

Thermal & Statistical Physics

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PHYS 343

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LECTURE 5

Heat Engines

- Thermodynamic processes and entropy
- Thermodynamic cycles
- Extracting work from heat

How do we define engine efficiency?

Carnot cycle --- best possible

Review: Entropy in Macroscopic Systems

Traditional thermodynamic entropy, S : $S \equiv k \ln(\Omega) \equiv k\sigma$

k = Boltzmann constant

- How can we find out about S from macrostate information (p , V , T , U , N , etc.) ?
 - start with expression defining temperature

$$\frac{1}{kT} \equiv \left(\frac{\partial \sigma}{\partial U} \right)_{V,N} \quad \text{so} \quad \frac{1}{T} \equiv \left(\frac{\partial S}{\partial U} \right)_{V,N}$$

Here's the entropy change when T changes from T_1 to T_2 , keeping V and N fixed:

$$dS = \frac{dU}{T} = \frac{C_V dT}{T} \Rightarrow \Delta S = \int_{T_1}^{T_2} \frac{C_V dT}{T}$$

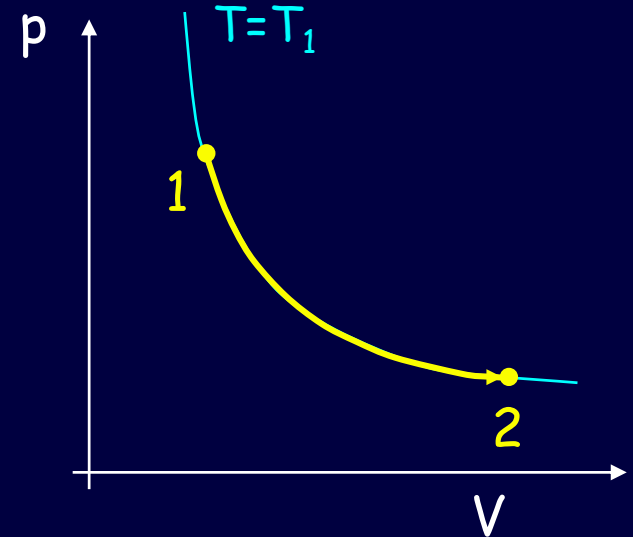
○ Special case: if C_V is constant $\Delta S = C_V \int_{T_1}^{T_2} \frac{dT}{T} = C_V \ln\left(\frac{T_2}{T_1}\right)$

Example: ΔS in Quasi-static Constant-Temperature Process

- Now suppose V & p change but T doesn't
 - is ΔS now zero??

- Work ($dW = -pdV$) is done
 - heat must enter to keep T constant

$$dS = \frac{dQ}{T} = \frac{dU - dW}{T} = \frac{dU + pdV}{T}$$



- Specialize to IDEAL GAS: Now if $dT = 0$, then $dU = 0$

$$dS = \frac{pdV}{T} = \frac{NkTdV}{VT} = \frac{NkdV}{V}$$

$$\Delta S = \int_{V_1}^{V_2} \frac{NkdV}{V} = Nk \ln \left(\frac{V_2}{V_1} \right)$$

ACT 1: Total entropy change in isothermal processes

1. We just saw that the entropy of a gas increases during a quasi-static isothermal expansion. What happens to the entropy of the environment during this process?

a. $\Delta S_{\text{env}} < 0$

b. $\Delta S_{\text{env}} = 0$

c. $\Delta S_{\text{env}} > 0$

2. Consider instead the 'free' expansion (i.e., not quasi-static) of a gas. What happens to the total entropy during this process?

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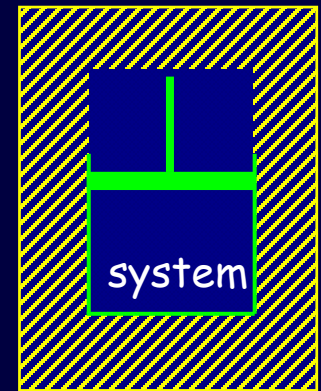


In this case, there is no work at all done on the gas (so its T doesn't change). Its entropy increases because the volume of allowed states does, but there's no change at all to the environment, since $Q = 0$. Therefore $\Delta S_{\text{tot}} > 0$.

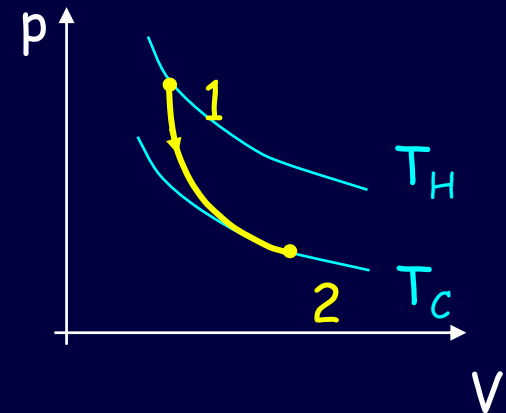
Quasi-static Processes

- Let's find ΔS for “quasi-static” processes
 - everything stays very close to being in equilibrium, i.e., V , T , p , etc. not changing rapidly
- Example: **ADIABATIC** process, i.e., no Q
 - V changes as applied p changes
- In equilibrium, the system must pick V to maximize its own S : $dS/dV = 0$ (no Q)
- WHY?
 - because no other S is changing
 - if, for example, it expands, GAIN in S from bigger V is exactly cancelled by LOSS in S due to reduced T .
- quasi-static **adiabatic** process

$$\Delta S = 0$$



Insulated Cylinder



Quasi-static Heat Flow and Entropy

- In quasi-static reversible process, total S (of system plus environment) doesn't change
 - So dS (of system) must cancel dS_E of environment
- In quasi-static reversible process, environment is at the same T (and p, if volume changes) as the system

so

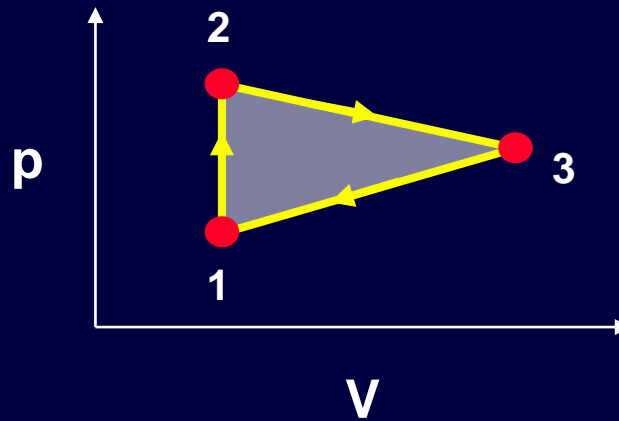
$$0 = dS + dS_E = dS + \frac{dU_E}{T} = dS - \frac{dU + dW_{by}}{T} = dS - \frac{dQ}{T}$$

$$dS = \frac{dQ}{T}$$

for quasi-static processes of ANY type

Closed Thermodynamic Cycles

A closed cycle is one in which the system is returned to the initial state (same p , V , and T), for example:



Since U is a state function:

$$\Delta U = 0$$

The net work done is the area enclosed by the cycle:

$$W = \oint p dV$$

First Law of Thermodynamics:

$$Q = W$$

Closed cycles will form the basis for our discussion of heat engines.

Thermodynamic processes of an α -ideal gas

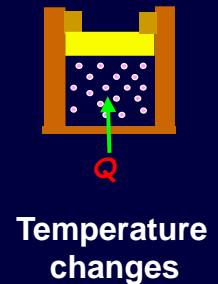
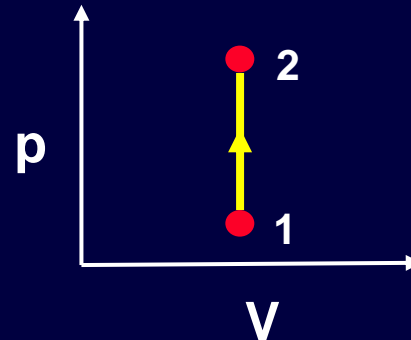
(FLT: $Q = \Delta U + W_{by}$)

□ Isochoric (constant volume)

$$W_{by} = \int p dV = 0$$

$$\Delta U = \alpha Nk \Delta T = \alpha V \Delta p$$

$$\text{FLT: } Q = \Delta U$$

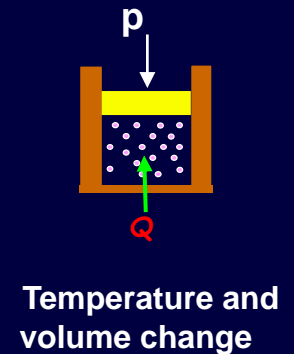
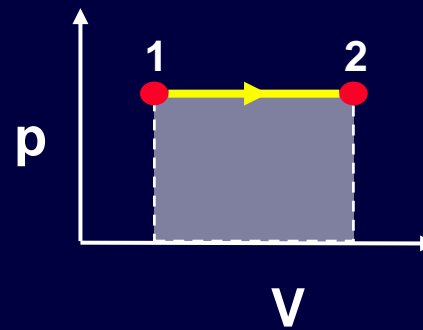


□ Isobaric (constant pressure)

$$W_{by} = \int p dV = p \Delta V$$

$$\Delta U = \alpha Nk \Delta T = \alpha p \Delta V$$

$$\text{FLT: } Q = \Delta U + W_{by} = (\alpha + 1) p \Delta V$$



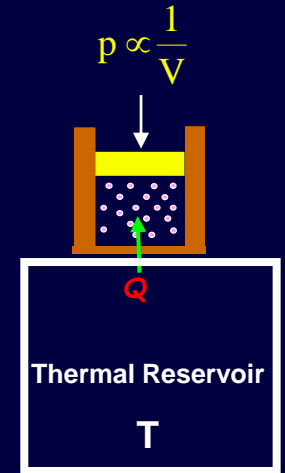
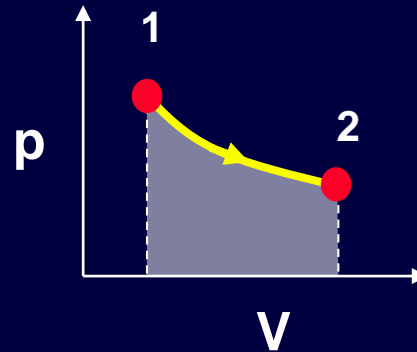
(FLT: $Q = \Delta U + W_{by}$)

□ **Isothermal** (constant temperature)

$\Delta U = 0$

$$W_{by} = \int_{V_1}^{V_2} p dV = \int_{V_1}^{V_2} \frac{NkT}{V} dV = NkT \ln\left(\frac{V_2}{V_1}\right)$$

FLT: $Q = W_{by}$



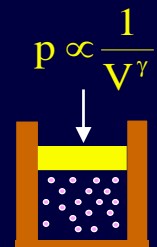
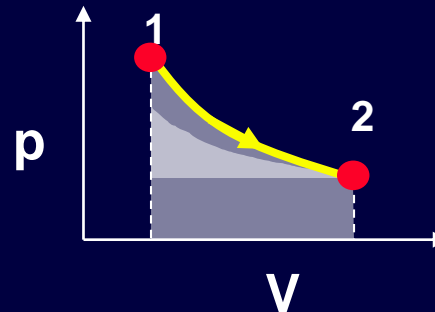
Volume and pressure change

□ **Adiabatic** (isolated - no heat input)

□(but what's constant? Stay tuned!)

$Q = 0$

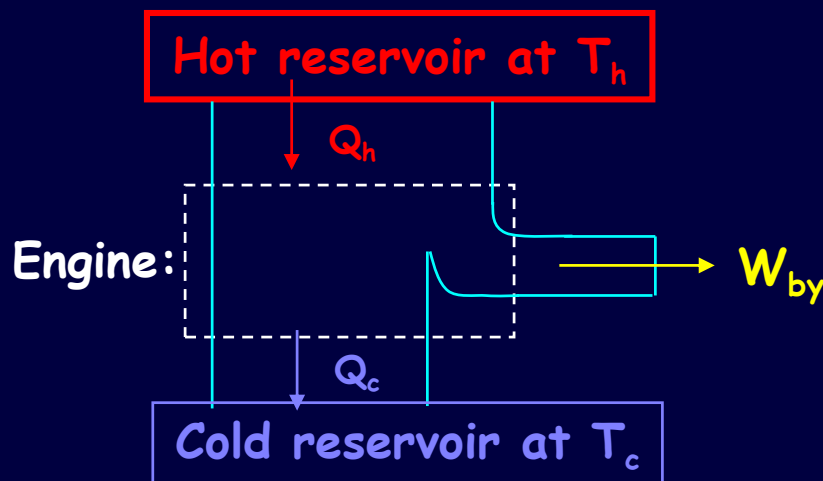
FLT: $W_{by} = -\Delta U = \alpha Nk(T_1 - T_2)$
 $= \alpha (p_1 V_1 - p_2 V_2)$



Volume, pressure and temperature change

Introduction to Heat Engines

- One of the primary applications of thermodynamics is to **Turn heat into work**
- The standard heat engine works on a cyclic process:
 1. extract heat from a hot reservoir,
 2. perform work,
 3. dump excess heat into a cold reservoir (often the environment).Recycle over and over. We represent this process with a diagram:

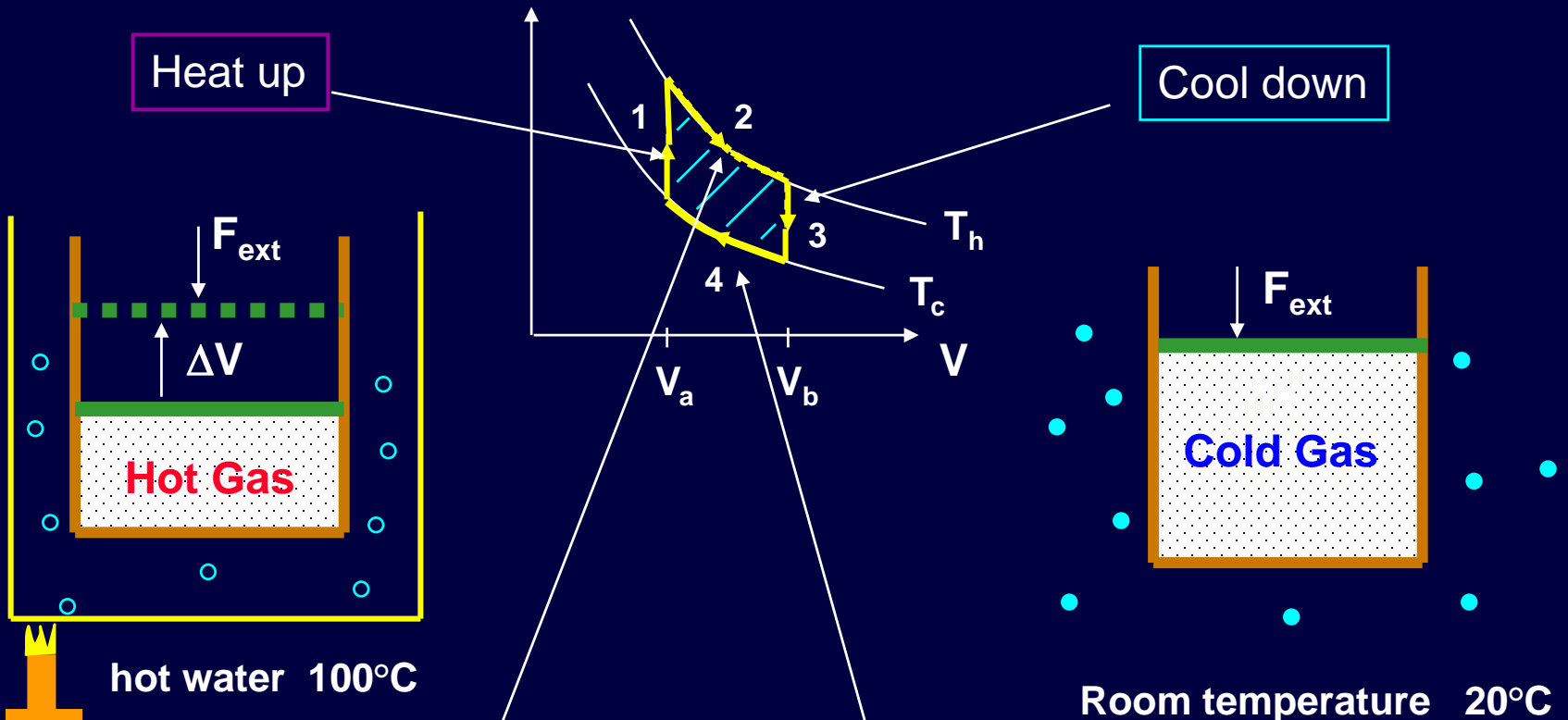


A "reservoir" is a large body whose temperature doesn't change when it absorbs or gives up heat

For heat engines we will define Q_h , Q_c and W_{by} as positive.

- Diagram shows the energy balance: $Q_h = Q_c + W_{by}$

A simple heat engine- the Stirling Cycle



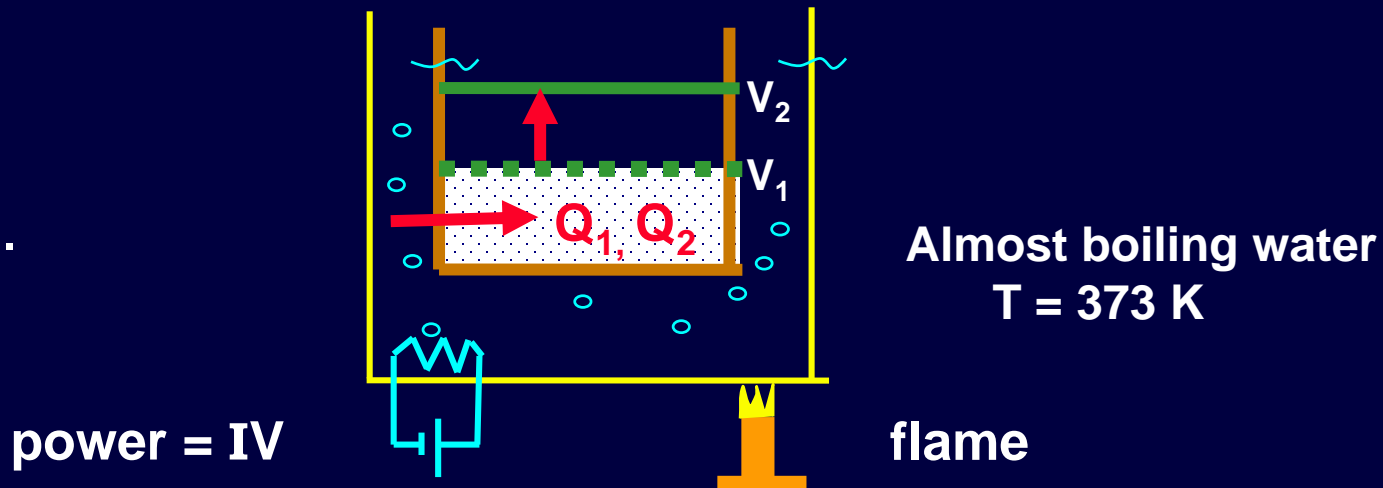
- Gas does work by expanding when hot
- Large pressure means large positive work

- Gas is reset to the original volume when cold
- Small pressure means small negative work

Where does the energy come from to do the work ?

Answer: We kept the reservoir at T_h while heat was being extracted by the engine (say as a piston does isothermal work)

E.G.



Electrical energy or Chemical energy

FLT: $\Delta U = Q_{\text{tot}} - W_{\text{by}} = 0$ for closed cycle:

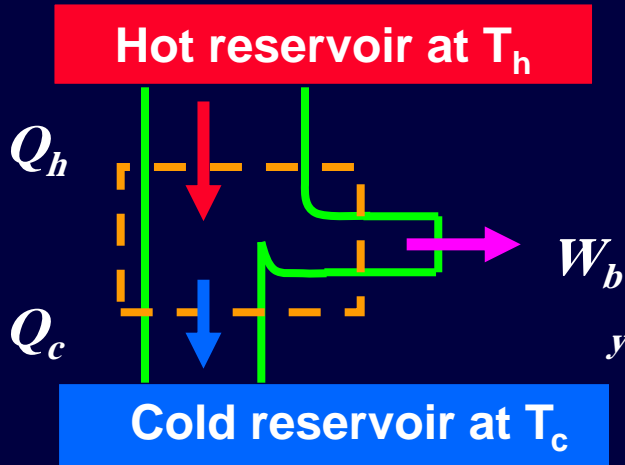
$$W_{\text{by}} = Q_{\text{tot}} = Q_h - Q_c$$

Important: The energy to do work does not come from the engine. After the engine completes one cycle, it has the same energy as when it started! U is a state function. $\rightarrow \Delta U = 0$.

Heat engine efficiency

General picture of a heat engine:

We paid for the heat input, Q_H .



Define the efficiency ε

$$\varepsilon \equiv \frac{\text{work done by system}}{\text{heat extracted from reservoir}} = \frac{\text{"work"}}{\text{"cost"}}$$

$$\varepsilon \equiv \frac{W_{by}}{Q_h} = \frac{Q_h - Q_c}{Q_h} = 1 - \frac{Q_c}{Q_h}$$

Valid for all heat engines.

($\Delta U = 0$ for closed cycle)

Remember: We define Q_h and Q_c as *positive*. The arrows in this diagram, and signs in equations, define direction of flow.

What's the best we can do?

Second Law sets Maximum Efficiency (1)

$$\Delta S_{tot} \geq 0$$

- How to calculate ΔS_{tot} ?


$$\Delta S_{tot} = \Delta S_{engine} + \Delta S_{env} = \Delta S_{env} = \Delta S_H + \Delta S_C$$

($\Delta S_{eng} = 0$ (cycle!), the only NET changes are in the reservoirs.)

- Remember

- Q_H is total heat taken from the environment at T_H
- Q_C is total heat added to the environment at T_C

Second Law

$$0 \leq \Delta S_{tot} = \Delta S_H + \Delta S_C = -\frac{Q_H}{T_H} + \frac{|Q_C|}{T_C} \Rightarrow \frac{|Q_C|}{Q_H} \geq \frac{T_C}{T_H}$$


$$\Delta S = Q/T, \text{ from definition of } T$$

Second Law sets Maximum Efficiency (2)

$$\text{efficiency} = \varepsilon = \frac{W}{Q_H} = 1 - \frac{|Q_C|}{Q_H}$$

$$\text{but } \mathbf{SLT} \Rightarrow \frac{|Q_C|}{Q_H} \geq \frac{T_C}{T_H}$$

therefore

$$\varepsilon \leq 1 - \frac{T_C}{T_H}$$

• **This limit holds in general**

not just for ideal gas! E.g., for

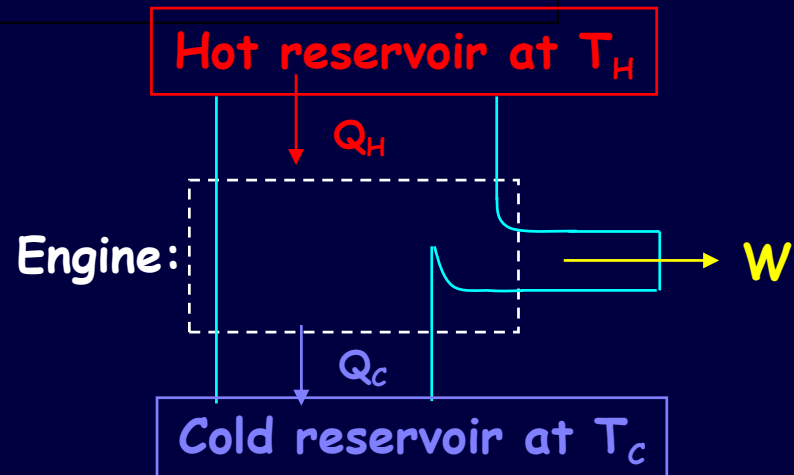
- electrical thermopower devices with no moving parts
- rubber-band engines
- shape-memory metal pumps
- ...

When ε is less than maximum

$$\Delta S_{tot} = -\frac{Q_H}{T_H} + \frac{|Q_C|}{T_C} = -\frac{Q_H}{T_H} + \frac{Q_H - W}{T_C}$$

$$\text{so } W = Q_H \left(1 - \frac{T_C}{T_H} \right) - T_C \Delta S_{tot}$$

$$\varepsilon \equiv \frac{W}{Q_H} = \left(1 - \frac{T_C}{T_H} \right) - \frac{T_C \Delta S_{tot}}{Q_H}$$



This is GENERAL.
It gives
how much ε is less than
the Carnot optimum.

Lesson: avoid any irreversible processes,
(ones that increase S_{tot}).

- direct heat flow from hot to cold
- free expansion
- sliding friction

Irreversible Processes

- Irreversibility is equivalent to entropy-increasing, e.g.,
 - free-expansion
(particle flow between regions at different density)
 - contact between two systems with different temperatures.
(heat flow between regions at different T)

Isothermal: Heat flow but no T difference.

Adiabatic: $Q = 0$. No heat flow at all.

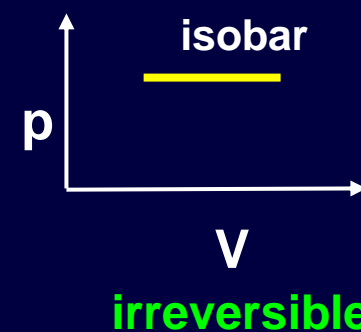
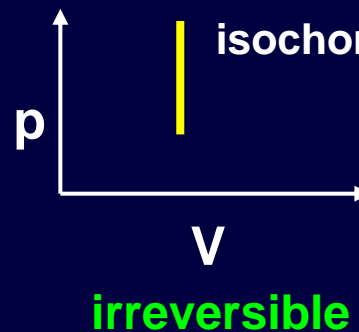
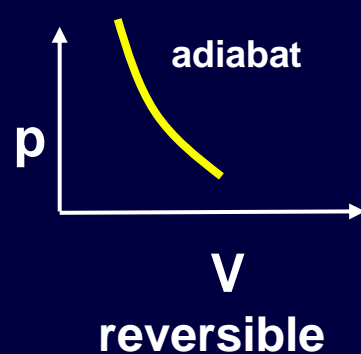
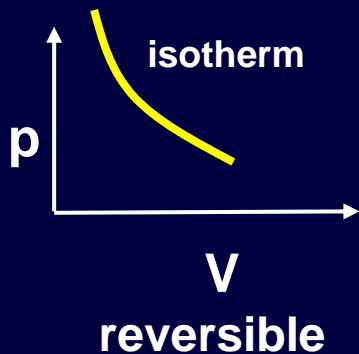
Isochoric & Isobaric: Heat flow between different T's. Irreversible

(Here we assume that there are only two reservoirs.)

Reversible

Reversible

Irreversible

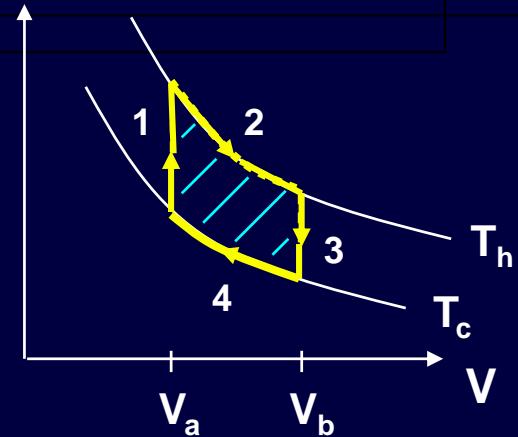


Act 2: Stirling efficiency

Will our simple Stirling engine
achieve Carnot efficiency?

a) Yes

b) No



Act 2: Stirling efficiency

Will our simple Stirling engine achieve Carnot efficiency?

a) Yes

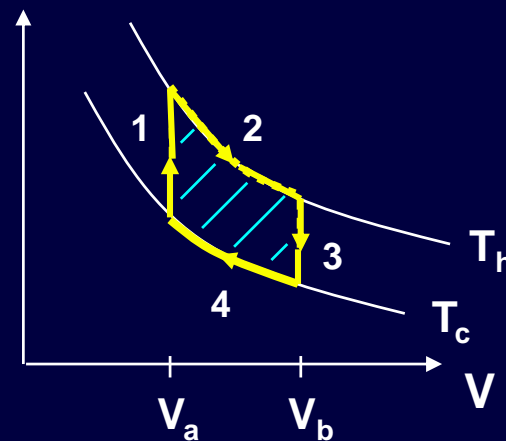
b) No

Steps 1 and 3

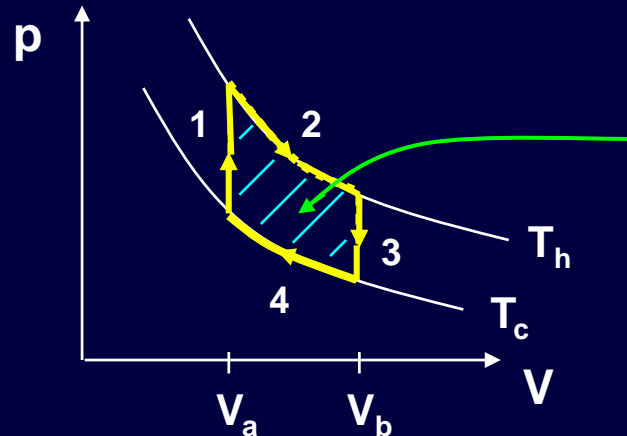
(heating and cooling)
are irreversible.

Cold gas put in hot bath.

Hot gas put in cold bath.



Supplement: Efficiency of Stirling Cycle



Area enclosed =

$$W_{\text{by}} = \oint p dV$$

Total work done by the gas in the entire cycle (see Appendix):

$$W_{\text{by}} = W_2 + W_4 = Nk(T_h - T_c) \ln \frac{V_b}{V_a}$$

Heat extracted from the hot reservoir, exhausted to cold reservoir:

$$Q_1 + Q_2 = \alpha Nk(T_h - T_c) + NkT_h \ln \frac{V_b}{V_a} = Q_h$$

$$Q_3 + Q_4 = -\alpha Nk(T_h - T_c) - NkT_c \ln \frac{V_b}{V_a} = -Q_c$$

Supplement: Efficiency of Stirling Cycle

$$\text{Take: } V_b = 2V_a$$

$$\alpha = 3/2 \quad (\text{monatomic gas})$$

$$T_h = 373\text{K} \quad T_c = 293\text{K}$$

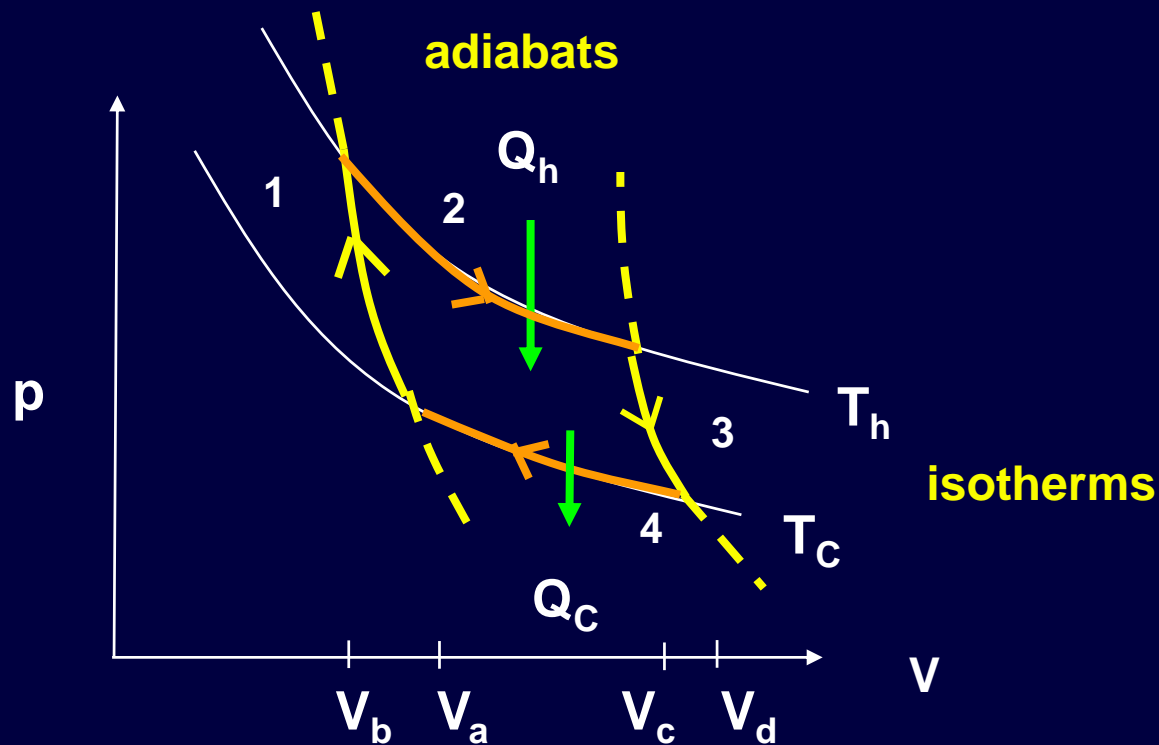
$$\begin{aligned} \text{Efficiency} = \varepsilon &\equiv \frac{W}{Q_H} = \frac{(T_h - T_c) \ln \frac{V_b}{V_a}}{\frac{3}{2}(T_h - T_c) + T_h \ln \frac{V_b}{V_a}} \quad (\ln 2 = 0.69) \\ &= \frac{80(0.69)}{120 + 373(0.69)} = 14.6\% = \frac{\text{work done}}{\text{heat supplied}} \end{aligned}$$

ε depends on the reservoir temperatures, volume ratio, and type of gas.

$$\varepsilon_{\text{carnot}} = 1 - 293/373 = 21.4\%$$

The Carnot Cycle

- **All steps are reversible** -- no thermal contact between systems at different temperatures.
- **No** engine is more efficient than the Carnot engine.

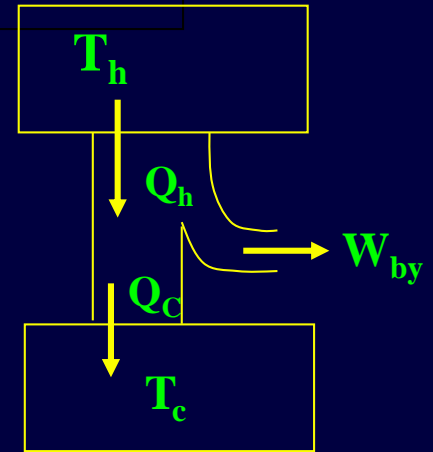


ACT 3: Entropy change in heat engine

Consider a Carnot heat engine.

1. What is the sign of the entropy change of the hot reservoir during one cycle?

- a. $\Delta S_h < 0$ b. $\Delta S_h = 0$ c. $\Delta S_h > 0$



2. What is the sign of the entropy change of the cold reservoir?

- a. $\Delta S_c < 0$ b. $\Delta S_c = 0$ c. $\Delta S_c > 0$

3. Compare the magnitudes of the two changes.

- a. $|\Delta S_c| < |\Delta S_h|$ b. $|\Delta S_c| = |\Delta S_h|$ c. $|\Delta S_c| > |\Delta S_h|$

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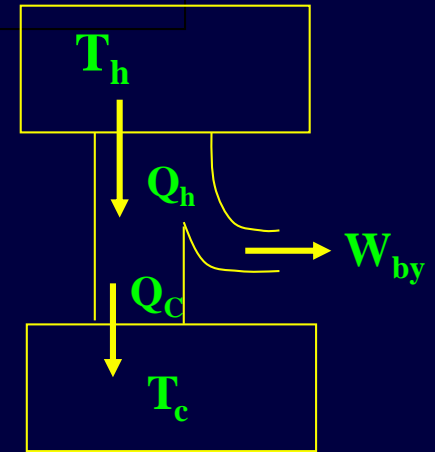
Because energy is flowing into the cold reservoir, its entropy (number of microstates) is increasing.

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a. $|\Delta S_c| < |\Delta S_h|$

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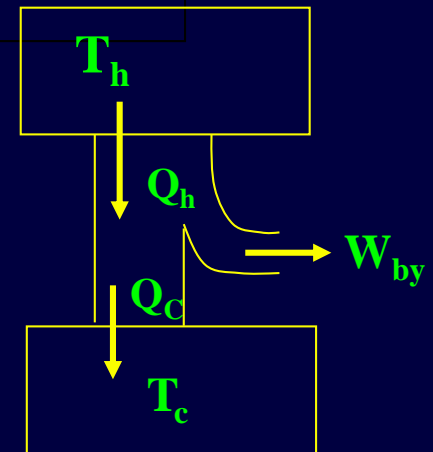
c. $|\Delta S_c| > |\Delta S_h|$

$$\Delta S_c = Q_c/T_c$$

$$\Delta S_h = Q_h/T_h$$

$$\Delta S_c / \Delta S_h = (Q_c/T_c)/(Q_h/T_h) = 1,$$

since $Q_c/Q_h = T_c/T_h$ for a Carnot cycle.



Efficiency of heat engines -- summary

For all engines

$$\varepsilon = 1 - \frac{Q_c}{Q_h}$$

For Carnot cycle

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

(best possible value)

Carnot efficiency

$$\varepsilon = 1 - \frac{T_c}{T_h}$$

The lost energy is dumped in the cold reservoir

In practice, Carnot engines are hard/impossible to realize → require very slow processes, and perfect insulation. When there's a net entropy increase, efficiency is reduced:

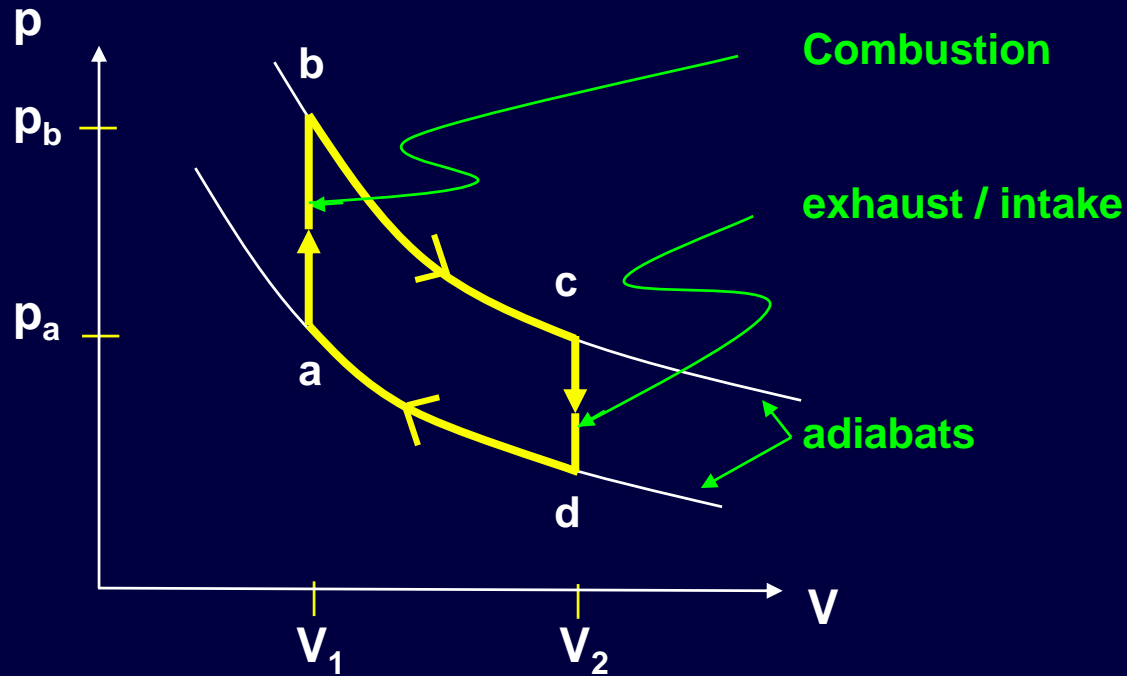
$$\varepsilon = \left(1 - \frac{T_C}{T_H} \right) - \frac{T_C \Delta S_{tot}}{Q_H}$$

Supplements: Gasoline and Diesel Engines

- **These are not really heat engines because the input energy is via fuel injected directly into the engine, not via heat flow. There is no clear hot reservoir. However, one can still calculate work and energy input for particular gas types...**

FYI: Gasoline Engine

- Find the efficiency for the gasoline engine (Otto cycle):



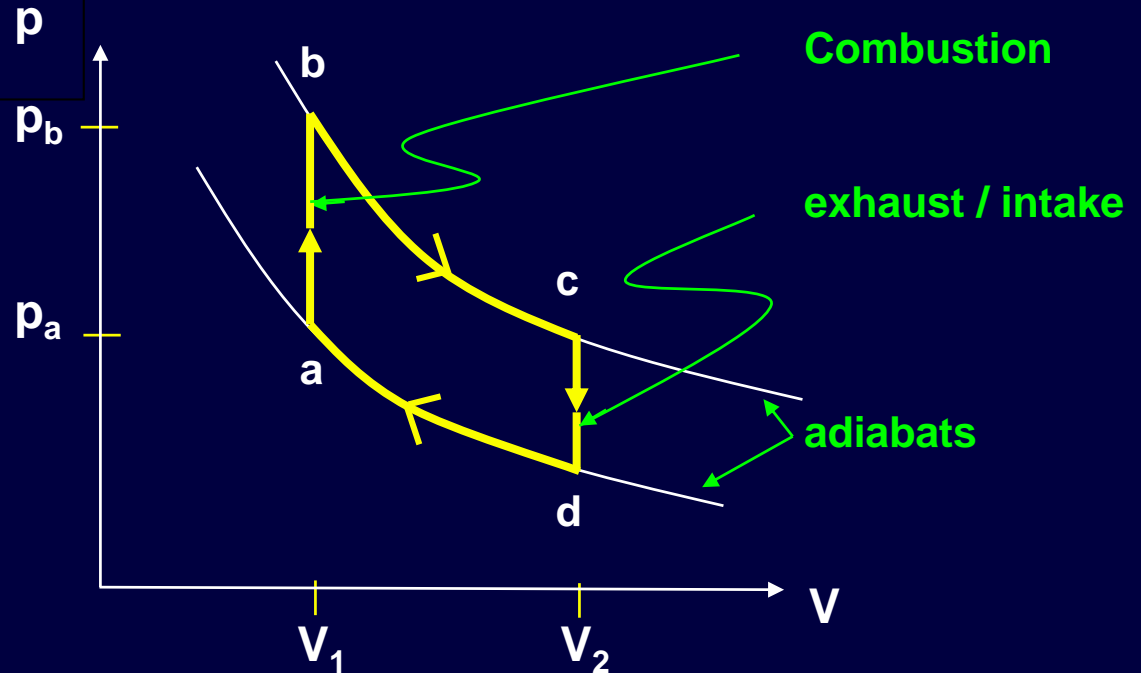
Let's calculate the efficiency...

FYI: Gasoline Engine

$$\varepsilon = \frac{W_{by}}{Q_{in}}$$

$$Q_{in} = C_v(T_b - T_a)$$

$$W_{by} = W_{b \rightarrow c} - |W_{d \rightarrow a}|$$



$$Q_{b \rightarrow c} = 0 \text{ (adiabatic)} \Rightarrow W_{b \rightarrow c} = U_b - U_c = C_v(T_b - T_c)$$

$$\text{similarly } W_{d \rightarrow a} = U_d - U_a = C_v(T_d - T_a)$$

$$W_{by} = C_v(T_b - T_c) - C_v(T_a - T_d)$$

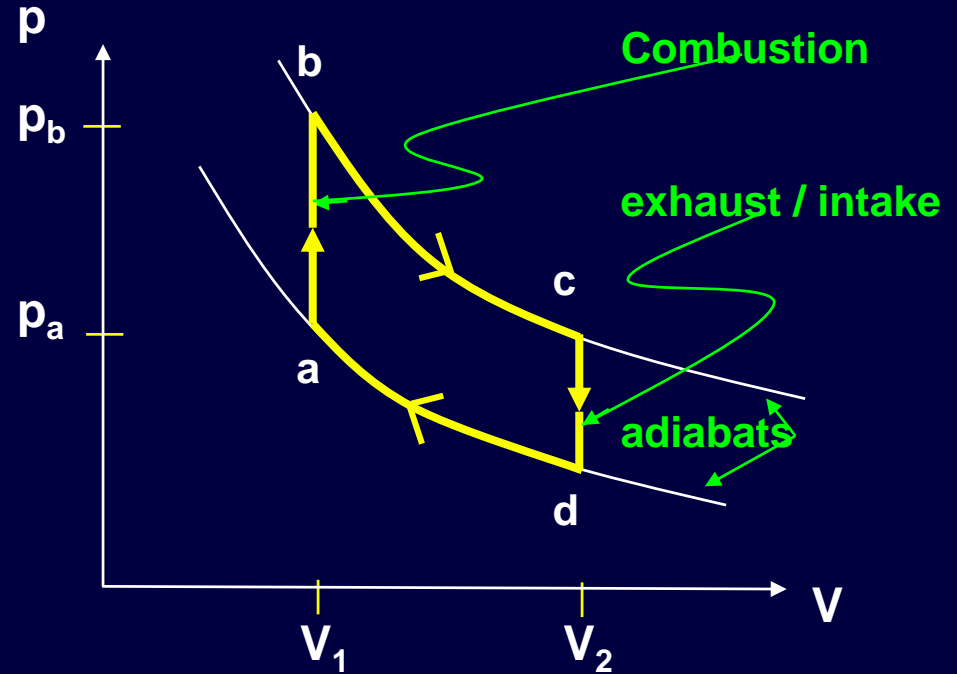
$$\varepsilon = \frac{C_v(T_b - T_c) - C_v(T_a - T_d)}{C_v(T_b - T_a)} = 1 - \frac{(T_c - T_d)}{(T_b - T_a)}$$

FYI: Gasoline Engine, cont.

$$\varepsilon = 1 - \frac{(T_c - T_d)}{(T_b - T_a)}$$

$$T_c^\alpha V_2 = T_b^\alpha V_1 \Rightarrow T_c = T_b (V_1/V_2)^{1/\alpha}$$

$$T_d^\alpha V_2 = T_a^\alpha V_1 \Rightarrow T_d = T_a (V_1/V_2)^{1/\alpha}$$



$$\therefore \frac{(T_c - T_d)}{(T_b - T_a)} = \frac{(T_b - T_a)(V_1/V_2)^{1/\alpha}}{(T_b - T_a)} = \left(\frac{V_1}{V_2}\right)^{1/\alpha} = \left(\frac{V_2}{V_1}\right)^{-1/\alpha} = \left(\frac{V_2}{V_1}\right)^{1-\gamma}$$

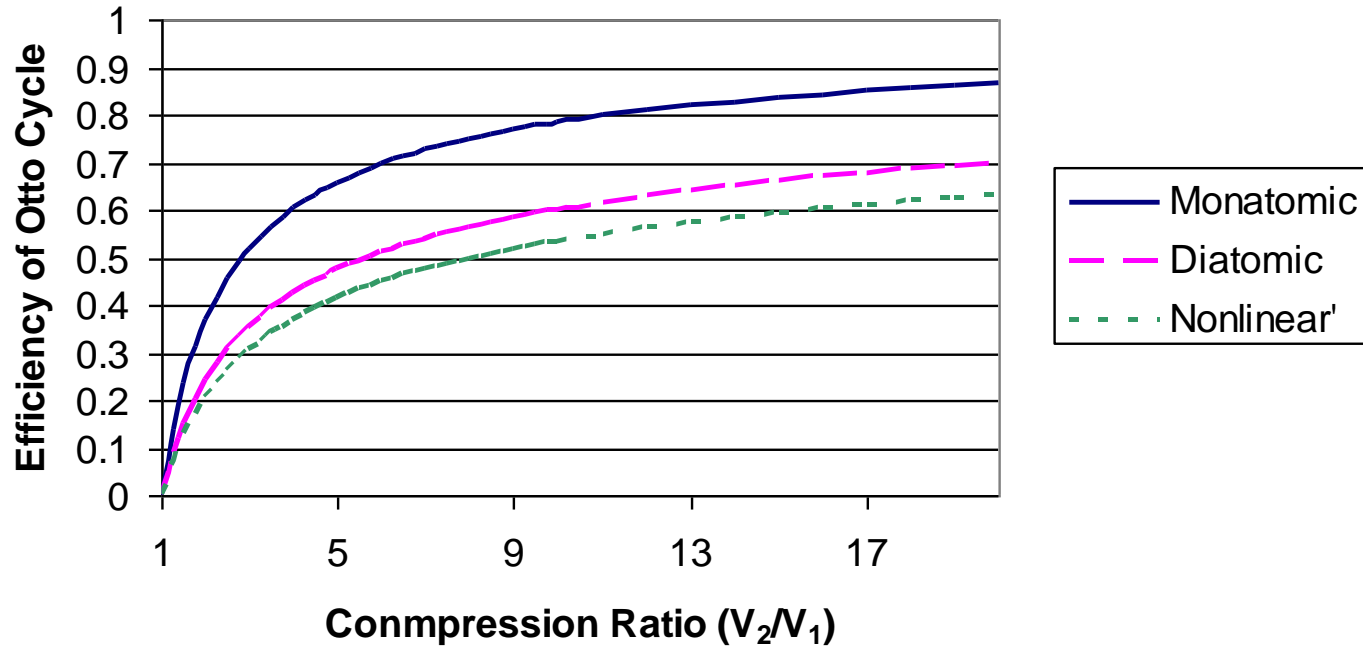
$$\varepsilon = 1 - \left(\frac{V_2}{V_1}\right)^{1-\gamma}$$

CR = $V_2/V_1 = 10$ (compression ratio)

$\gamma = 1.4$ (diatomic gas) $\rightarrow \varepsilon = 60\%$

(in reality about 30%, due to friction, turbulence, etc.)

FYI: Gasoline Engine



- Why not simply use a higher compression ratio?
 - V_2 big \rightarrow huge, heavy engine
 - V_1 small \rightarrow temp. gets too high \rightarrow premature ignition \rightarrow need to use octane in gas to raise combustion temperature

Supplement: Efficiency of the Carnot cycle

example calculation assumes α -ideal gas for convenience

$$\varepsilon = 1 - \frac{Q_c}{Q_h}$$

For all engines

Isothermal processes:

$$Q_h = W_{by} = NkT_h \cdot \ln \frac{V_b}{V_c}$$

$$Q_c = -W_{on} = NkT_c \cdot \ln \frac{V_a}{V_d}$$

Adiabatic processes:

$$T^\alpha V = \text{constant}$$

$$T_h^\alpha V_b = T_c^\alpha V_a$$

$$T_h^\alpha V_c = T_c^\alpha V_d$$

$$\frac{V_b}{V_c} = \frac{V_a}{V_d}$$

$$\ln \frac{V_b}{V_c} = \ln \frac{V_a}{V_d}$$

Therefore:

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

For Carnot cycle

$$\varepsilon = 1 - \frac{T_c}{T_h}$$

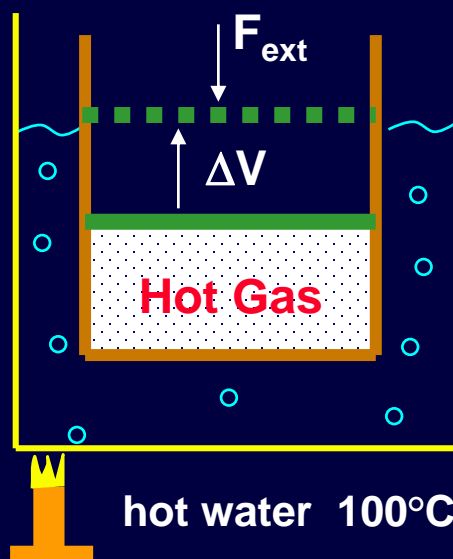
Carnot efficiency

For a Carnot engine working between boiling water and room temperature:

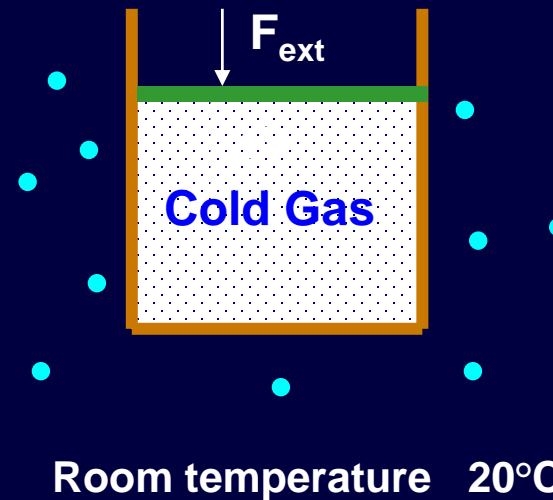
$$\varepsilon = 1 - \frac{293}{373} = 21.4\%$$

Appendix: A simple heat engine- the Stirling Cycle illustrated with an α -ideal gas

- Function: Convert heat into work using a cyclic process
- Operation: Cycle a piston of gas between hot and cold reservoirs



- Gas does work by expanding when hot
- Large pressure means large positive work

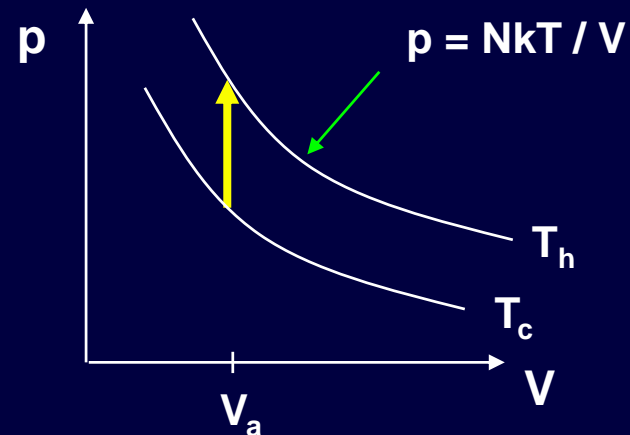
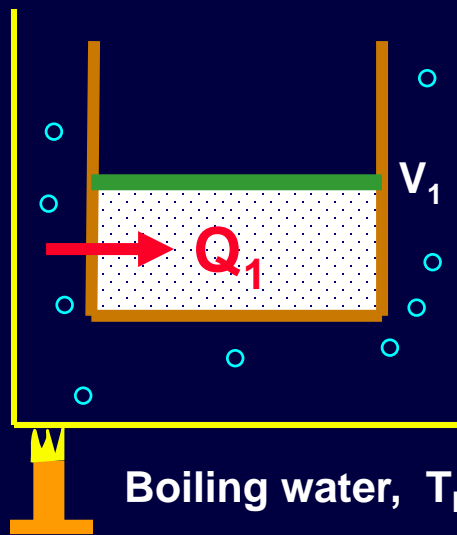


- Gas is reset to the original volume when cold
- Small pressure means small negative work

Appendix: Stirling Cycle: Step 1

- Isochoric process:

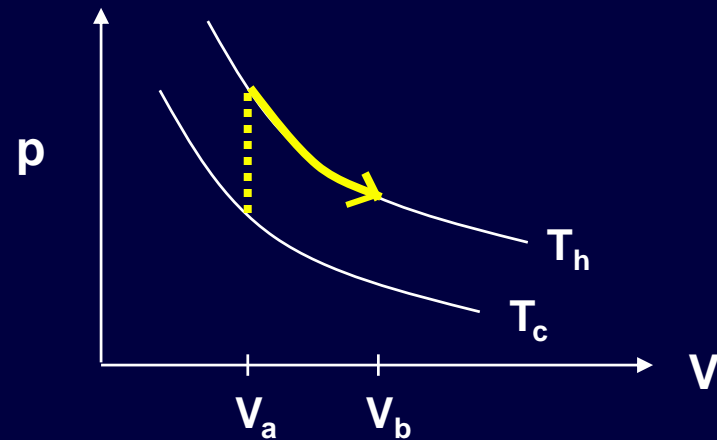
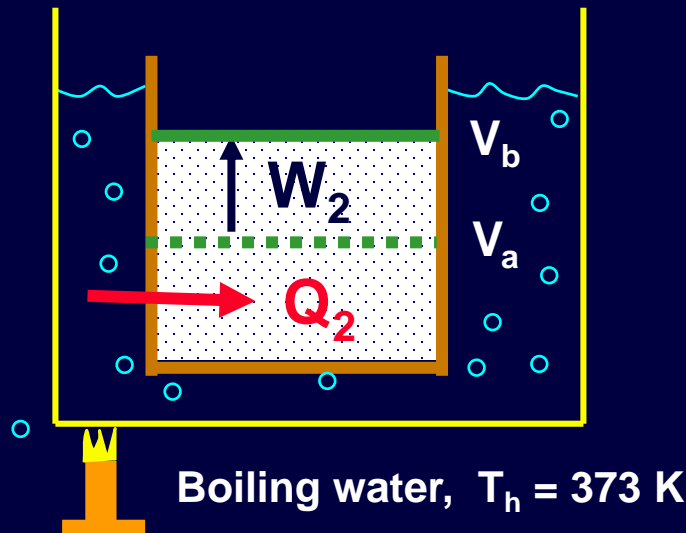
Start with gas container at room temperature T_c and volume V_a
place container in heat bath at T_h and let gas warm up to T_h



- Heat flow: $Q_1 = \Delta U = \alpha Nk (T_h - T_c)$ ($U = \alpha NkT$ for ideal gas)
- This is an irreversible process. The gas will never transfer this heat back to the bath.
- Heat travels from hot to cold (**Second Law**)

Appendix: Stirling Cycle: Step 2

- **Isothermal expansion:** expand gas at constant temperature T_h
- The gas does work on the environment



$$W_2 = \text{Work done by gas} = \int_{V_a}^{V_b} p dV = NkT_h \int_{V_a}^{V_b} \frac{dV}{V} = NkT_h \ln \frac{V_b}{V_a}$$

This is a **reversible** process. The gas and water are at the same T .

Appendix: Stirling Cycle: Step 2 (cont'd)

- Heat must be supplied to the gas while it expands, in order to keep it at the bath temperature, T_h . Heat added = Q_2 .
- The internal energy of the gas does not change (constant T).

FLT: $\Delta U_2 = Q_2 - W_2 = 0$ First Law of Thermodynamics

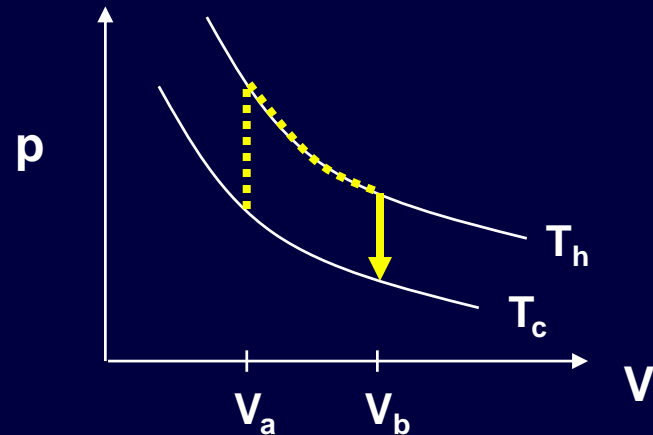
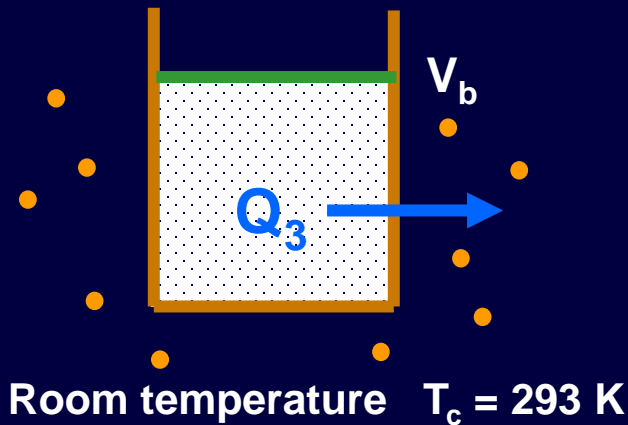
Therefore, $Q_2 = W_2 = NkT_h \ln \frac{V_b}{V_a}$

- The total heat extracted from the hot reservoir in **Steps 1 and 2** is:

$$Q_h = Q_1 + Q_2 = \alpha Nk(T_h - T_c) + NkT_h \ln \frac{V_b}{V_a}$$

Appendix: Stirling Cycle: Step 3

- **Isochoric process:** remove the gas container from the heat bath and allow it to come to room temperature, T_c

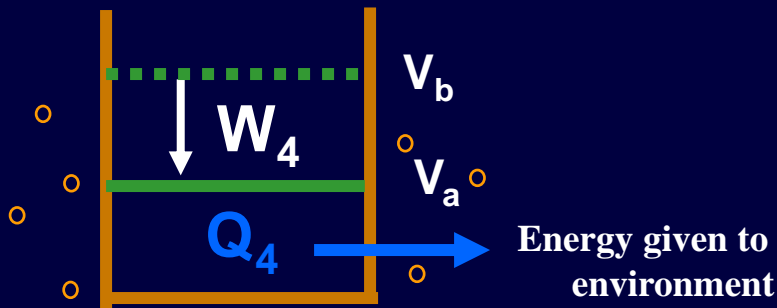


- This is an **irreversible** process. The gas cannot re-heat spontaneously.
- Q_3 is energy lost to the environment.

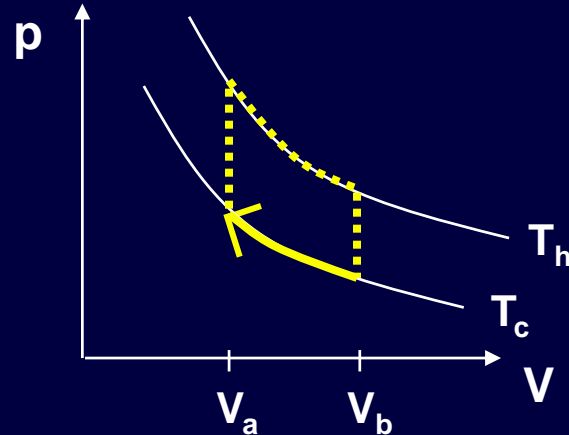
$$Q_3 = \Delta U_3 = \alpha Nk(T_h - T_c) \quad (W_3 = 0)$$

Appendix: Stirling Cycle: Step 4

- Compress the gas to its original volume V while it is in thermal contact with air at T_c .



Room temperature $T_c = 273 \text{ K}$



$$W_4 = \int_{V_b}^{V_a} p dV = NkT_c \int_{V_b}^{V_a} \frac{dV}{V} = NkT_c \ln \frac{V_a}{V_b} = -NkT_c \ln \frac{V_b}{V_a}$$

- Negative because positive work is done on the gas.
- Q_4 is calculated as for Q_2 .
- This is a **reversible** process.

$$Q_4 = W_4 = -NkT_c \ln \frac{V_b}{V_a}$$

Example Problem (1)

How much heat is absorbed by 3 moles of helium when it expands from $V = 10$ liters to $V = 20$ liters and the temperature is kept at a constant 350 K? What are the initial and final pressures?

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How much heat is absorbed by 3 moles of helium when it expands from $V = 10$ liters to $V = 20$ liters and the temperature is kept at a constant 350 K? What are the initial and final pressures?

Solution:

$$Q = -W_{\text{on}}$$

$$\begin{aligned} W_{\text{on}} &= -nRT \ln(V_f/V_i) \\ &= -6048 \text{ J} \end{aligned}$$

$$\begin{aligned} p_i &= nRT/V_i = 8.72 \times 10^5 \text{ Pa} \\ p_f &= p_i/2 = 4.36 \times 10^5 \text{ Pa} \end{aligned}$$

Remember the first law. For an ideal gas, isothermal means $\Delta U = 0$. Positive Q means heat flows **into** the gas.

This was derived in lecture.
 $R = 8.31 \text{ J/mole}\cdot\text{K}$

$$pV = nRT$$

Where is the heat coming from? In order to keep the gas at a constant temperature, it must be put in contact with a large object having that temperature. That object is called a "heat reservoir", and it supplies heat to the gas (or absorbs heat, if necessary) in order to keep the gas temperature constant.

Example Problem 2

Suppose a mole of a diatomic gas, such as O_2 , is compressed adiabatically so the final volume is half the initial volume. The starting state is $V = 1$ liter, $T = 300$ K. What are the final temperature and pressure?

$$p_i V_i^\gamma = p_f V_f^\gamma$$

$$\gamma = \frac{7/2}{5/2} = 1.4$$

$$p_f = p_i \left(\frac{V_i}{V_f} \right)^\gamma$$

$$= \frac{nRT_i}{V_i} \left(\frac{V_i}{V_f} \right)^\gamma$$

$$= 6.57 \times 10^6 \text{ Pa}$$

$$T_f = \frac{p_f V_f}{nR}$$

$$= 395 \text{ K}$$

$$T_i^\alpha V_i = T_f^\alpha V_f$$

$$T_f = T_i \left(\frac{V_i}{V_f} \right)^{\frac{1}{\alpha}}$$

$$= 395 \text{ K}$$

Equation relating p, V for adiabatic process in α -ideal gas

γ is the ratio of C_p/C_v for diatomic gas in this case

Solve for p_f from first equation

Substitute for p_i

Use ideal gas law to calculate final temperature

OR use the equation relating T, V for an adiabatic process to get the final temperature ($\alpha = 5/2$ for diatomic gas)

Solve for T_f