

Thermodynamics

PHY 215
Thermodynamics and
Modern Physics

Spring 2026
MSU

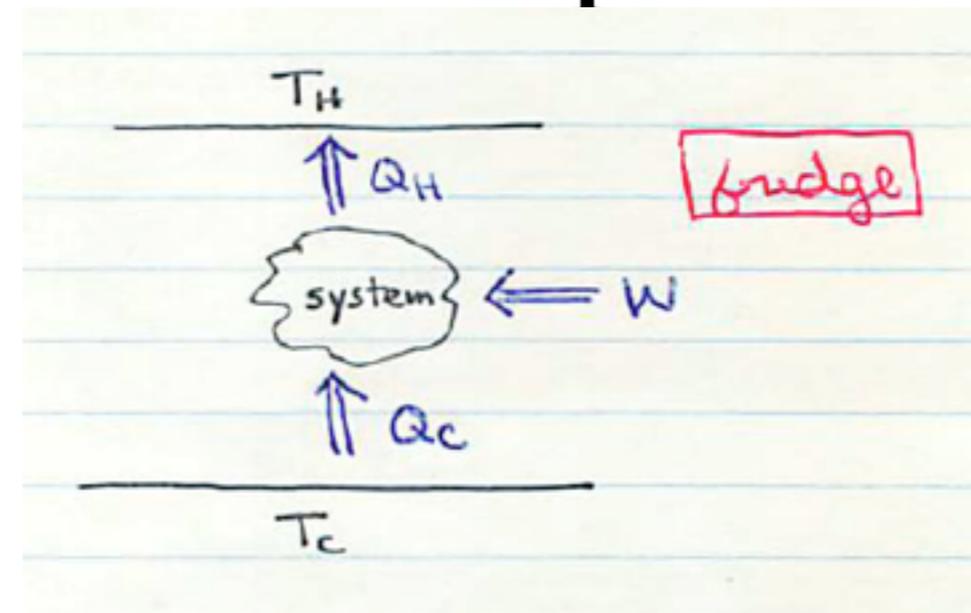
Outline

- 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 2nd law

Concept Test

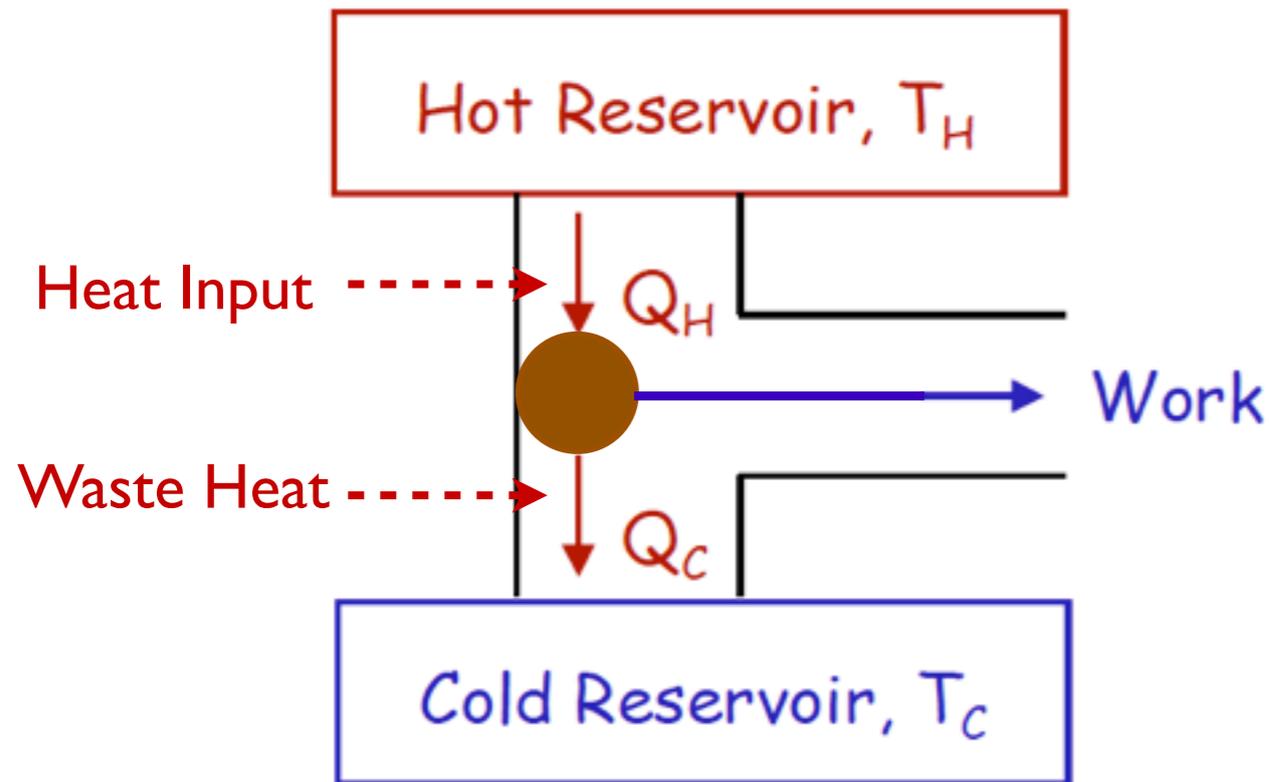
Air conditioners are placed in windows because:

- 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

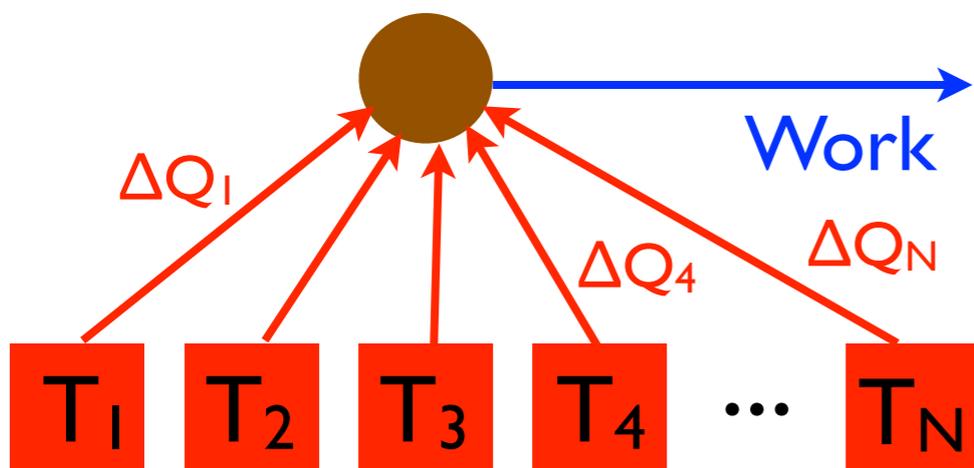


$$\eta = \frac{W}{Q_H} = \frac{Q_H - Q_C}{Q_H} \leq \eta_{Carnot} = 1 - \frac{T_C}{T_H}$$

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

$$\sum_{i=1,2} \frac{\Delta Q_i}{T_i} \leq 0, \Delta Q_i = \text{“absorbed” heat}$$

“N-Step” Heat Engine:



Compare to “N” Carnot Engines:

“Kelvin” 2nd law \Rightarrow

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

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

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

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

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

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

(for the "absorbed" heat ΔQ_i at T_i)

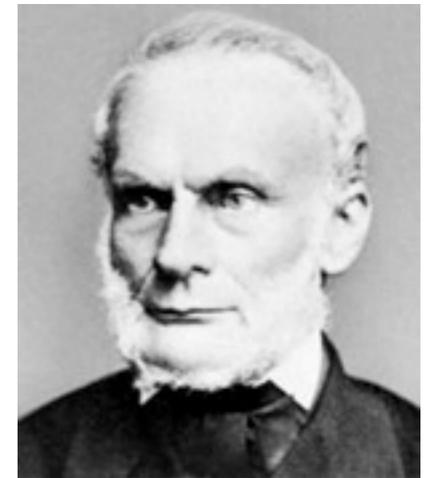
Clausius's Theorem II

Statement of Theorem:

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

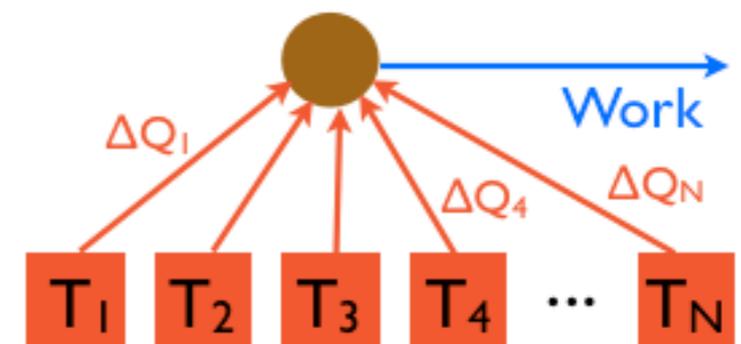
$$\sum_{i=1}^N \frac{\Delta Q_i}{T_i} \leq 0$$

- ΔQ_i heat “absorbed” in i^{th} step
- T_i temperature of i^{th} reservoir
- Equality holds only if all steps reversible!



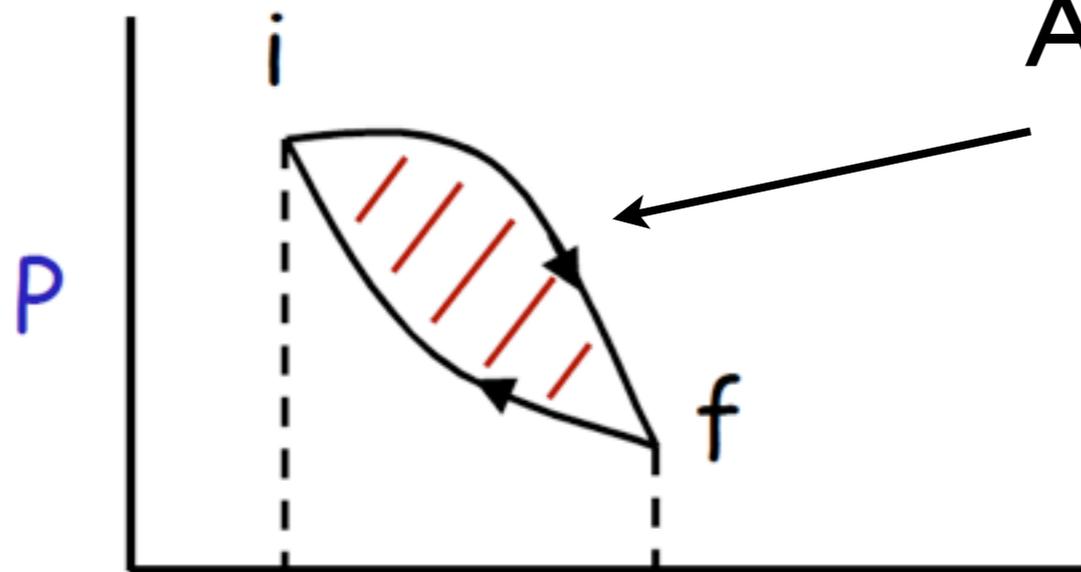
Rudolf Clausius
1822-1888

“N-Step” Heat Engine:



Follows, logically, from 2nd law of thermodynamics.

Clausius's Theorem III

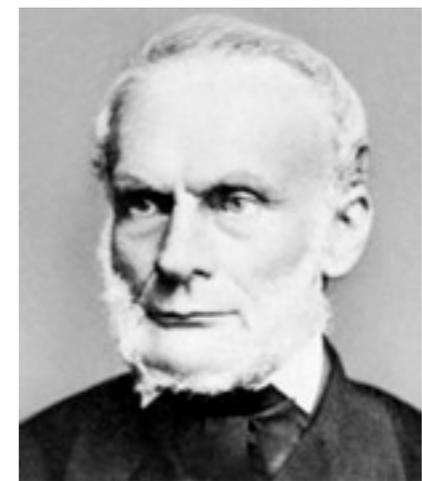


A continuous cycle is an “∞-Step” process!

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

For a reversible cycle:

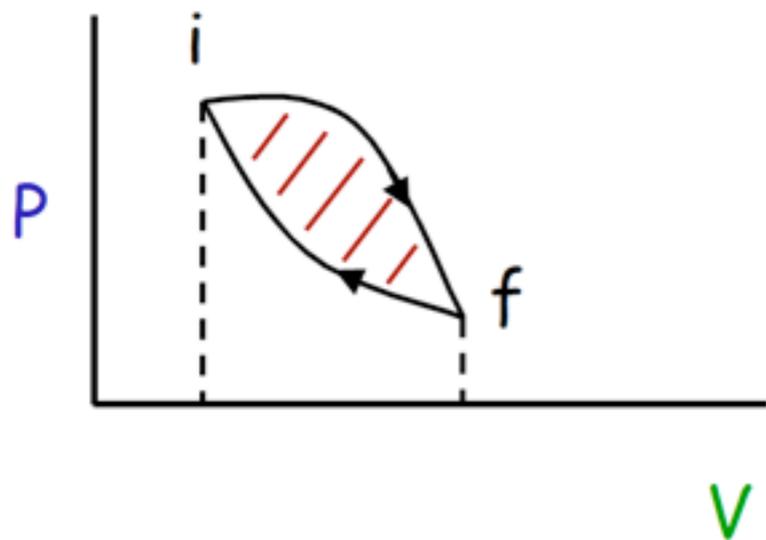
$$\oint \frac{dQ_{rev}}{T} = 0$$



Rudolf Clausius
1822-1888

Clausius Consequences: All Cycles

$$\oint \frac{dQ}{T} \leq 0 \quad \Rightarrow \quad dQ_{\text{rev}} \text{ must have both positive and negative contributions!}$$



The system must both absorb heat from and reject heat to the environment!

Kelvin form of 2nd law.

Recall: “State Functions”

- “State Functions” depend only on the parameters which define an equilibrium state, e.g. p, V, T, n, \dots
- 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:

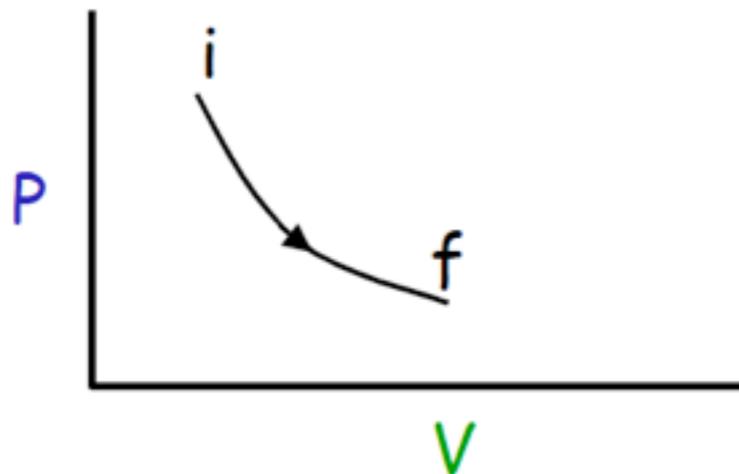
$$\oint \frac{dQ_{rev}}{T} = 0$$



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!

Ideal Gas Entropy I

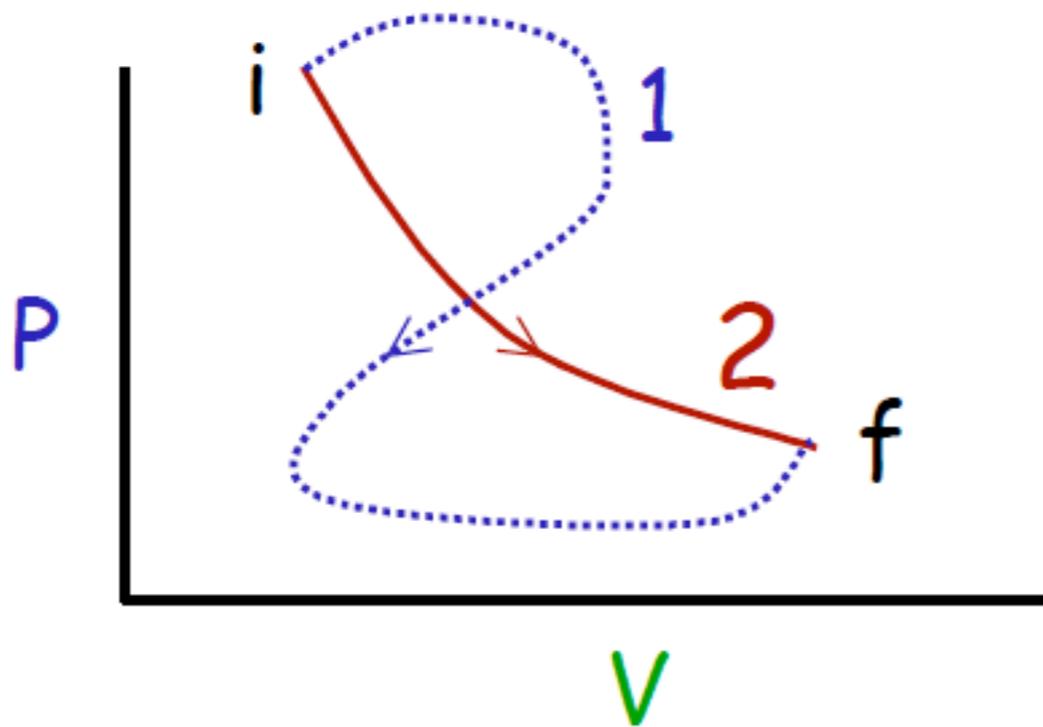
$$\begin{aligned}dQ_{rev} &= dU + dW = nC_V dT + pdV \\ &= nC_V dT + nRT \frac{dV}{V}\end{aligned}$$

$$\begin{aligned}\frac{dQ_{rev}}{T} &= nC_V \frac{dT}{T} + nR \frac{dV}{V} \\ &= nC_V d \log T + nR d \log V\end{aligned}$$

$$\begin{aligned}S_f - S_i &= \int_i^f \frac{dQ_{rev}}{T} \\ &= nC_V \log \left(\frac{T_f}{T_i} \right) + nR \log \left(\frac{V_f}{V_i} \right)\end{aligned}$$

Ideal Gas Entropy II

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

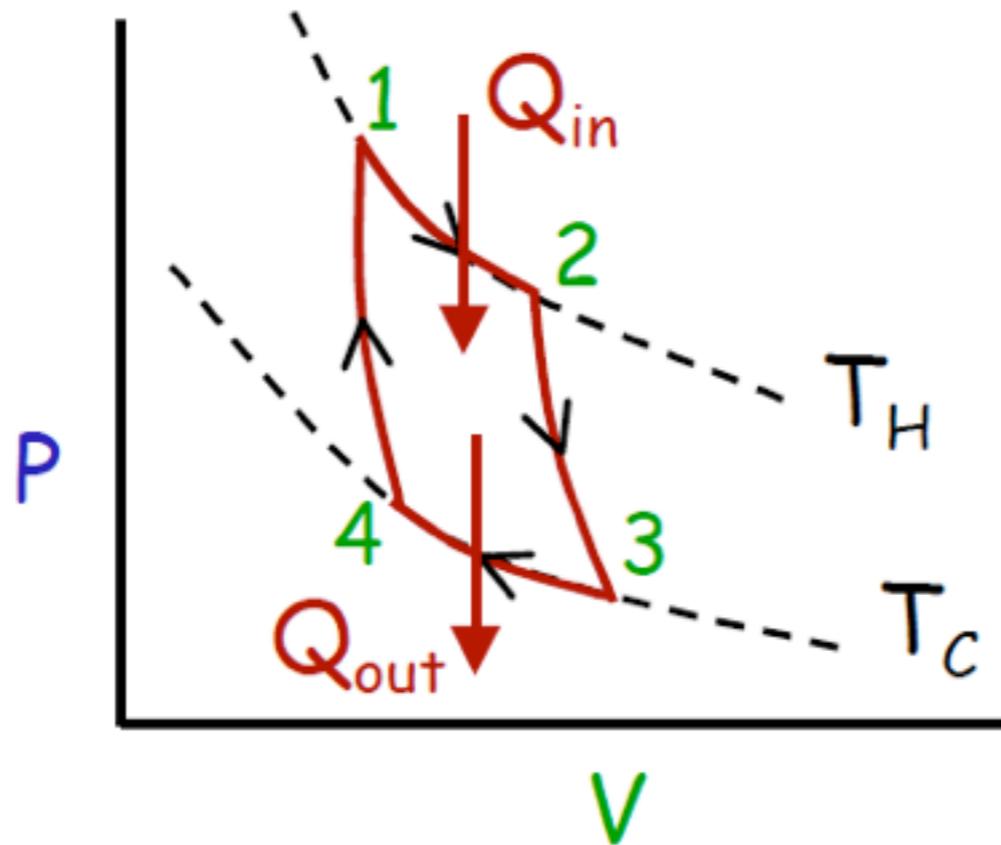


NB: Depends only on initial and final states!

Hence: any path can be used to define ΔS !

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

The Carnot Engine



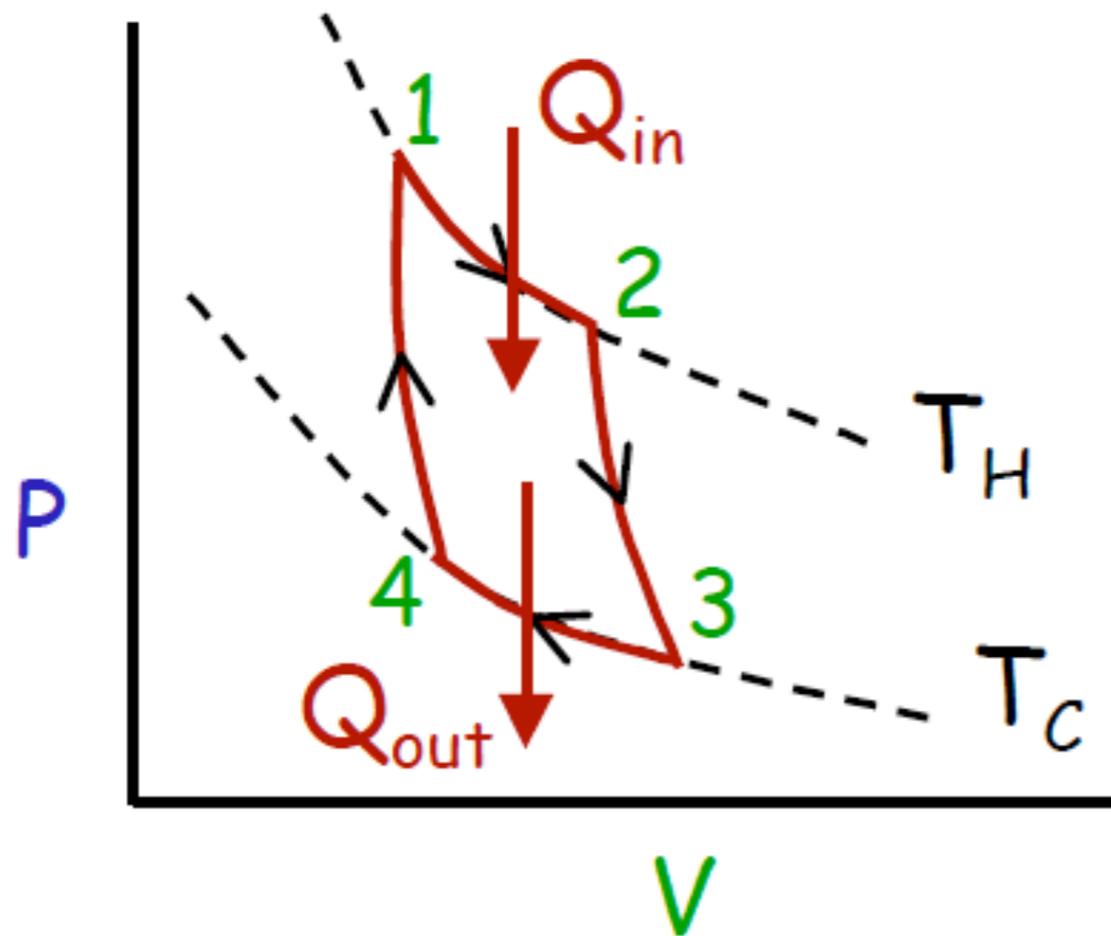
$1 \rightarrow 2$ & $3 \rightarrow 4$
isothermal

$2 \rightarrow 3$ & $4 \rightarrow 1$
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

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

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 \rightarrow 2	$nRT_H \ln\left(\frac{V_2}{V_1}\right)$	T_H	$nR \ln\left(\frac{V_2}{V_1}\right)$
2 \rightarrow 3	0		0
3 \rightarrow 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 \rightarrow 1	0	T_C	0
Total			0

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

$(\Delta S)_{\text{total}} = 0$ 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

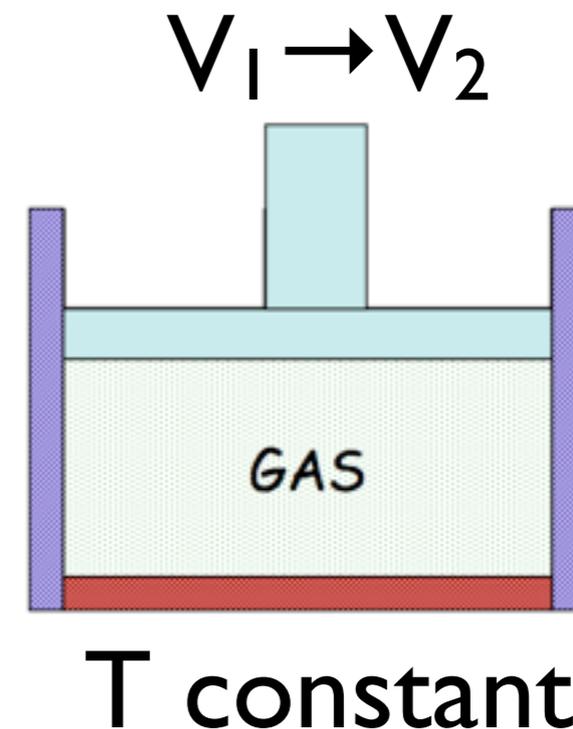
$$\Delta S_{\text{gas}} = + Q/T = n R \ln(V_f/V_i).$$

The entropy change of the reservoir is

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

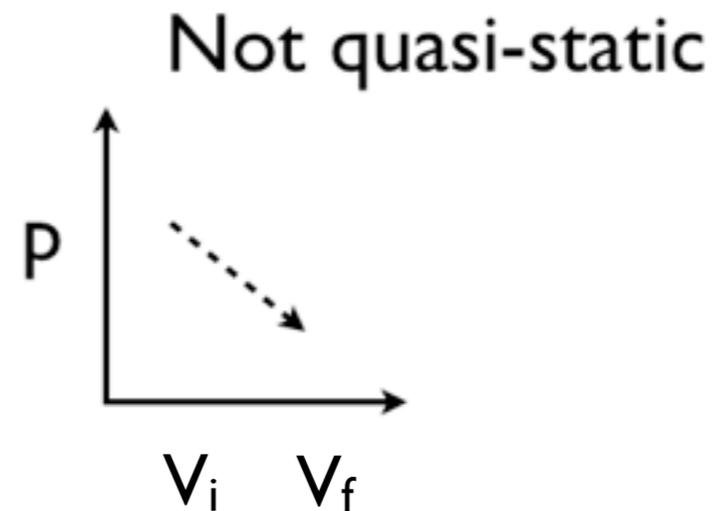
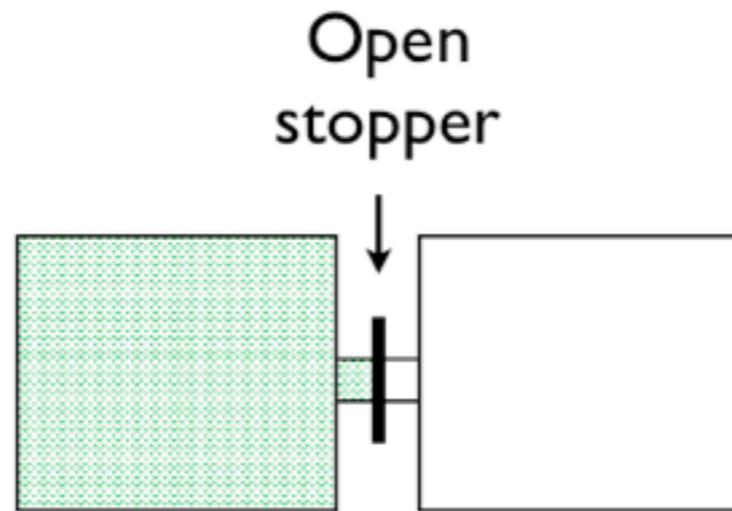
The net entropy change is

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



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

Entropy Change: Adiabatic Free Expansion



$$\begin{aligned}\Delta Q &= 0 \quad (\text{adiabatic}) \\ \Delta W &= 0 \quad (\text{nothing to work against}) \\ \Rightarrow \Delta U &= 0\end{aligned}$$

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

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

Entropy Increases!

- BUT: no heat transfer from environment!

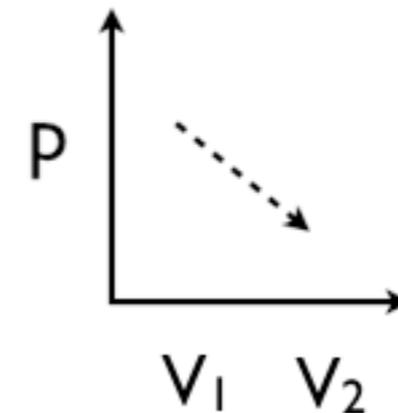
- $\Delta S_{\text{reservoir}} = 0$

- $\Delta S_{\text{universe}} = \Delta S_{\text{gas}} + \Delta S_{\text{reservoir}} > 0!$

- 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 $\Delta S_{\text{universe}} \geq 0$.
- The equal sign only applies to reversible processes.
- Entropy increases, but does not decrease
⇒ “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: $\Delta S_{universe} \geq 0$