What is an Engine?

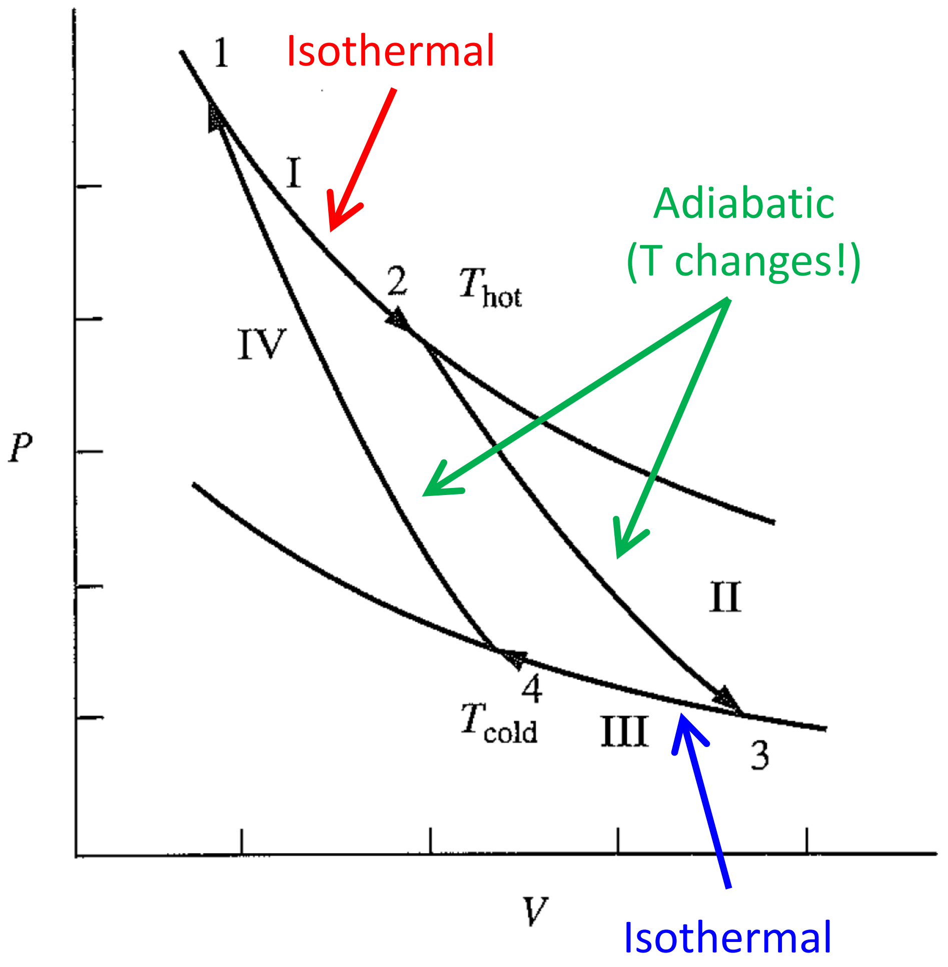
- Anything that transforms Heat → Work
  - *Inherently a thermodynamic device!*
- Parts of an engine
  - Heat source
  - Pistons (the system)
  - Cooling mechanism (where does excess heat go?)
- Efficiency (per cycle):

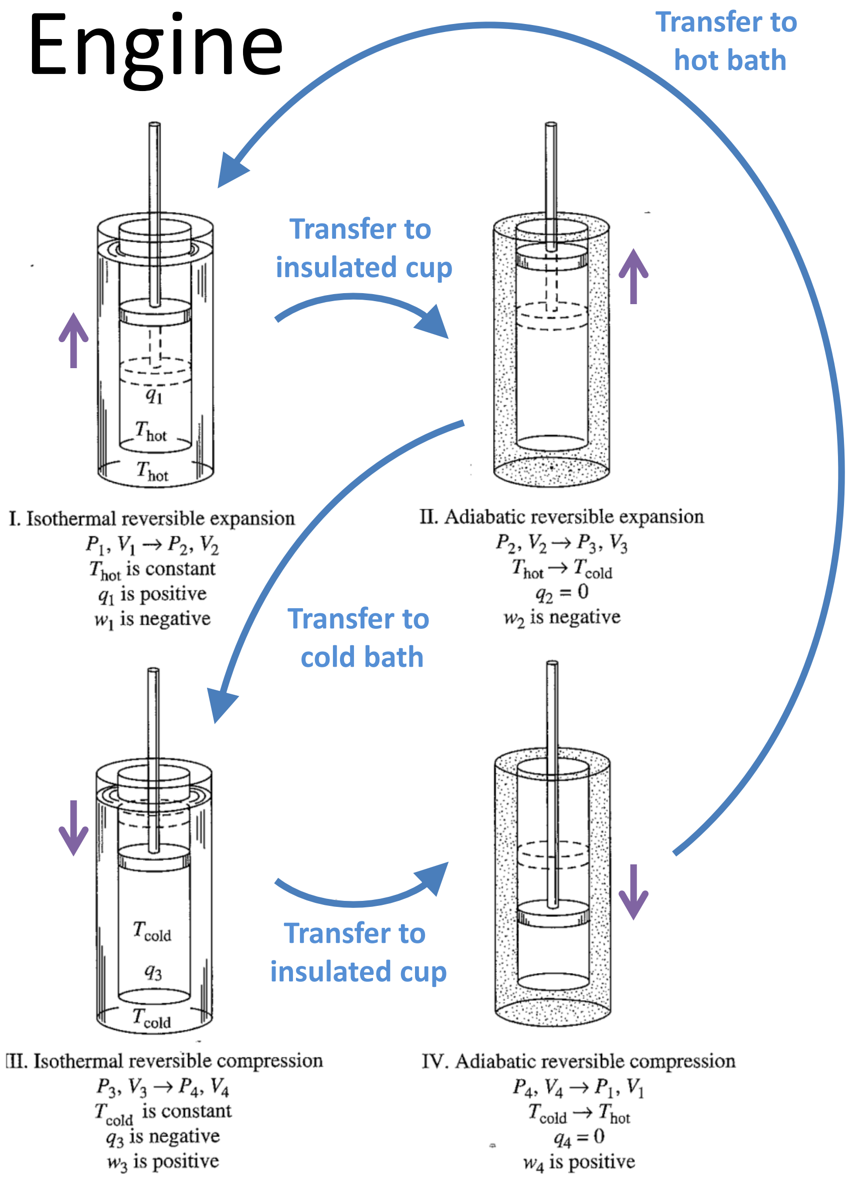
$$\text{efficiency} = \frac{(-w)}{q_{abs}}$$

Work done **by** system is *negative*, but efficiency is *positive*, hence the negative sign

http://www.allpar.com/mopar/new-mopar-hemi.html

The Carnot Engine





I. Isothermal reversible expansion
$P_1, V_1 \rightarrow P_2, V_2$
T_{hot} is constant
q_1 is positive
w_1 is negative

II. Adiabatic reversible expansion
$P_2, V_2 \rightarrow P_3, V_3$
$T_{\text{hot}} \rightarrow T_{\text{cold}}$
$q_2 = 0$
w_2 is negative

III. Isothermal reversible compression
$P_3, V_3 \rightarrow P_4, V_4$
T_{cold} is constant
q_3 is negative
w_3 is positive

IV. Adiabatic reversible compression
$P_4, V_4 \rightarrow P_1, V_1$
$T_{\text{cold}} \rightarrow T_{\text{hot}}$
$q_4 = 0$
w_4 is positive

Tinoco, p. 71.

Carnot Engine: Heat

- **Given:** T_{hot}, T_{cold}, P_1, V_1, V_2
  - V_1, V_2 define the "stroke" of the engine

Path I	(Isothermal, T_{hot})	$q_I = -w_I = nRT_{hot} \ln \frac{V_2}{V_1}$
Path II	(Adiabatic, $T_{hot} \rightarrow T_{cold}$)	$q_{II} = 0$
Path III	(Isothermal, T_{cold})	$q_{III} = -\mathrm{w}_{\mathrm{III}} = nRT_{cold} \ln \frac{V_4}{V_3}$
Path IV	(Adiabatic, $T_{cold} \rightarrow T_{hot}$)	$q_{IV} = 0$

Carnot Engine: Work

- **Given:** T_{hot}, T_{cold}, P_1, V_1, V_2
  - V_1, V_2 define the “stroke” of the engine

Path I	(Isothermal, T_{hot})	$w_I = -nRT_{hot} \ln \frac{V_2}{V_1}$
Path II	(Adiabatic, $T_{hot} \rightarrow T_{cold}$)	$w_{II} = n\bar{C}_V(T_{cold} - T_{hot})$
Path III	(Isothermal, T_{cold})	$\mathrm{w}_{\mathrm{III}} = -nRT_{cold} \ln \frac{V_4}{V_3}$
Path IV	(Adiabatic, $T_{cold} \rightarrow T_{hot}$)	$w_{IV} = n\bar{C}_V(T_{hot} - T_{cold})$

Aside: How to calculate $V_{3,}$ V_4

- Given without further proof (see p. 70, eq. 3.1a)

$$C_V \ln \frac{T_f}{T_i} = -nR \ln \frac{V_f}{V_i}$$

- Applies for adiabatic expansion/compression
- So:

$C_V \ln \frac{T_{cold}}{T_{hot}} = -nR \ln \frac{V_3}{V_2}$ and $C_V \ln \frac{T_{hot}}{T_{cold}} = -nR \ln \frac{V_1}{V_4}$

Aside: How to calculate $V_{3,}$ V_4

- Review of logarithms:

$$\ln A + \ln B =$$

$$\ln A - \ln B =$$

$$-\ln B =$$

$$e^{\ln A} =$$

$$\ln e^{A} =$$

$$\ln A^{x} =$$

Aside: How to calculate $V_{3,}$ V_4

- Review of logarithms:

$$\ln A + \ln B = \ln AB$$

$$\ln A - \ln B = \ln \frac{A}{B}$$

$$-\ln B = \ln \frac{1}{B}$$

$$e^{\ln A} = A$$

$$\ln e^{A} = A$$

$$\ln A^{x} = x \ln A$$

Aside: How to calculate $V_{3,}$ V_4

$$
\begin{array}{rr}
 & C_V \ln \frac{T_{cold}}{T_{hot}} = -nR \ln \frac{V_3}{V_2} \\
+ & C_V \ln \frac{T_{hot}}{T_{cold}} = -nR \ln \frac{V_1}{V_4} \\
\hline
 & 0 = -nR \ln \frac{V_1 V_3}{V_2 V_4}
\end{array}
$$

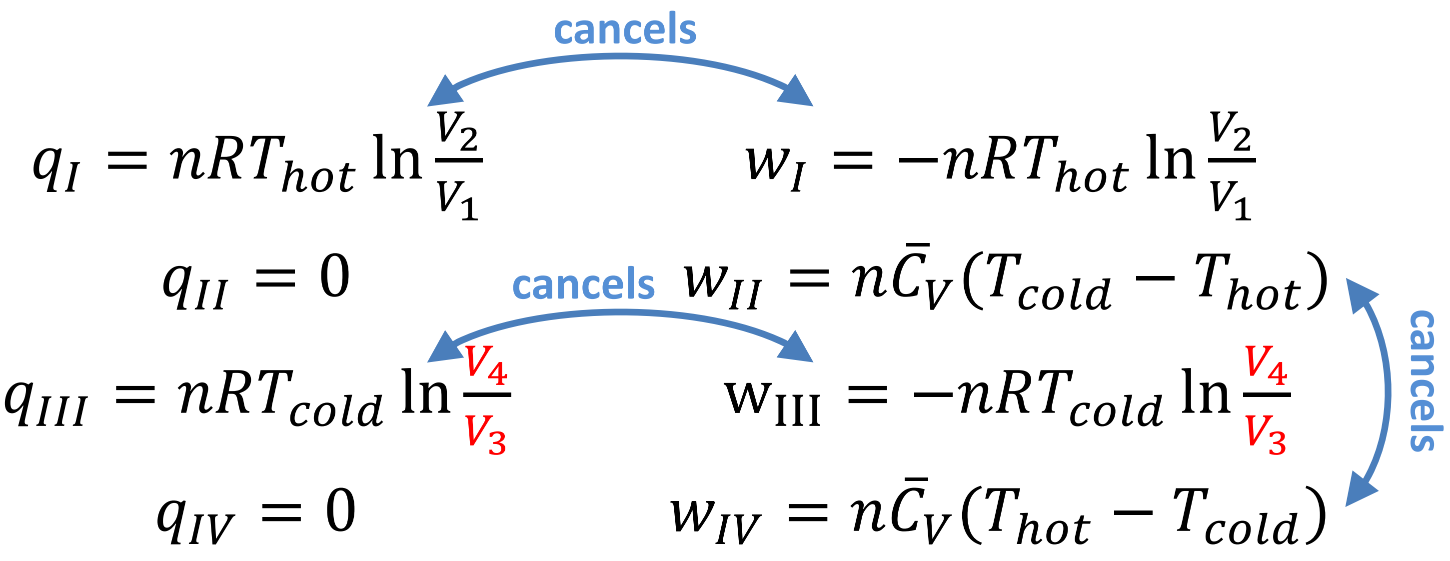
Carnot Engine: Summary

- **Given:** T_{hot}, T_{cold}, P_1, V_1, V_2
  - – V_1, V_2 define the “stroke” of the engine

Path I	$q_I = nRT_{hot}\ln\frac{V_2}{V_1}$	$w_I = -nRT_{hot}\ln\frac{V_2}{V_1}$
Path II	$q_{II} = 0$	$w_{II} = n\bar{C}_V(T_{cold} - T_{hot})$
Path III	$q_{III} = nRT_{cold}\ln\frac{V_4}{V_3}$	$\mathrm{w}_{\mathrm{III}} = -nRT_{cold}\ln\frac{V_4}{V_3}$
Path IV	$q_{IV} = 0$	$w_{IV} = n\bar{C}_V(T_{hot} - T_{cold})$

Carnot Engine: Summary

- **Given:** T_{hot}, T_{cold}, P_1, V_1, V_2
  - – V_1, V_2 define the “stroke” of the engine



Path I	$q_I = nRT_{hot}\ln\frac{V_2}{V_1}$	$w_I = -nRT_{hot}\ln\frac{V_2}{V_1}$
Path II	$q_{II} = 0$	$w_{II} = n\bar{C}_V(T_{cold} - T_{hot})$
Path III	$q_{III} = nRT_{cold}\ln\frac{V_4}{V_3}$	$\mathrm{w_{III}} = -nRT_{cold}\ln\frac{V_4}{V_3}$
Path IV	$q_{IV} = 0$	$w_{IV} = n\bar{C}_V(T_{hot} - T_{cold})$

So $\Delta E_{path} = 0$, as we expect!

Carnot Engine: Analysis

- No net change in E around path
  - Therefore: $w_{path} = -q_{path}$
- "S" function also shows no net change:
  - Defined as: $\int dS = \int \frac{dq_{rev}}{T}$
  - Specifically: $\frac{q_I}{T_{hot}} + \frac{q_{III}}{T_{cold}} = 0$
- Efficiency depends only on temperature difference:
  - Given by: $\text{efficiency} = 1 - \frac{T_{cold}}{T_{hot}}$
- Reversibility: Put in work, create a temperature difference

What is Efficiency?

- Assume engine is 60% “efficient”
  - When it absorbs 100 kJ of heat at “hot” stage, 60 kJ are converted to work, 40 kJ are lost to “cold” stage

  - When operating in reverse, 60 kJ of work would emit 100 kJ of heat at hot stage, transferring 40 kJ of heat from “cold” stage.

A Subtle Argument

- **Question:** Do all reversible cycles operating between T_{hot} and T_{cold} have the same efficiency ($1 - \frac{T_{cold}}{T_{hot}}$), or is that true only for Carnot cycle?

- If true for all cycles, then ΔS must be a state function (because ΔS = 0 → $\text{efficiency} = 1 - \frac{T_{cold}}{T_{hot}}$)
  - If everything has the same efficiency, everything must have the same ΔS

Proof By Contradiction

- Assume a premise is true
- Combine premise with known facts
- If you arrive at a contradiction, then premise must be false

Proof By Contradiction

- Assume a premise is true

All beagles are cats.

- Combine premise with known facts

Known fact #1: *Beagles are dogs.*
Known fact #2: *Dogs are not cats.*

Suppose all beagles are cats. We know that beagles are dogs (#1). Therefore, some dogs must be cats.

- Our logic above contradicts known fact #2, so our premise must be false.

Entropy Is a State Function

- **Premise:** Cycle 1 has efficiency of 75%, and cycle 2 has efficiency of 50% (for same T_{hot}, T_{cold})
- Cycle 1: 100 kJ of heat absorbed from hot bath will generate 75 kJ work transfer 25 kJ to cold bath.
- Use work from cycle 1 to drive cycle 2 in reverse.
- Cycle 2: 75 kJ of work will take 75 kJ from cold stage and add 150 kJ to hot stage.
- Net heat added to hot stage is 50 kJ.
- **Contradiction: Heat spontaneously flows from hot to cold, not vice-versa! Cycles *cannot* differ in their efficiencies!**

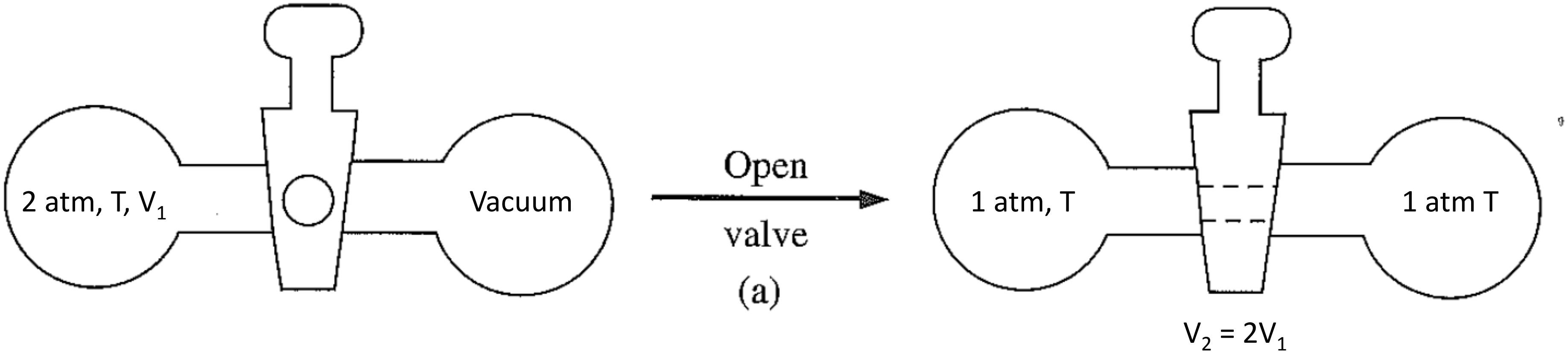
Implications of Carnot Reasoning

- Entropy is a state function: $\Delta S = \int \frac{dq_{rev}}{T}$

  $H_2O(l) \rightarrow H_2O(s) \rightarrow H_2O(l)$, ΔS=0

  - Entropy is just like ΔH for chemical reactions!
- Entropy (S) is extensive, molar entropy ($\bar{S}$) is intensive
- Temperature *T* of the ideal gas law is the "correct" temperature to make S a state function
- Units: energy per temperature (kJ/K, similar to heat capacity

Example 3.1 From Tinoco



- First path: Irreversible expansion
  - Calculate q, ΔS_{system}, $\Delta S_{surroundings}$
- Second path: Reversible expansion
  - Calculate q, ΔS_{system}, $\Delta S_{surroundings}$

Tinoco, pp. 75-77.

Calculating Entropy

- Find a reversible path between states
- Use first law, etc. to calculate q_{rev}. Then:

$$\Delta S_{sys} = \int \frac{dq_{rev}}{T}$$

Reversible heat transfer is greater (more efficient) than irreversible heat transfer

- Cannot use $q_{irreversible}$, because:

$$\Delta S_{sys} > \int \frac{dq_{irrev}}{T}$$

- For all spontaneous processes *total entropy* (system *and* surroundings) must increase.