoir is

$\Delta S_{reservoir} = - Q/T$.

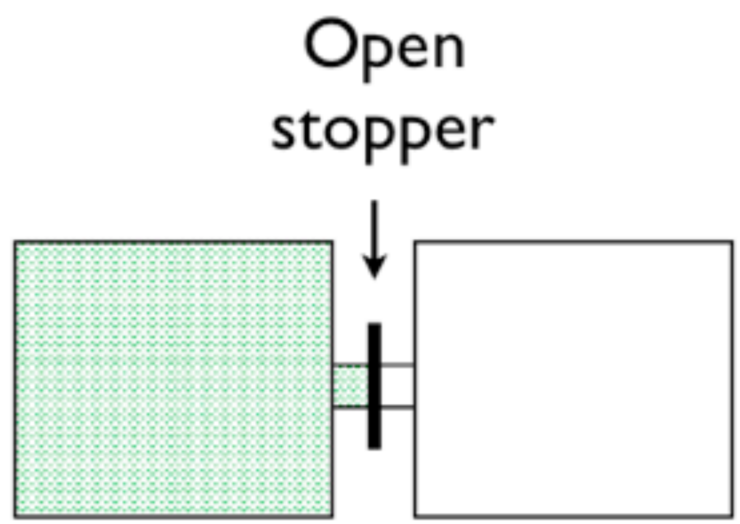
The net entropy change is

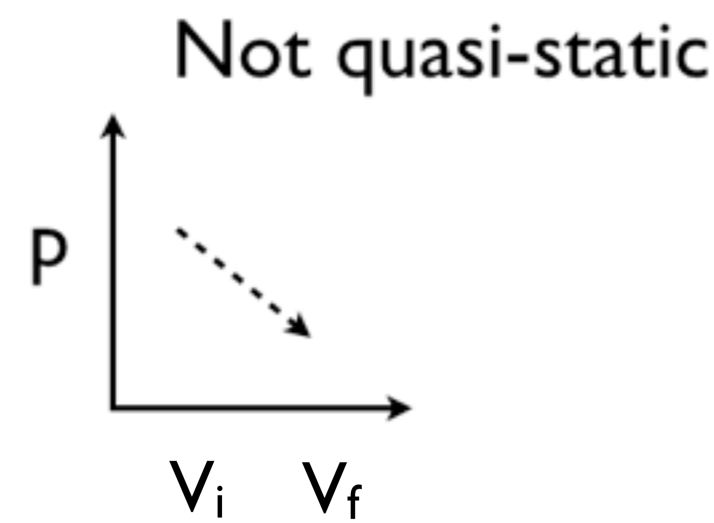
$\Delta S_{universe} = \Delta S_{gas} + \Delta S_{reservoir} = 0$.



In a reversible process, the entropy change of the universe (system + surroundings) is zero.

Entropy Change: Adiabatic Free Expansion





$\Delta Q = 0$ (adiabatic)

$\Delta W = 0$ (nothing to work against)

$\Rightarrow \Delta U = 0$

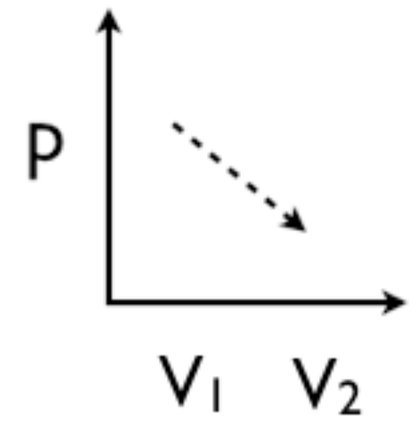
NB: Beginning and ending states of system are the same as isothermal expansion!

$$\Delta S_{gas} = + Q/T = n\,R\,\ln(V_f/V_i).$$

Entropy Increases!

- BUT: no heat transfer from environment!
  - $\Delta S_{reservoir} = 0$
  - $\Delta S_{universe} = \Delta S_{gas} + \Delta S_{reservoir} > 0!$
- Irreversible Processes: Entropy increases.
- NB: In an irreversible process

$$S_f - S_i \neq \int_i^f \frac{dQ}{T}$$



No path in state “space”

2nd Law: Entropy Form

- The entropy of the universe, or any *isolated*, system satisfies $\Delta S_{universe} \geq 0$.
- The equal sign only applies to reversible processes.
- Entropy increases, but does not decrease $\Rightarrow$ "The Arrow of Time"

Sir Arthur Eddington
1882-1944

Image: http://en.wikipedia.org

Entropy: Interpretation

Entropy ~ a measure of the disorder of a system.

A state of high order = low probability
A state of low order = high probability

In an irreversible process, the universe moves from a state of low probability to a state of higher probability.

More in next lecture...

Summary

- Clausius Theorem $$\sum_{i=1}^{N} \frac{\Delta Q_i}{T_i} \leq 0$$
- Reversible Processes $$\oint \frac{dQ_{rev}}{T} = 0$$
- Entropy $$S_f - S_i = \int_i^f \frac{dQ_{rev}}{T}$$
- Ideal Gas Entropy

$$S_f - S_i = nC_V \log\left(\frac{T_f}{T_i}\right) + nR\log\left(\frac{V_f}{V_i}\right)$$

- 2nd Law: $\Delta S_{universe} \geq 0$