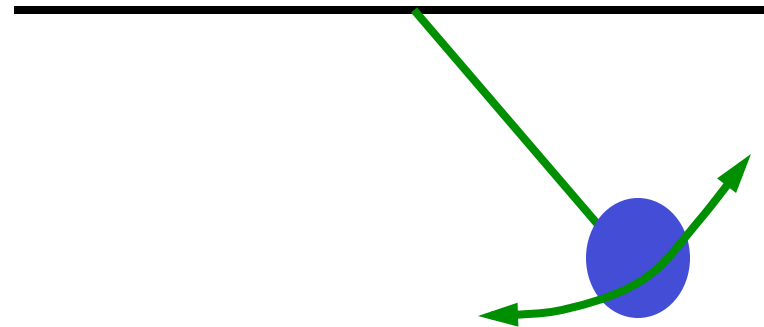# Chapter 20: Entropy and the Second Law of Thermodynamics

The Conservation of Energy law allows energy to flow bi-directionally between its various forms. For example in a pendulum, energy continually goes to/from kinetic energy and potential energy.
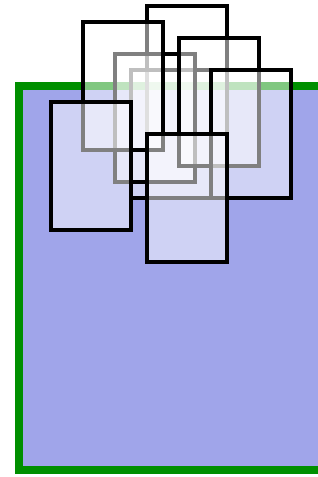
Entropy is different: No conservation law – the entropy change ΔS associated with an irreversible process in a closed system is always greater than or equal to zero.

👉 If an irreversible process occurs in a *closed* system, the entropy *S* of the system always increases; it never decreases.

Ice in water

Consider putting some ice into a glass of water.

**Conservation of energy would allow energy to flow:**

1. only from ice into water
2. only from water into ice
3. both ways

Entropy and the Second Law of Thermodynamics

Consider putting some ice into a glass of water.

Conservation of energy would allow:
- ice getting **colder** and water getting **hotter**.
- ice getting **warmer** and water getting **cooler**.
- both ice and water staying at their initial temperatures.
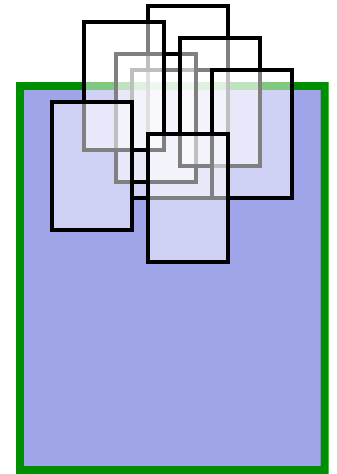
Only one of these scenarios happens, so something must be controlling the *direction* of energy flow.
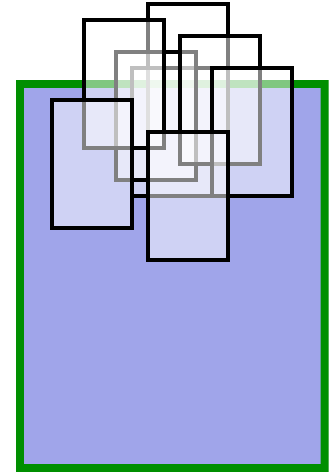
That direction is set by a quantity called **entropy**

Entropy and the Second Law of Thermodynamics

But what about the ice?

The ice is a very ordered state with all of the molecules in specific locations in the crystal. **(W small)**

Liquid water has many states for the water molecules. **(W large)**

Nature will maximize number of energetically-allowed microstates.

Thus, heat (energy) always flows from the water to the ice.

Two equivalent ways to define the entropy in a system:

(1) In terms of the system's temperature and the energy change the system gains or loses as heat,

or;

(1) By counting the ways in which the components of the system can be arranged. (huh?)

Relationship between entropy and heat

Entropy is a state property…. It does not depend on the process, only depends on the initial and final states.
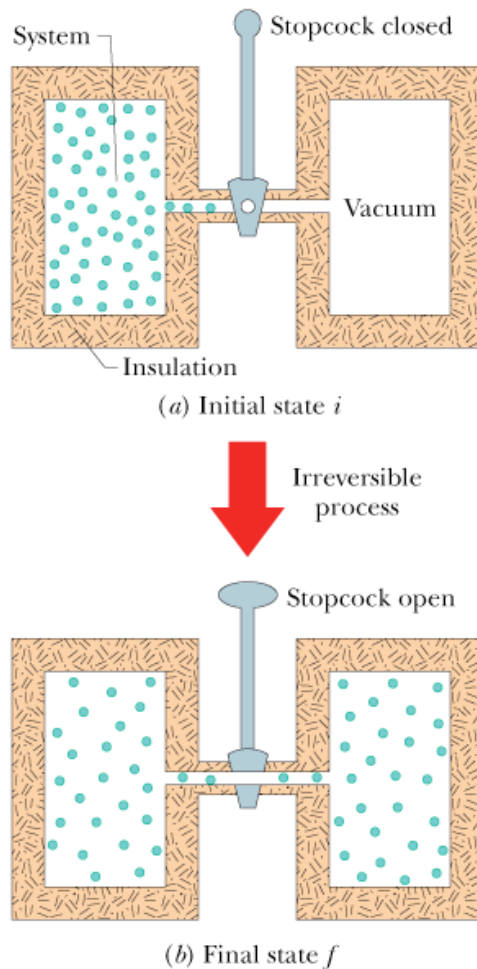
Definition of change in entropy:

$$\Delta S = S_f - S_i = \int_i^f \frac{dQ}{T}$$

Q: energy transferred as heat

T: temperature in **Kelvin**

sign of ΔS and Q SI unit of S: J/K

What are some other state properties? ….*p, V, E, and T*…?

Entropy and the Small View (statistical thermodynamics)

(a)

— Insulation

(b)

Let's bring the numbers down to illustrate the relationship between entropy and probability.

Consider an insulated box containing six molecules (N=6). The box is divided into the left half and the right half. Let n_1 be the number of molecules in the left half and n_2 be the number of molecules in the right half.
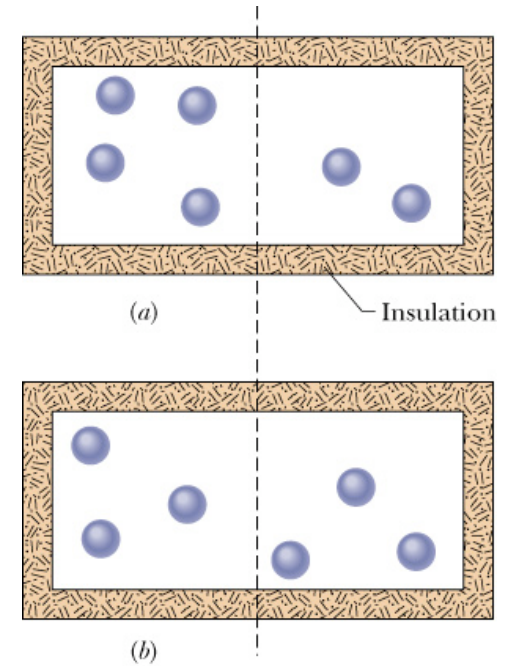
Note: $N = n_1 + n_2$

We now selectively pick molecules to be placed in the left half.

1st molecule we can pick any of the six available molecules.
2nd molecule we can pick any of the five remaining molecules.
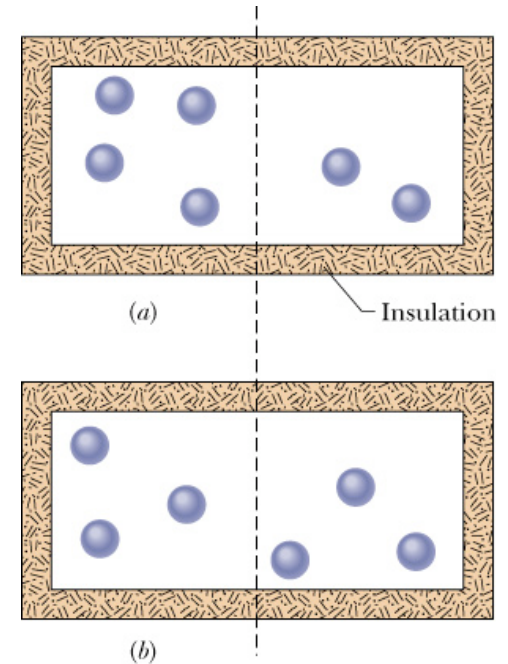
etc.......

Total number of ways we can select the six molecules = 6! = 720

Entropy and Probability (Section 20-8)

Six **indistinguishable** molecules can be selected to be located 720 (6 ! or "six factorial") different ways.

There are 4! (=24) different ways we could have put four molecules in the left side and 2! (=2) different ways we could have out the other two molecules in the right half.

Multiplicity W is the resulting number of microstates.

$$W = \frac{N!}{n_1! \, n_2!} \qquad W_{III} = \frac{6!}{4! \, 2!} = \frac{720}{24 \cdot 2} = 15$$
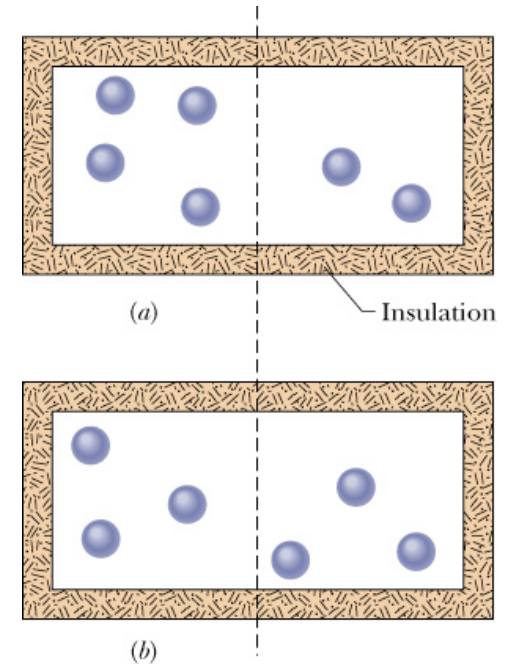
Note: $0! = 1$ and $6! = 6 \cdot 5 \cdot 4 \cdot 3 \cdot 2 \cdot 1 = 720$

This W is *NOT* work: Many books use W for multiplicity)

Entropy

Continuing with all possible combinations of the six molecules in the two halves:

(a)
— Insulation

(b)

Label	n_1	n_2	Multiplicity W
I	6	0	$6!/(6!\cdot0!) = 1$
II	5	1	$6!/(5!\cdot1!) = 6$
III	4	2	$6!/(4!\cdot2!) = 15$
IV	3	3	$6!/(3!\cdot3!) = 20$
V	2	4	$6!/(2!\cdot4!) = 15$
VI	1	5	$6!/(1!\cdot5!) = 6$
VII	0	6	$6!/(0!\cdot6!) = 1$

$$W = \frac{N!}{n_1!\, n_2!} = \frac{N!}{n_1!\, (N - n_1)!}$$

The most likely state (highest probability) is the state with the greatest multiplicity, W_{IV} with three molecules in each half (most disordered).

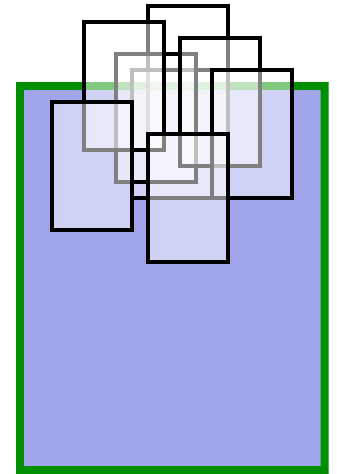# Entropy

So, ...   How does this play out in Thermodynamics?

Entropy is the Boltzmann constant (k = $1.38\text{x}10^{-23}$ J/K) times the natural log of W.

$$S = k \ln W$$

Chapter 20 Entropy and the Second Law of Thermodynamics

Example with the ice and water

Suppose 0.1 kg ice at 0^oC (273K) is in 0.5kg water at 20^oC (293K).

Calculate Heat transfers:

$$Q_{melt} = m_{ice}L_f = (0.1kg)(3.33 \times 10^5 J/kg) = 3.33 \times 10^4 J$$

$$Q_{water} = m_{water}c_w \Delta T \Rightarrow \Delta T = Q_{water}/m_{water}c_w = -15.9K$$

$$Q_{water} = m_{water}c_w(277.1 - T_f) = m_{icewater}c_w(T_f - 273)$$

$$T_f = (277.1m_{water} + 273m_{icewater})/(m_{icewater} + m_{water}) = 276.4K$$

Chapter 20 Entropy and the Second Law of Thermodynamics

Example with the ice and water

Suppose 0.1 kg ice at 0^oC (273K) is in 0.5kg water at 20^oC (293K). What is the change in entropy of the ice as it melts at 0^oC?
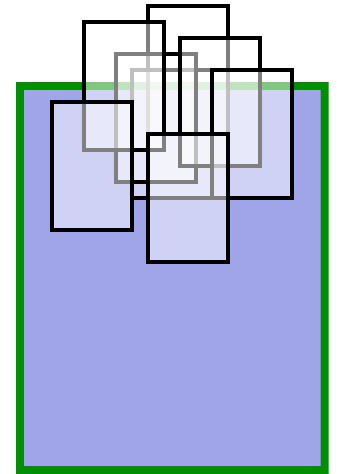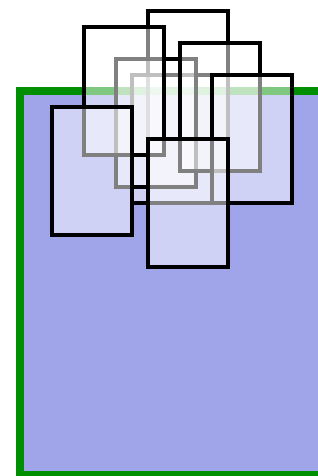
Convert all temperatures into Kelvin!!

$$\Delta S_{melt} = S_f - S_i = \int_i^f \frac{dQ}{T} = \frac{m_{ice}L_f}{T}$$

$$= \frac{(0.1kg)(3.33x10^5 J/kg)}{273K} = +122.0 J/K$$

Chapter 20 Entropy and the Second Law of Thermodynamics

Example with the ice and water

Suppose 0.1 kg ice at 0°C (273K) is in 0.5kg water at 20°C (293K).

What is the change in entropy of the ice water as it warms up to the final temperature?

$$\Delta S_{icewater} = S_f - S_i = \int_i^f \frac{dQ}{T} = \int_i^f \frac{m_{icewater}c_w dT}{T} = m_{icewater}c_w \int_i^f \frac{dT}{T}$$

$$= m_{icewater}c_w \ln\left(\frac{T_f}{T_i}\right) = (0.1\,kg)(4186\,J/kg{\cdot}K)\ln\left(\frac{276.4K}{273K}\right) = +5.2\,J/K$$

Chapter 20 Entropy and the Second Law of Thermodynamics

Example with the ice and water

Suppose 0.1 kg ice at 0°C (273K) is in 0.5kg water at 20°C (293K).

What is the change in entropy of the water as it melted the ice?
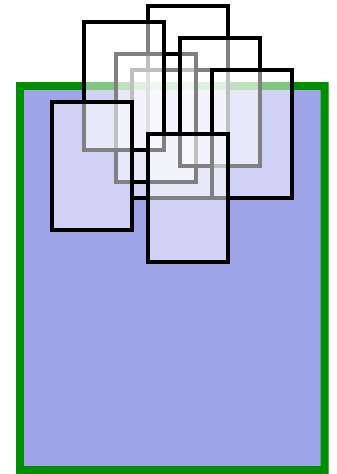
$$\Delta S_{watermelt} = S_f - S_i = \int_i^f \frac{dQ}{T} = \int_i^f \frac{m_{water}c_w dT}{T} = m_{water}c_w \int_i^f \frac{dT}{T}$$

$$= m_{water}c_w \ln\left(\frac{T_f}{T_i}\right) = (0.5\,kg)(4186\,J/kg\cdot K) \ln\left(\frac{277.1K}{293K}\right) = -116.8\,J/K$$

Chapter 20 Entropy and the Second Law of Thermodynamics

Example with the ice and water

Suppose 0.1 kg ice at 0°C (273K) is in 0.5kg water at 20°C (293K).

What is the change in entropy of the water as it cooled down to the final temperature?
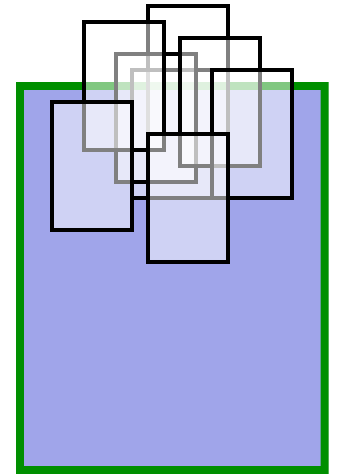
$$\Delta S_{watercooled} = S_f - S_i = \int_i^f \frac{dQ}{T} = \int_i^f \frac{m_{water}c_w dT}{T} = m_{water}c_w \int_i^f \frac{dT}{T}$$

$$= m_{water}c_w \ln\left(\frac{T_f}{T_i}\right) = (0.5\,kg)(4186\,J/kg\cdot K)\ln\left(\frac{276.4K}{277.1K}\right) = -5.3\,J/K$$

Chapter 20 Entropy and the Second Law of Thermodynamics

Example with the ice and water

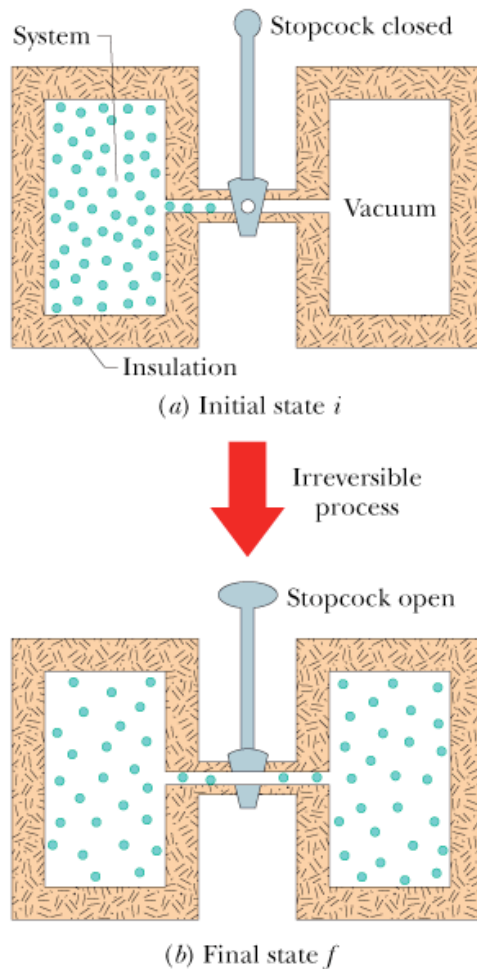Suppose 0.1 kg ice at 0°C (273K) is in 0.5kg water at 20°C (293K).

Total change in entropy of the ice / water system as it came to thermal equilibrium
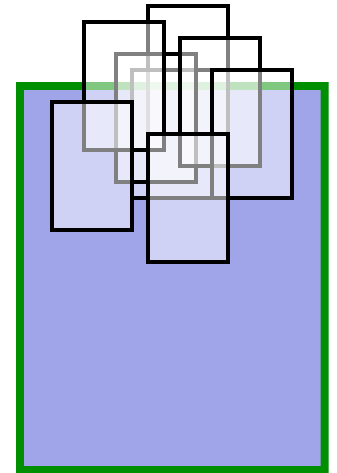
$$\Delta S_{total} = \quad \Delta S_{melt} + \Delta S_{icewater} + \Delta S_{watermelt} + \Delta S_{watercooled}$$
$$= (+122.0 \quad + 5.2 \qquad + -116.8 \quad + -5.3) \text{ J/K}$$
$$= +5.1 \text{ J/K}$$

Relationship between entropy and heat

Entropy is a state property…. It does not depend on the process, only depends on the initial and final states.

System — Stopcock closed

Vacuum

Insulation

(a) Initial state *i*

Irreversible process

Stopcock open

(b) Final state *f*

Definition of change in entropy:

$$\Delta S = S_f - S_i = \int_i^f \frac{dQ}{T}$$

Q: energy transferred as heat

T: temperature in **Kelvin**

sign of ΔS and Q SI unit of S: J/K

What are some other state properties? ….*p, V, E, and T*…?

Reversible and Irreversible Processes

An **irreversible process** is one that cannot be reversed by means of small changes in the environment. Entropy increases. $\Delta S > 0$

e.g. A broken egg can not go back to being a whole egg. Heat does not transfer from the ice to the water (though this would not violate the law of energy conservation).

Note: ALL _real_ processes are **irreversible**!

If an irreversible process occurs in a closed system, the entropy S of the system always increases, it never decreases. (entropy postulate)

Sample Problem

Water is heated on a stove. Which of the following temperature changes results in the greatest change in entropy?
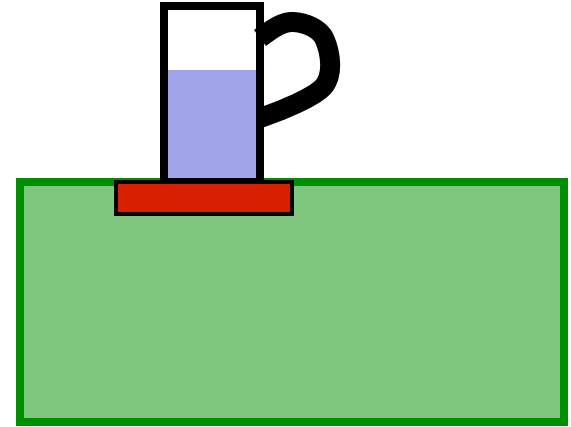
1. from 10°C to 20°C
2. from 45°C to 55°C
3. from 80°C to 90°C
4. all have the same entropy change

Sample Problems

$$\Delta S_{water} = \int_i^f \frac{dQ}{T} = \int_i^f \frac{m_{water} c_w dT}{T} = m_{water} c_w \int_i^f \frac{dT}{T} = m_{water} c_w \ln\left(\frac{T_f}{T_i}\right)$$

Water is heated on a stove. Which of the following temperature changes results in the greatest change in entropy?

(1) from 10ºC to 20ºC => 283K to 293K => ln(293/283) = 0.035
(2) from 45ºC to 55ºC => 318K to 328K => ln(328/318) = 0.031
(3) from 80ºC to 90ºC => 353K to 363K => ln(363/353) = 0.028
(4) all have the same entropy change.

The Second Law of Thermodynamics

For the free expansion, we have $\Delta S > 0$. It is an irreversible process in a closed system.

For the reversible isothermal process, for the gas $\Delta S > 0$ for expansion and $\Delta S < 0$ for compression. However, the gas itself is not a closed system. It is only a closed system if we include both the gas and the reservoir.

during expansion:
$$\Delta S_{gas} = \frac{|Q|}{T} \qquad \Delta S_{res} = -\frac{|Q|}{T}$$

So: $\Delta S_{total} = 0$

$$\boxed{\Delta S \geq 0 \quad \text{(Second Law of Thermodynamics)}}$$

If a process occurs in a *closed* system, the entropy of the system increases for irreversible processes and remains constant for reversible processes. It never decreases.

Reversible and Irreversible Processes

A **reversible process** is one that can be reversed by means of small changes in the environment. In this case, DS = 0.

e.g. An isothermal expansion/compression of an ideal gas.

The Second Law says that <u>not only can't</u> you come out ahead -- you *can't* even break even!!?!!

Everything you do will increase the entropy of the universe!

$$\Delta S \geq 0 \longleftarrow$$ **Second Law of Thermodynamics**

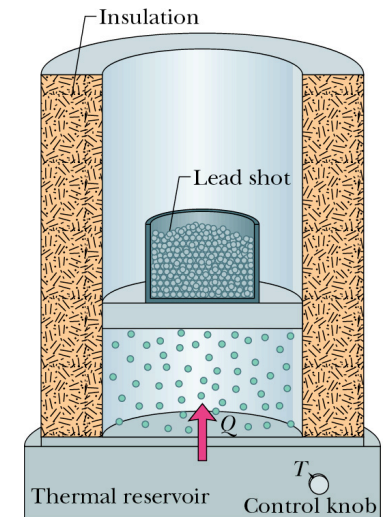$\Delta S = 0$ reversible process; $\Delta S > 0$ irreversible process

Calculate ΔS for the reversible isothermal process. since T = constant:

$$\Delta S = S_f - S_i = \frac{1}{T}\int_i^f dQ = \frac{Q}{T}$$

In isothermal expansion, Q > 0, therefore $\Delta S > 0$ that means $\Delta S > 0$ for free expansion

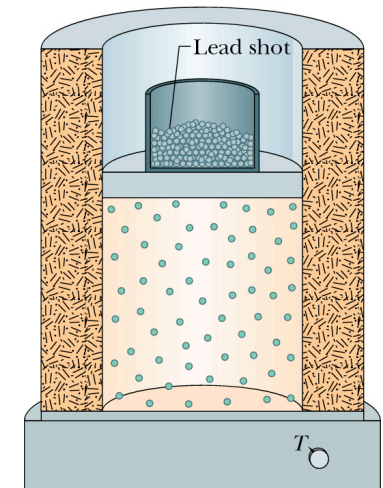For a process that ΔT is small compared to T :

$$\Delta S = S_f - S_i \approx \frac{Q}{T_{avg}}$$

Insulation

Lead shot

Q

T

Thermal reservoir   Control knob

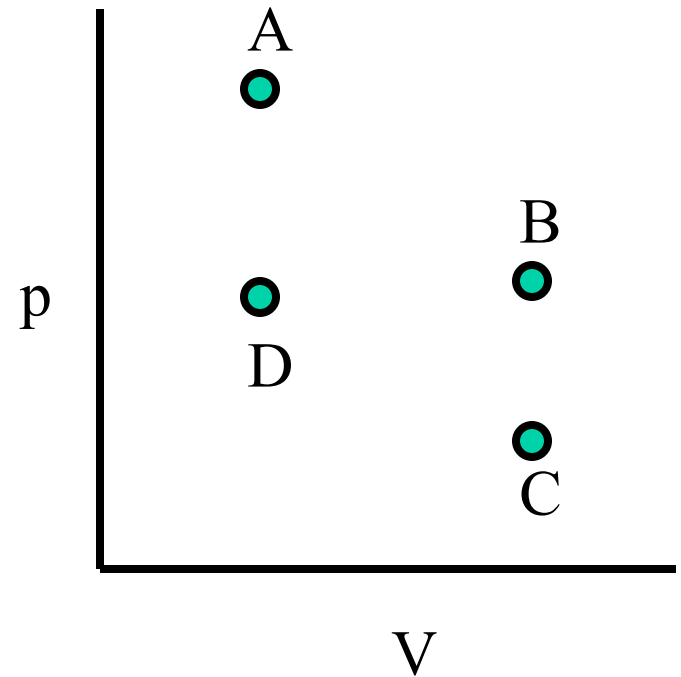(a) Initial state i

Reversible process
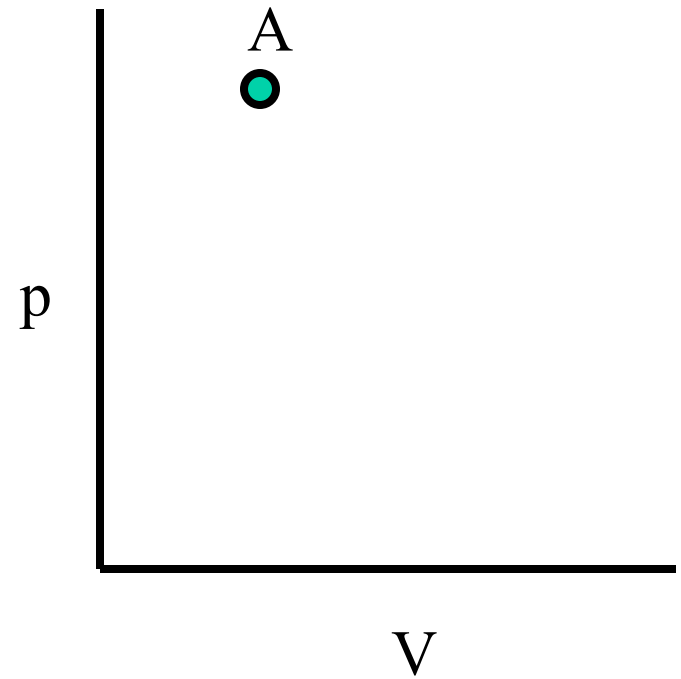
Lead shot

T

(b) Final state f

PROBLEM 2: (25pts) One mole of an ideal, monatomic gas is the working substance of an ideal heat engine. The system is initially at point A with pressure (p_A), volume (V_A), and temperature ($T_A = T_H$). It is then allowed to expand isothermally to point B, then cool isochorically to point C, then contract isothermally to point D, then finally warm-up isochorically back to the initial point A.

Let $p_A = 1.00 \times 10^5$ Pa, $V_B = 3.00 \ V_A$,

$T_H = 600$ K, and $T_L = 300$ K.

PROBLEM 2: (25pts) One mole of an ideal, monatomic gas is the working substance of an ideal heat engine. The system is initially at point A with pressure (p_A), volume (V_A), and temperature ($T_A = T_H$).

p

A

V

Let $p_A = 1.00 \times 10^5$ Pa, $V_B = 3.00\, V_A$,

$T_H = 600$ K, and $T_L = 300$ K.

A. What is the volume this gas occupies at point A?

Ideal gas Law

$$pV = nRT \implies p_A V_A = nRT_A \implies V_A = \frac{nRT_A}{p_A}$$

PROBLEM 2: (25pts) One mole of an ideal, monatomic gas is the working substance of an ideal heat engine. The system is initially at point A with pressure (p_A), volume (V_A), and temperature ($T_A=T_H$). It is then allowed to expand isothermally to point B
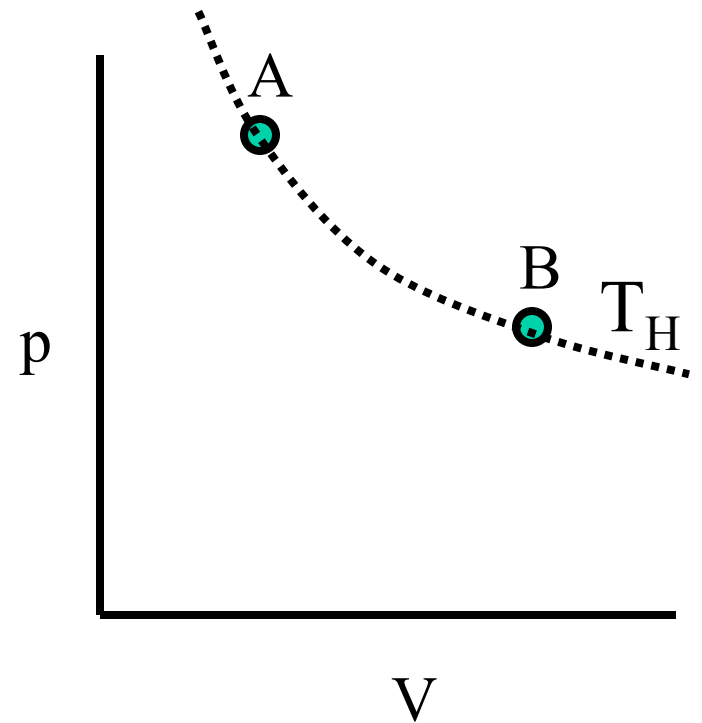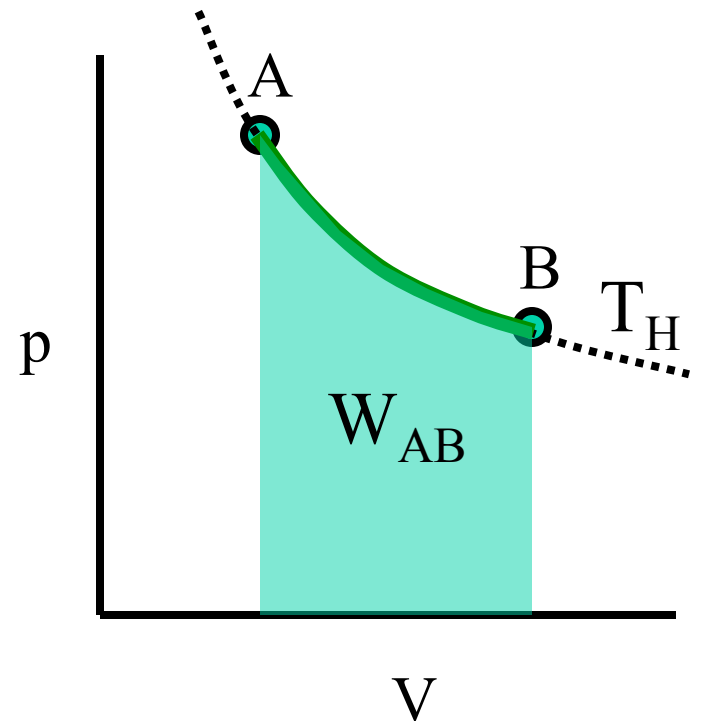

B. What is the work done by the gas W_{AB} in going from A to B?

How can it isothermally go from A to B?

$$pV = nRT \longleftarrow$$ Both p and V *must* change such that their product (nRT_H) is a constant.

PROBLEM 2: (25pts) One mole of an ideal, monatomic gas is the working substance of an ideal heat engine. The system is initially at point A with pressure (p_A), volume (V_A), and temperature ($T_A = T_H$). It is then allowed to expand isothermally to point B
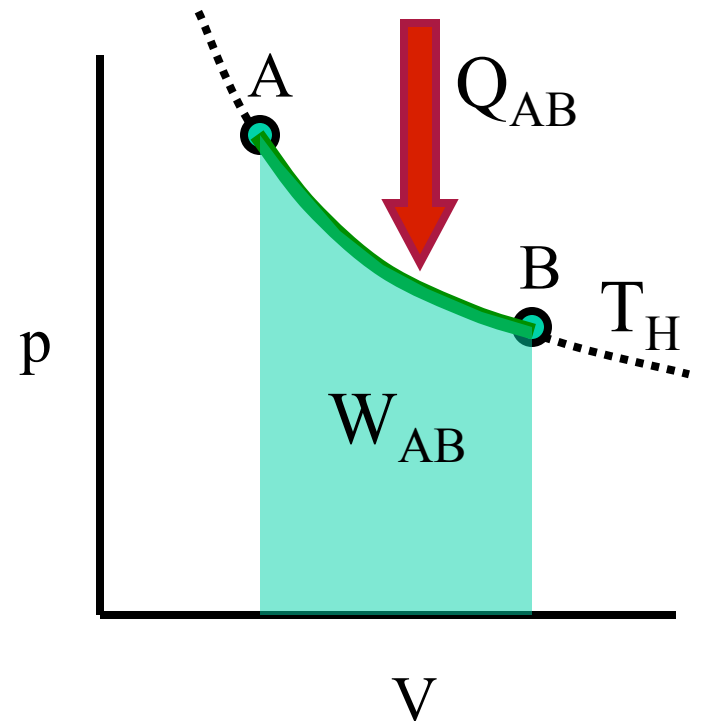

B. What is the work done by the gas W_{AB} in going from A to B?

But if V increases, the gas does positive work (i.e., energy leaves the gas).

$$pV = nRT \implies p = nRT/V$$

$$W_{AB} = \int_{V_A}^{V_B} p \, dV = \int_{V_A}^{V_B} \frac{nRT_H}{V} \, dV = nRT_H \int_{V_A}^{V_B} \frac{dV}{V}$$

$$= nRT_H \ln(V_B / V_A)$$

PROBLEM 2: (25pts) One mole of an ideal, monatomic gas is the working substance of an ideal heat engine. The system is initially at point A with pressure (p_A), volume (V_A), and temperature ($T_A=T_H$). It is then allowed to expand isothermally to point B
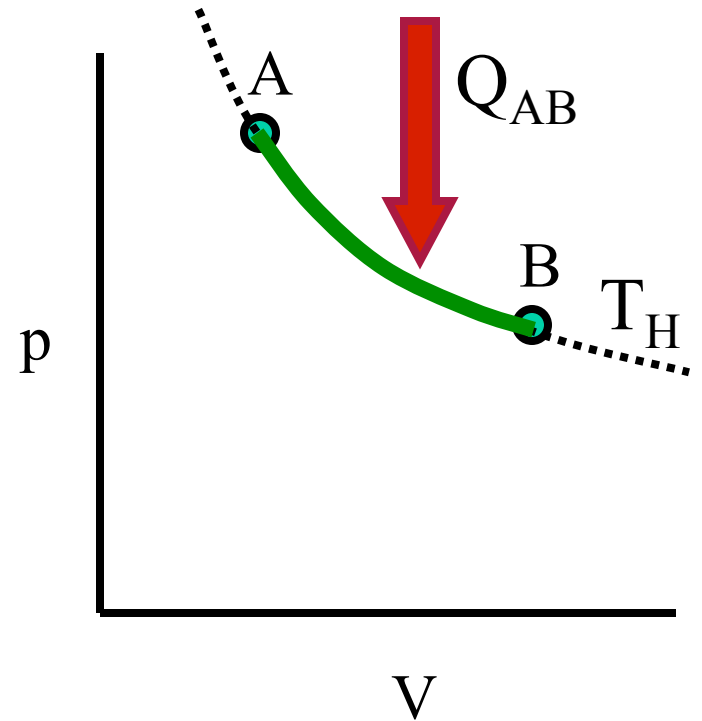

B. What is the work done by the gas W_{AB} in going from A to B?

Since the internal energy doesn't change, energy (heat) must be added to compensate for the work the gas does.

$$\Delta E_{int} = Q - W = 0 \Rightarrow Q_{AB} = W_{AB}$$

PROBLEM 2: (25pts) One mole of an ideal, monatomic gas is the working substance of an ideal heat engine. The system is initially at point A with pressure (p_A), volume (V_A), and temperature ($T_A=T_H$). It is then allowed to expand isothermally to point B

B*. What is the heat added to the gas Q_{AB} in going from A to B?

$$\Delta E_{int} = Q - W = 0 \implies Q_{AB} = W_{AB} = nRT_H \ln(V_B/V_A)$$

PROBLEM 2: (25pts) One mole of an ideal, monatomic gas is the working substance of an ideal heat engine. The system is initially at point A with pressure (p_A), volume (V_A), and temperature ($T_A = T_H$). It is then allowed to expand isothermally to point B
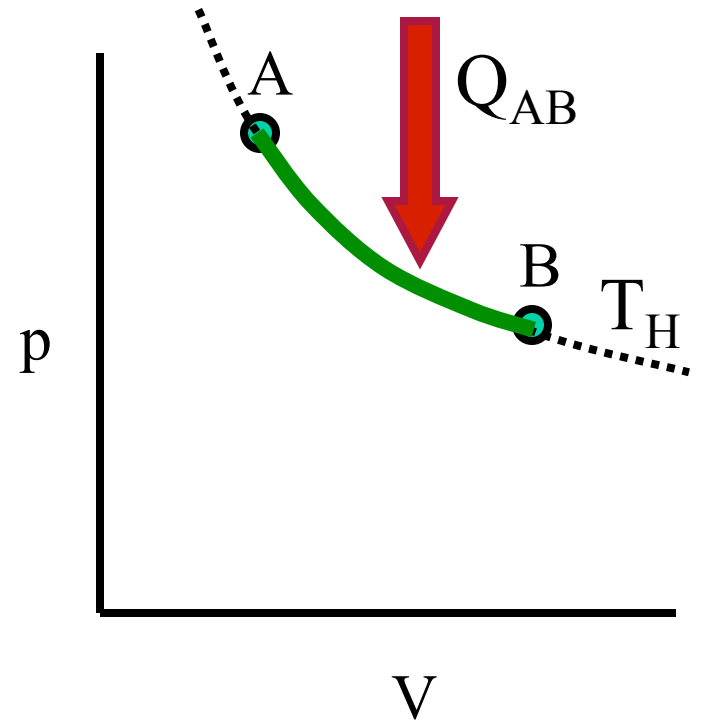

B*. What is the change in entropy of the gas DS_{AB} going from A to B?

$$\Delta E_{int} = Q - W = 0 \implies Q_{AB} = W_{AB} = nRT_H \ln(V_B/V_A)$$

$$\Delta S_{AB} = \int_A^B \frac{dQ}{T} = \frac{1}{T_H} \int_A^B dQ = \frac{Q_{AB}}{T_H}$$

$$\boxed{\Delta S_{AB} = nR \ln(V_B/V_A)} \qquad > 0$$

PROBLEM 2: (25pts) One mole of an ideal, monatomic gas is the working substance of an ideal heat engine. The system is initially at point A with pressure (p_A), volume (V_A), and temperature ($T_A = T_H$). It is then allowed to expand isothermally to point B, then cool isochorically to point C
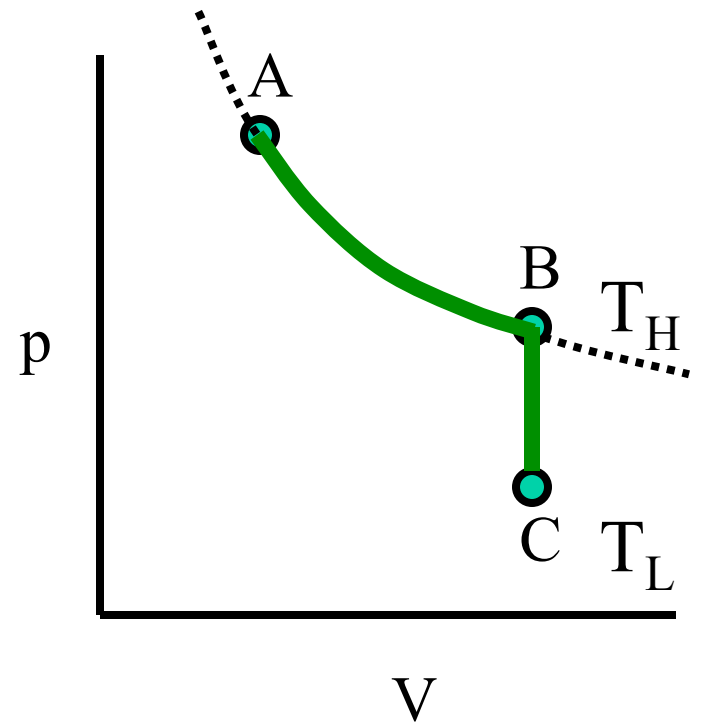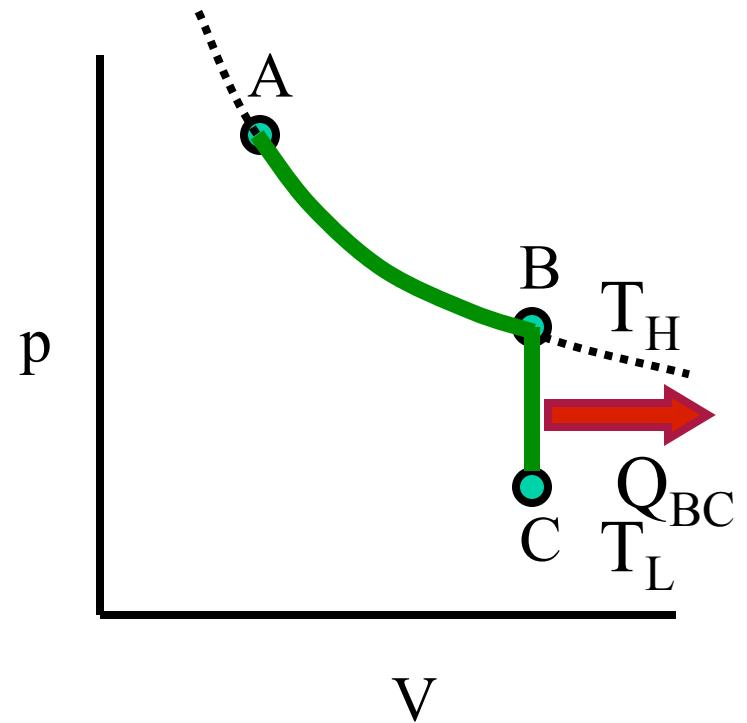

C. What is the work done by the gas W_{BC} in going from B to C?

No volume change => work = 0.

But that *doesn't* mean energy didn't change form!

How could the gas's temperature drop with no change in volume? ⟶ Energy has to leave the system!

PROBLEM 2: (25pts) One mole of an ideal, monatomic gas is the working substance of an ideal heat engine. The system is initially at point A with pressure (p_A), volume (V_A), and temperature ($T_A=T_H$). It is then allowed to expand isothermally to point B, then cool isochorically to point C

C*. What is the heat leaving the gas Q_{BC} in going from B to C?

Monatomic gas   No volume change

$\Rightarrow$ work = 0.

$\Delta E_{int} = 3/2 \; nR \; \Delta T = Q - W$

$\Rightarrow \quad \Delta E_{int} = Q_{BC} - 0 = Q_{BC} = 3/2 \; nR \; (T_L - T_H) \qquad < 0$

PROBLEM 2: (25pts) One mole of an ideal, monatomic gas is the working substance of an ideal heat engine. The system is initially at point A with pressure (p_A), volume (V_A), and temperature ($T_A = T_H$). It is then allowed to expand isothermally to point B, then cool isochorically to point C
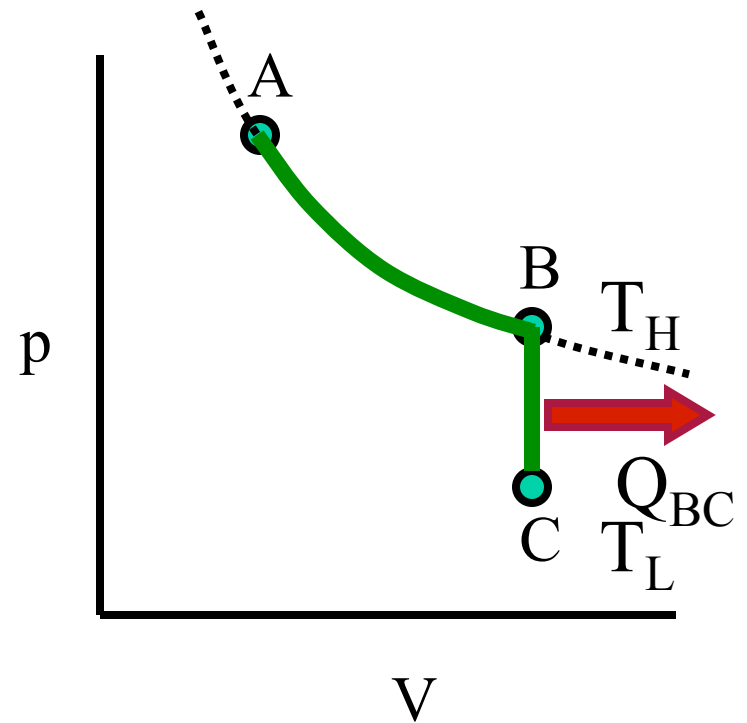

C*. What is the change in entropy of the gas ΔS_{BC} going from B to C?

$$\Delta E_{int} = Q_{BC} \quad \Rightarrow \quad dE_{int} = dQ_{BC} = 3/2\ nR\ dT$$

$$\Delta S_{BC} = \int_B^C \frac{dQ}{T} = \int_{T_H}^{T_L} \frac{3/2\ nR\ dT}{T} = 3/2\ nR\ \ln\left(T_L / T_H\right)$$

$$\boxed{\Delta S_{BC} = \frac{3}{2}\ nR\ \ln\left(T_L / T_H\right) = -\frac{3}{2}\ nR\ \ln\left(T_H / T_L\right)} \quad < 0$$

PROBLEM 2: (25pts) One mole of an ideal, monatomic gas is the working substance of an ideal heat engine. The system is initially at point A with pressure (p_A), volume (V_A), and temperature ($T_A=T_H$). It is then allowed to expand isothermally to point B, then cool isochorically to point C, then contract isothermally to point D
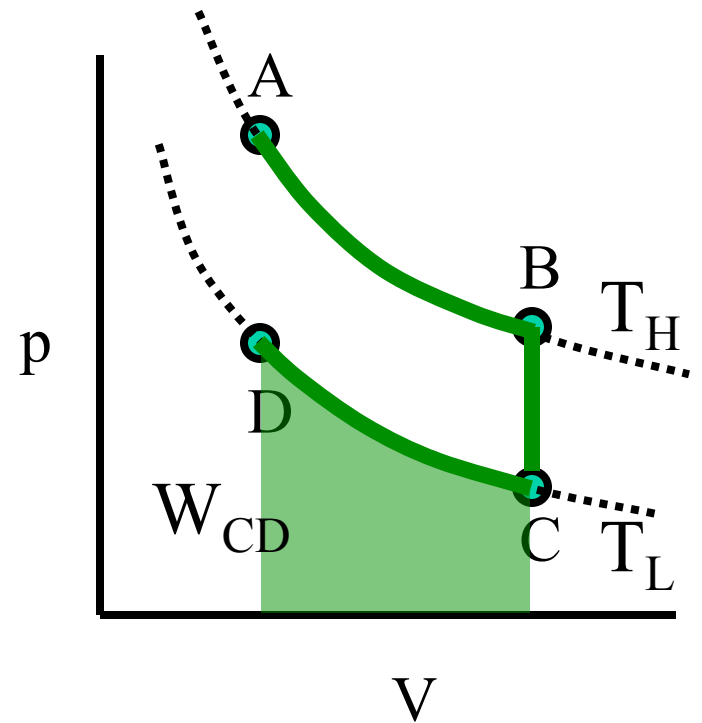

D. What is the work done by the gas W_{CD} in going from C to D?

But if V decreases, the gas does negative work (i.e., energy enters the gas). Note: $V_C=V_B$ and $V_D=V_A$

$$W_{CD} = \int_{V_C}^{V_D} p\,dV = \int_{V_C}^{V_D} \frac{nRT_L}{V}dV = nRT_L \int_{V_B}^{V_A} \frac{dV}{V} = nRT_L \ln(V_A/V_B)$$

$$= -nRT_L \ln(V_B/V_A) \qquad < 0$$

PROBLEM 2: (25pts) One mole of an ideal, monatomic gas is the working substance of an ideal heat engine. The system is initially at point A with pressure (p_A), volume (V_A), and temperature ($T_A = T_H$). It is then allowed to expand isothermally to point B, then cool isochorically to point C, then contract isothermally to point D
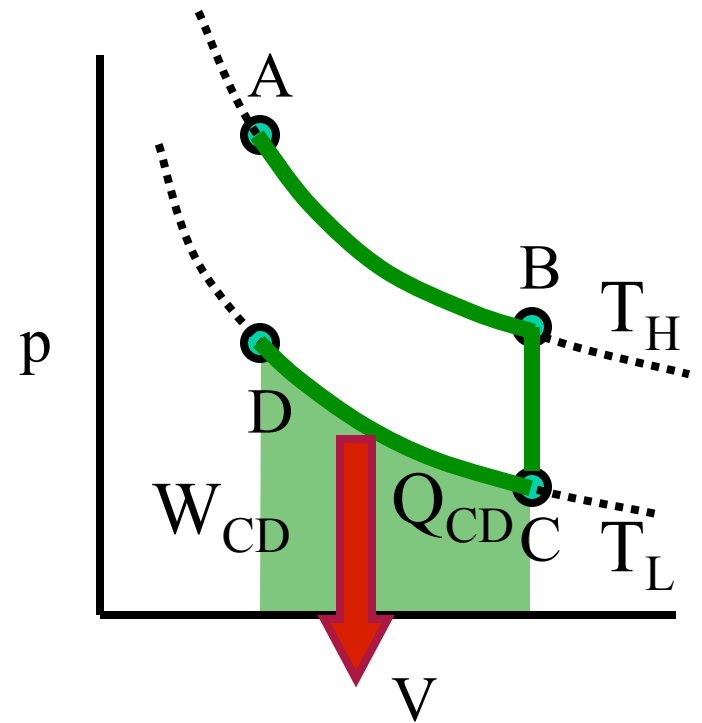
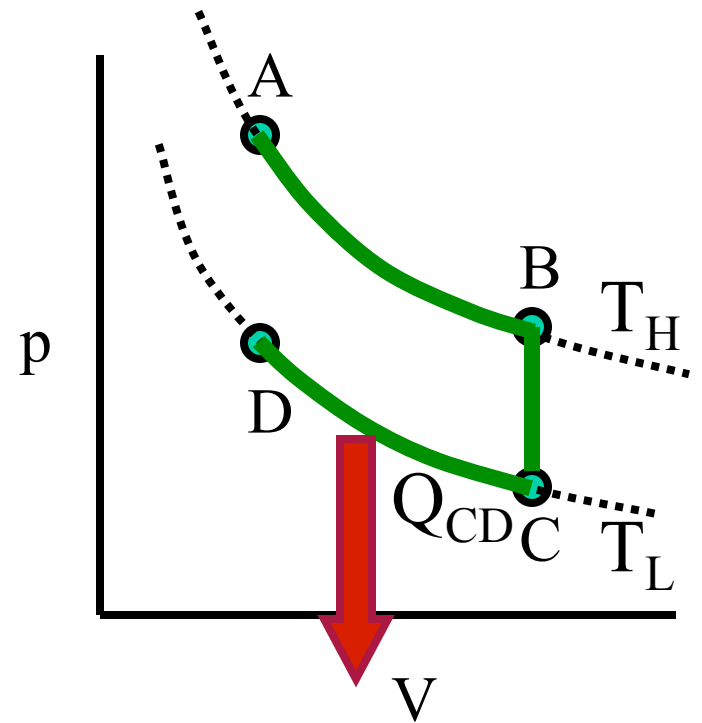D*. What is the heat change of the gas Q_{CD} in going from C to D?

How can it isothermally go from C to D?

Since the internal energy doesn't change, energy (heat) must leave the gas as the volume decreases.

$$\Delta E_{int} = Q - W = 0 \implies$$

$$Q_{CD} = W_{CD} = nRT_L \ln(V_A / V_B) = -nRT_L \ln(V_B / V_A)$$

PROBLEM 2: (25pts) One mole of an ideal, monatomic gas is the working substance of an ideal heat engine. The system is initially at point A with pressure (p_A), volume (V_A), and temperature ($T_A = T_H$). It is then allowed to expand isothermally to point B, then cool isochorically to point C, then contract isothermally to point D


D*. What is the heat leaving the gas Q_{CD} in going from C to D?

$$\Delta E_{int} = Q - W = 0$$

$$=> \quad Q_{CD} = W_{CD} = nRT_L \ln(V_A/V_B) = -nRT_L \ln(V_B/V_A)$$

PROBLEM 2: (25pts) One mole of an ideal, monatomic gas is the working substance of an ideal heat engine. The system is initially at point A with pressure (p_A), volume (V_A), and temperature ($T_A=T_H$). It is then allowed to expand isothermally to point B, then cool isochorically to point C, then contract isothermally to point D
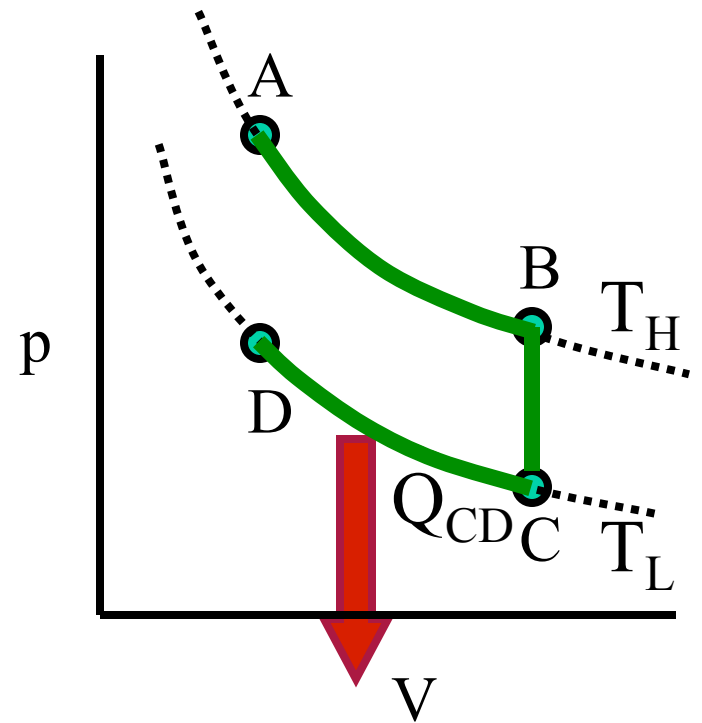
D*. What is the change in entropy of the gas ΔS_{CD} going from C to D?

$$\Delta E_{int} = Q - W = 0 \;\Rightarrow\; Q_{CD} = W_{CD} = nRT_L \ln(V_A/V_B)$$

$$\Delta S_{CD} = \int_C^D \frac{dQ}{T} = \frac{1}{T_L}\int_C^D dQ = \frac{Q_{CD}}{T_L}$$

$$\boxed{\Delta S_{CD} = nR\ln(V_A/V_B) = -nR\ln(V_B/V_A)} \quad < 0$$

PROBLEM 2: (25pts) One mole of an ideal, monatomic gas is the working substance of an ideal heat engine. The system is initially at point A with pressure (p_A), volume (V_A), and temperature ($T_A = T_H$). It is then allowed to expand isothermally to point B, then cool isochorically to point C, then contract isothermally to point D, then finally warm-up isochorically back to the initial point A.
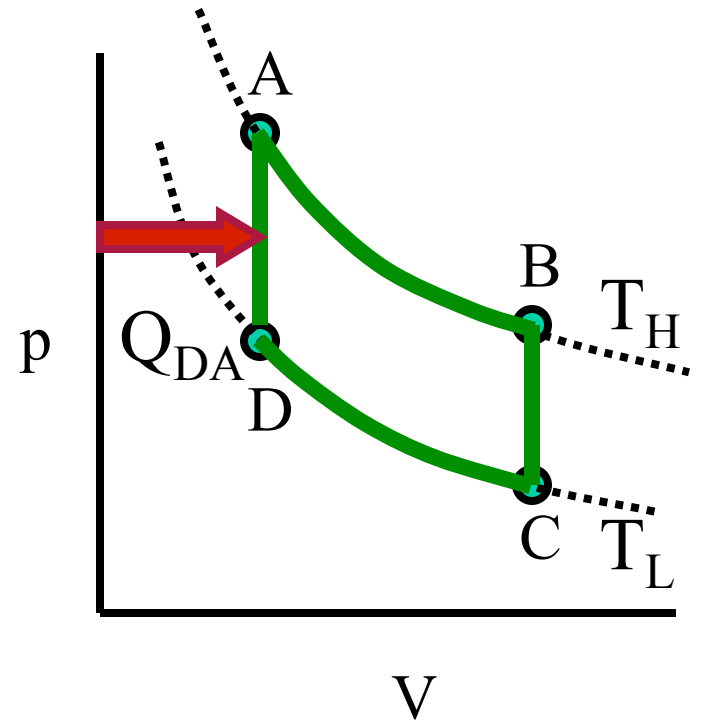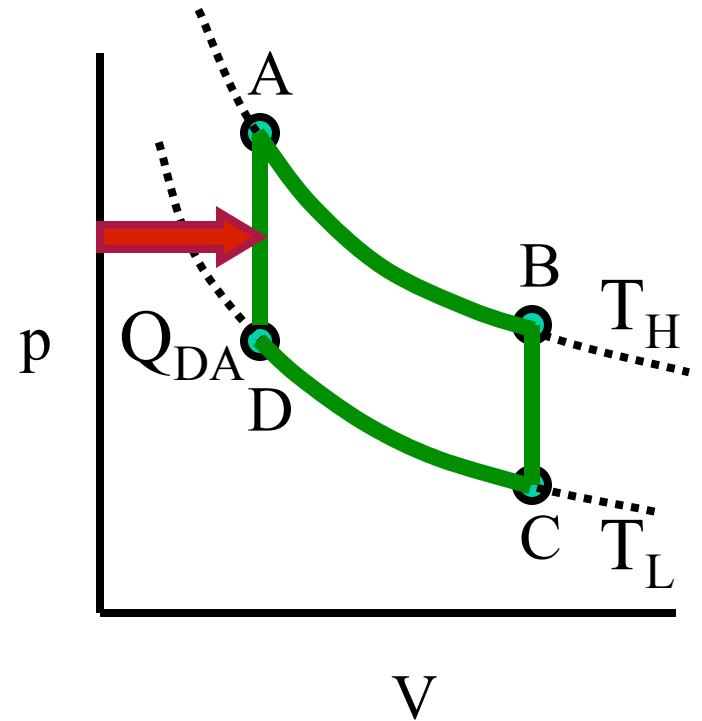

E. What is the work done by the gas W_{DA} in going from D back to A?

No volume change => work = 0.

But that *doesn't* mean energy didn't change form!
How could the gas's temperature increase with no change in volume? ⟶ Energy has to enter the system!

PROBLEM 2: (25pts) One mole of an ideal, monatomic gas is the working substance of an ideal heat engine. The system is initially at point A with pressure (p_A), volume (V_A), and temperature $(T_A=T_H)$. It is then allowed to expand isothermally to point B, then cool isochorically to point C, then contract isothermally to point D, then finally warm-up isochorically back to the initial point A.
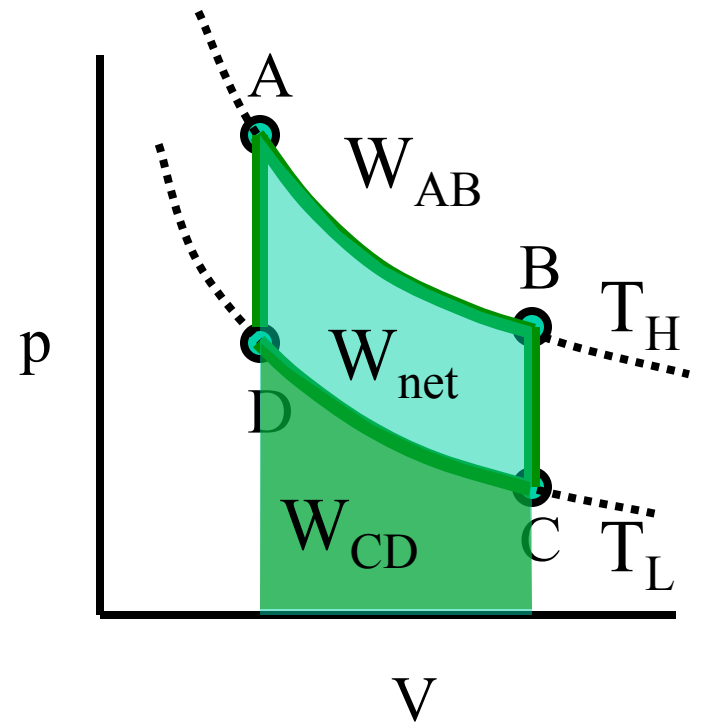

E*. What is the heat entering the gas Q_{DA} in going from D to A?

Monatomic gas

No volume change => work = 0.

$$\Delta E_{int} = 3/2 \, nR \, \Delta T = Q - W$$

$$=> \quad \Delta E_{int} = Q_{DA} - 0 = Q_{DA} = 3/2 \, nR \, (T_H - T_L) \quad > 0$$

PROBLEM 2: (25pts) One mole of an ideal, monatomic gas is the working substance of an ideal heat engine. The system is initially at point A with pressure (p_A), volume (V_A), and temperature $(T_A=T_H)$. It is then allowed to expand isothermally to point B, then cool isochorically to point C, then contract isothermally to point D, then finally warm-up isochorically back to the initial point A.
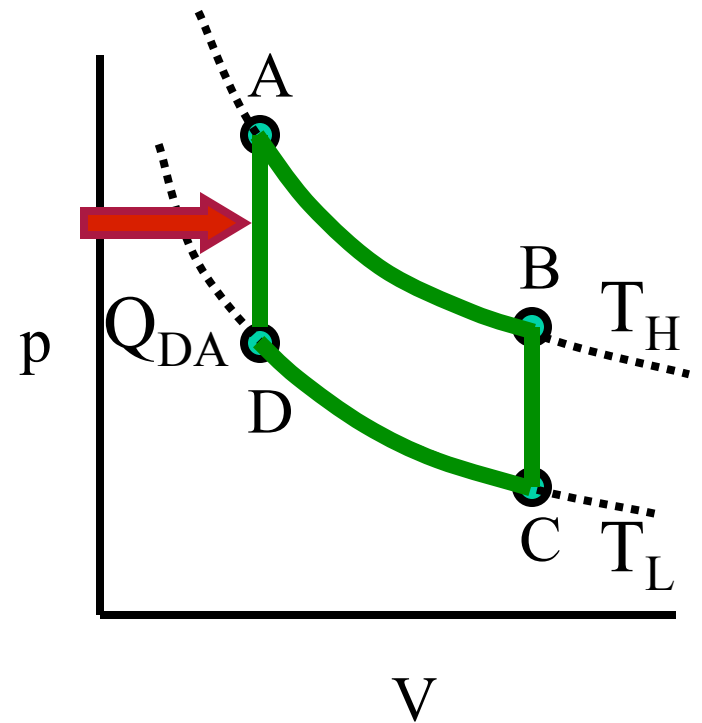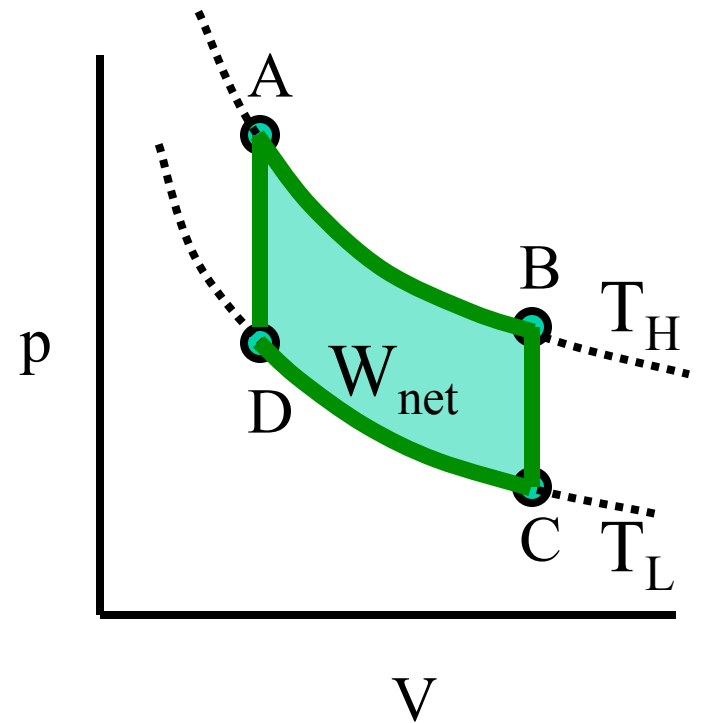

E*. What is the change in entropy of the gas ΔS_{DA} going from D to A?

$$\Delta E_{int} = Q_{DA} \implies dQ_{DA} = 3/2 \, nR \, dT$$

$$\Delta S_{DA} = \int_D^A \frac{dQ}{T} = \int_{T_L}^{T_H} \frac{3/2 \, nR \, dT}{T} = 3/2 \, nR \, \ln(T_H/T_L)$$

$$\boxed{\Delta S_{DA} = \tfrac{3}{2} nR \, \ln(T_H/T_L)} \quad > 0$$

PROBLEM 2: (25pts) One mole of an ideal, monatomic gas is the working substance of an ideal heat engine. The system is initially at point A with pressure (p_A), volume (V_A), and temperature ($T_A = T_H$). It is then allowed to expand isothermally to point B, then cool isochorically to point C, then contract isothermally to point D, then finally warm-up isochorically back to the initial point A.
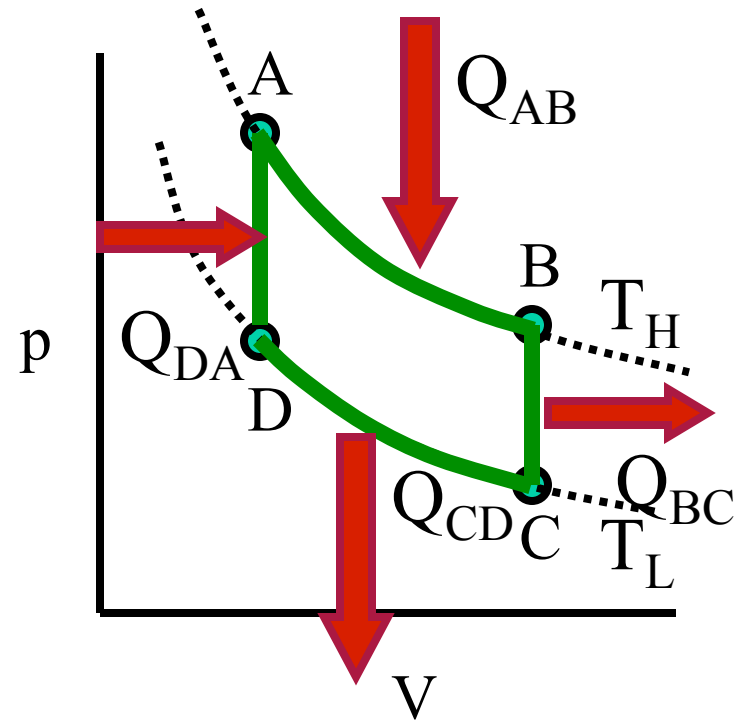

F. What is the net work done in one cycle?

$$W_{net} = W_{AB} \qquad + \qquad W_{BC} \qquad + \qquad W_{CD} \qquad + \qquad W_{DA}$$

$$nRT_H \ln(V_B/V_A) \qquad 0 \qquad -nRT_L \ln(V_B/V_A) \qquad 0$$

$$W_{net} = nR(T_H - T_L)\ln(V_B/V_A)$$

PROBLEM 2: (25pts) One mole of an ideal, monatomic gas is the working substance of an ideal heat engine. The system is initially at point A with pressure (p_A), volume (V_A), and temperature ($T_A = T_H$). It is then allowed to expand isothermally to point B, then cool isochorically to point C, then contract isothermally to point D, then finally warm-up isochorically back to the initial point A.

F. What is the net work done in one cycle?

$$W_{net} = W_{AB} + W_{BC} + W_{CD} + W_{DA}$$

$$nRT_H \ln(V_B/V_A) \quad 0 \quad -nRT_L \ln(V_B/V_A) \quad 0$$

$$\boxed{W_{net} = nR(T_H - T_L)\ln(V_B/V_A)}$$

PROBLEM 2: (25pts) One mole of an ideal, monatomic gas is the working substance of an ideal heat engine. The system is initially at point A with pressure (p_A), volume (V_A), and temperature ($T_A = T_H$). It is then allowed to expand isothermally to point B, then cool isochorically to point C, then contract isothermally to point D, then finally warm-up isochorically back to the initial point A.


G. What is the net heat transferred in one cycle
$$ (i.e., Q_{net} = Q_{AB} + Q_{BC} + Q_{CD} + Q_{DA})? $$

Two different ways to approach this question.

Easy way: $DE_{int} = Q_{net} - W_{net} = 0$ for a cycle

$$ \Rightarrow \ Q_{net} = W_{net} \qquad \boxed{Q_{net} = W_{net} = nR(T_H - T_L)\ln(V_B/V_A)} $$

PROBLEM 2: (25pts) One mole of an ideal, monatomic gas is the working substance of an ideal heat engine. The system is initially at point A with pressure (p_A), volume (V_A), and temperature ($T_A = T_H$). It is then allowed to expand isothermally to point B, then cool isochorically to point C, then contract isothermally to point D, then finally warm-up isochorically back to the initial point A.
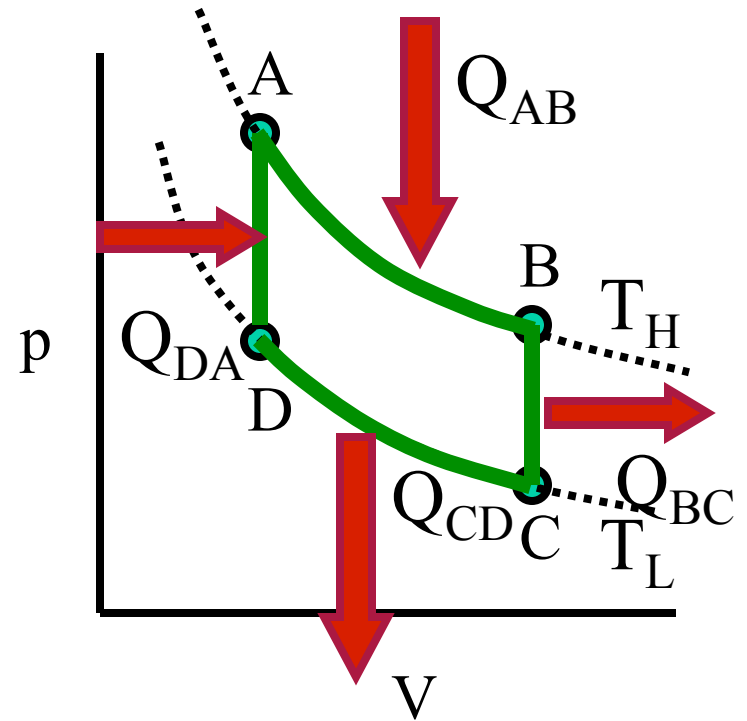
G. What is the net heat transferred in one cycle?

Harder way: $Q_{net} = Q_{AB} + Q_{BC} + Q_{CD} + Q_{DA}$

$nRT_H \ln(V_B/V_A)$ ~~$3/2\, nR\,(T_L - T_H)$~~ $-nRT_L \ln(V_B/V_A)$ ~~$3/2\, nR\,(T_H - T_L)$~~

$$Q_{net} = nR\left(T_H - T_L\right)\ln\left(V_B / V_A\right) = W_{net}$$

PROBLEM 2: (25pts) One mole of an ideal, monatomic gas is the working substance of an ideal heat engine. The system is initially at point A with pressure (p_A), volume (V_A), and temperature ($T_A = T_H$). It is then allowed to expand isothermally to point B, then cool isochorically to point C, then contract isothermally to point D, then finally warm-up isochorically back to the initial point A.
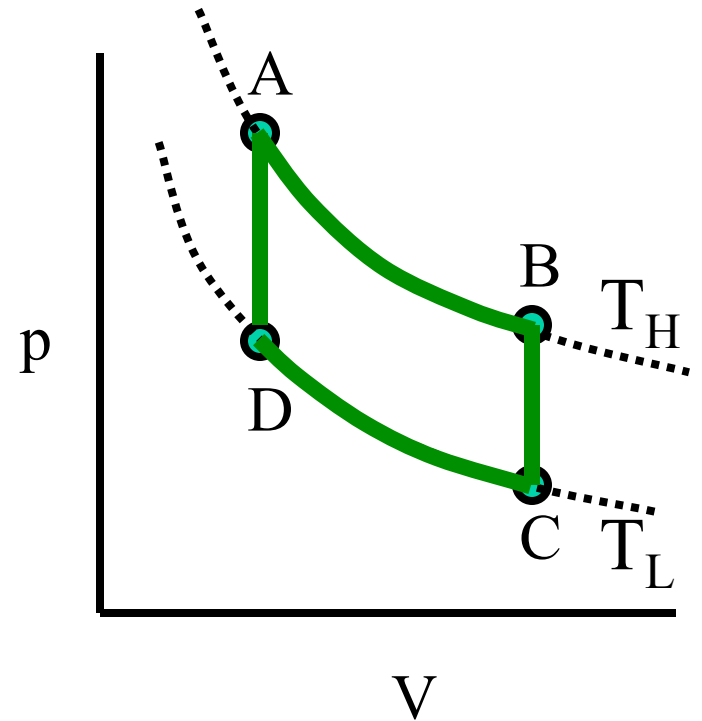
G. What is the net entropy change in one cycle?

Easy way: $\Delta S|_{cycle} = 0$!

PROBLEM 2: (25pts) One mole of an ideal, monatomic gas is the working substance of an ideal heat engine. The system is initially at point A with pressure (p_A), volume (V_A), and temperature ($T_A = T_H$). It is then allowed to expand isothermally to point B, then cool isochorically to point C, then contract isothermally to point D, then finally warm-up isochorically back to the initial point A.
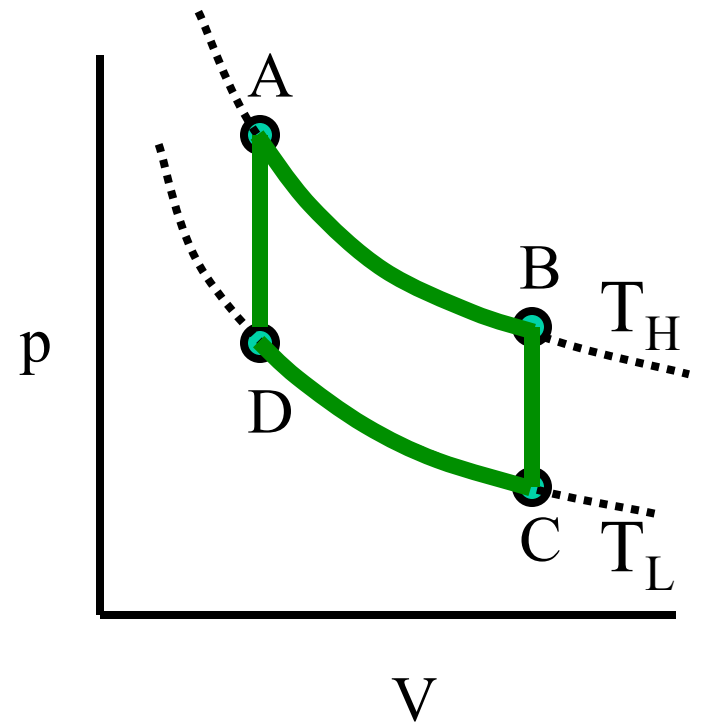
G. What is the net entropy change in one cycle?

Harder way: $\Delta S_{net} = \Delta S_{AB} + \Delta S_{BC} + \Delta S_{CD} + \Delta S_{DA}$

$$nR\ln(V_B/V_A) \quad -\tfrac{3}{2}nR\ln(T_H/T_L) \quad -nR\ln(V_B/V_A) \quad \tfrac{3}{2}nR\ln(T_H/T_L)$$

$$\Delta S_{net} = \Delta S_{cycle} = 0 \quad !$$

$$\Delta S = \int_i^f \frac{dQ}{T}$$

$$\Delta S = \int_i^f \frac{dQ}{T} = \frac{Q_H}{T_H}$$

Q_H

Pressure

Volume
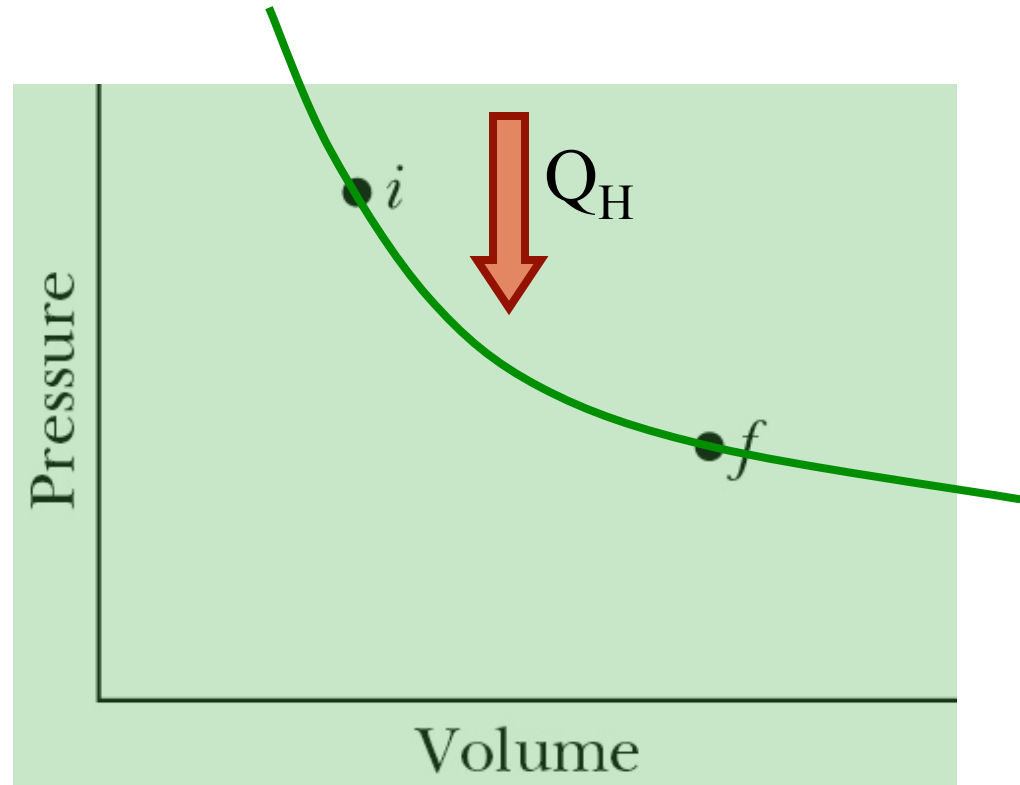
Various methods to take the system from point i to point f

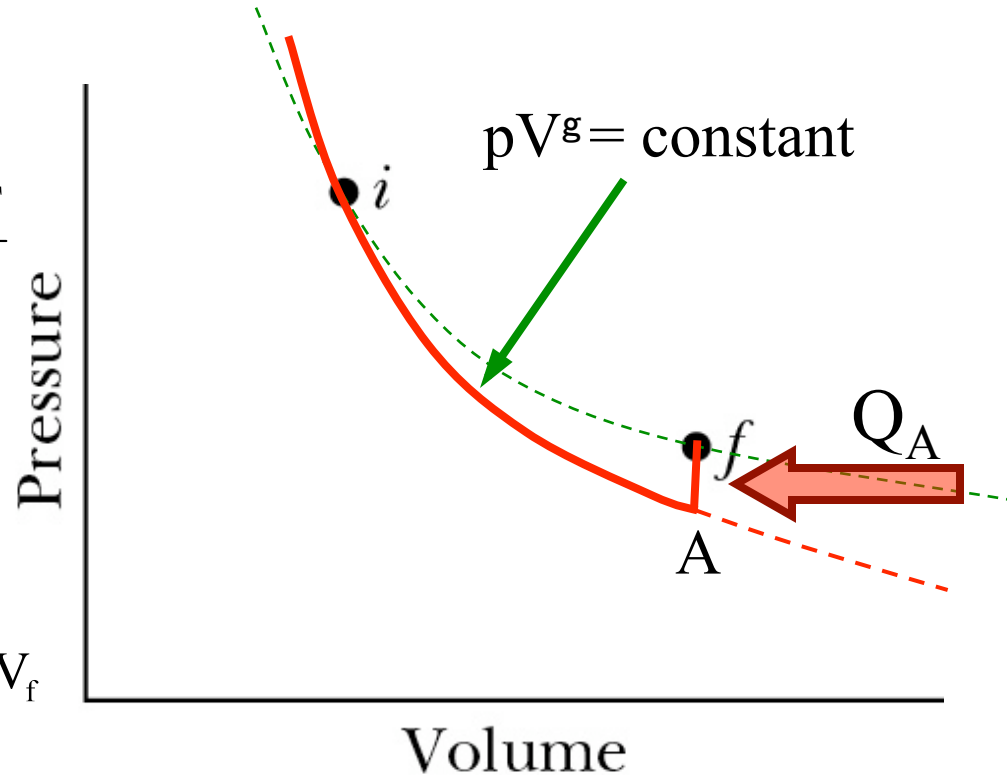——— Isothermal: Heat needs to be absorbed to maintain constant temperature.

$$\Delta S = \int_i^f \frac{dQ}{T}$$

$$\Delta S = \int_i^f \frac{dQ}{T} = \int_i^f \frac{mc_V dT}{T} = mc_V \int_A^f \frac{dT}{T}$$

$$= mc_V \ln \frac{T_f}{T_A} = mc_V \ln \frac{p_f}{p_A}$$

$$Q_A = mc_V \int_A^f mc_V dT$$

$$= mc_V (T_f - T_A) = \frac{mc_V}{nR}(p_f - p_A)V_f$$

$pV^g =$ constant

Q_A

Pressure

Volume

i

f

A

Various methods to take the system from point i to point f

———— Adiabatic: No heat transfer. But the system is at a lower temperature than it needs to be at the volume f. Input heat system isochorically (constant volume)

$$\Delta S = \int_i^f \frac{dQ}{T}$$

$$\Delta S = \int_i^A \frac{dQ}{T} = \int_i^f \frac{mc_V dT}{T} = mc_V \int_i^A \frac{dT}{T}$$

$$= mc_V \ln \frac{T_A}{T_i} = -mc_V \left(\ln \frac{p_i}{p_A} \right)$$

$$\Delta S = \int_A^f \frac{dQ}{T} = \int_A^f \frac{mc_P dT}{T} = mc_P \int_A^f \frac{dT}{T}$$

$$= mc_P \ln \frac{T_f}{T_A} = mc_P \left(\ln \frac{V_f}{V_A} \right)$$
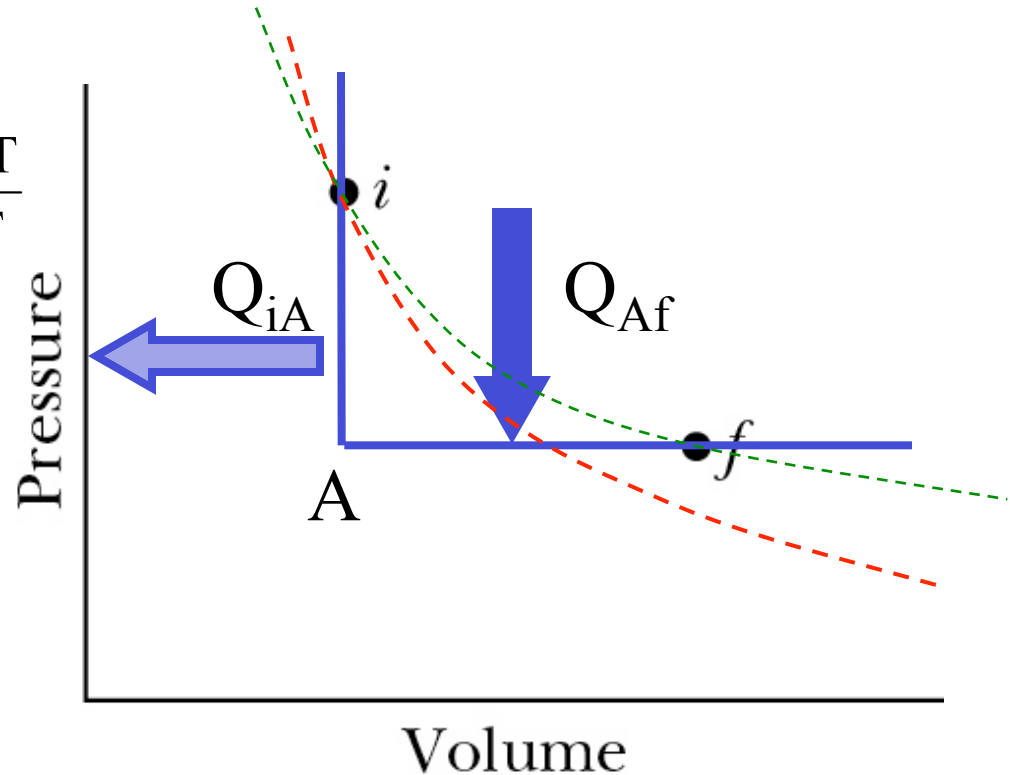
Various methods to take the system from point i to point f

————— Isochorically then isobarically: Heat removed to bring system down to final pressure, then heat added to bring system to final volume.

$$\Delta S = \int_i^f \frac{dQ}{T}$$
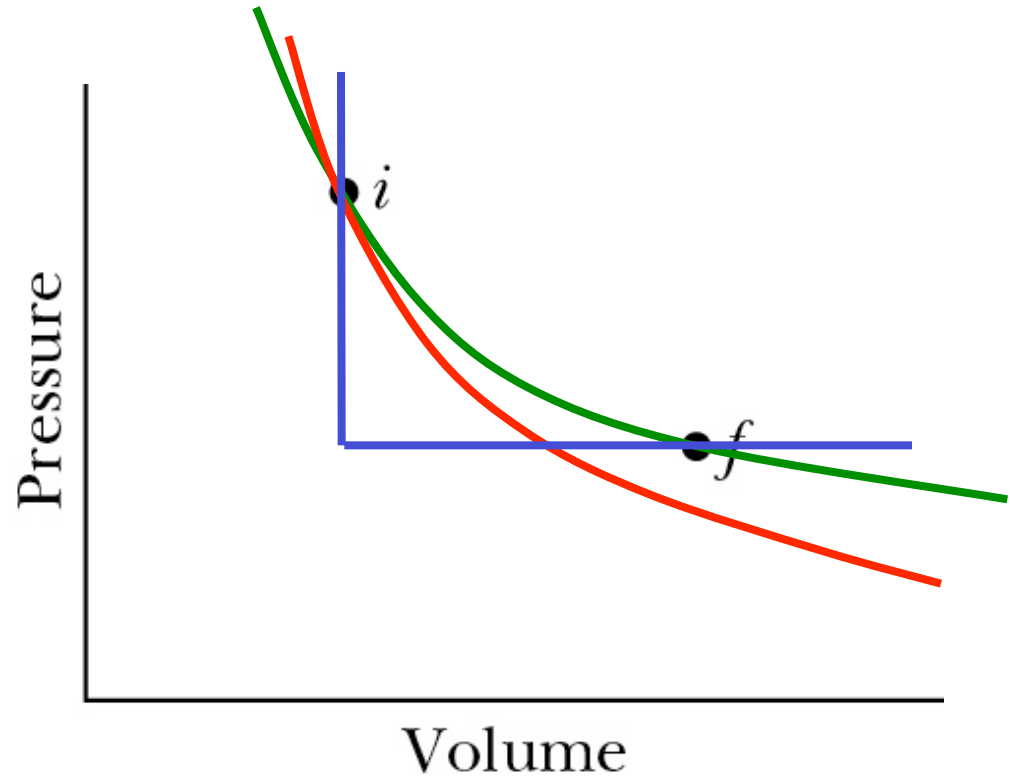
Various methods to take the system from point i to point f

——	Isothermal
——	Adiabatic
——	isochoric-isobaric

Entropy in real world: Engines

Let's explore how entropy affects energy
flow in devices -- (i.e., engines).

A heat engine is a device that:

absorbs heat from a hot reservoir **(1)**

does work on something **(2)**

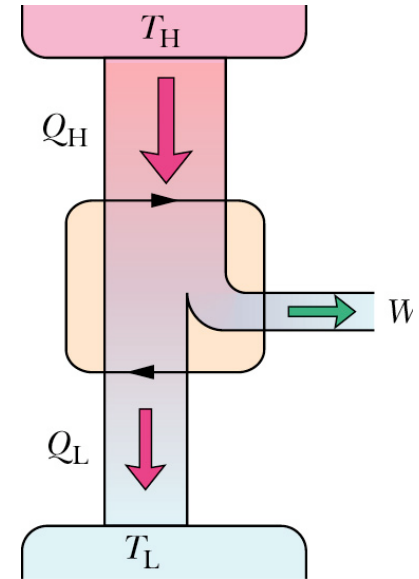then expels heat to a cold reservoir **(3)** to return to the
engine's starting conditions.

This constitutes one cycle (and the process repeats itself).

In an ideal engine, all processes are reversible.
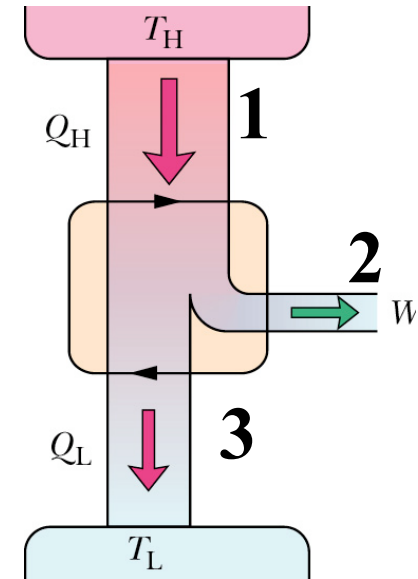
Entropy in real world: Engines

A heat engine is a device that extracts heat from its environment and does useful work.

Consider a p-V diagram with an ideal gas as the working substance for our engine.

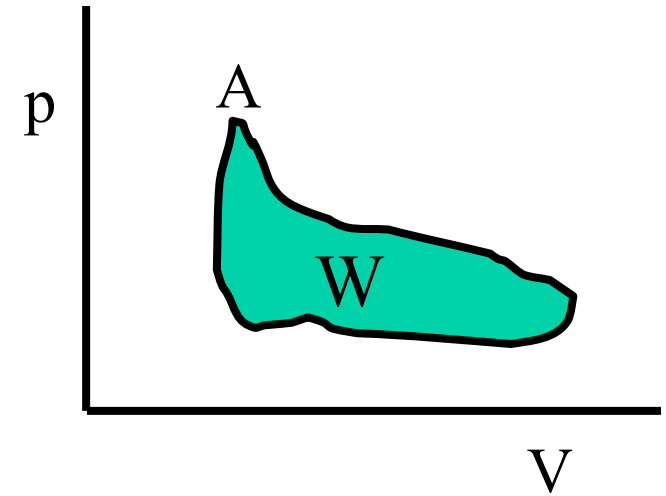The cycle starts at A and must return to A at the end of the cycle.

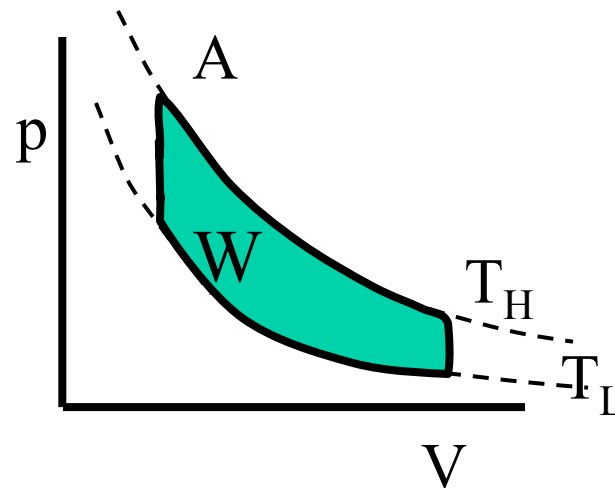The area enclosed by the cycle is the net work the engine does.
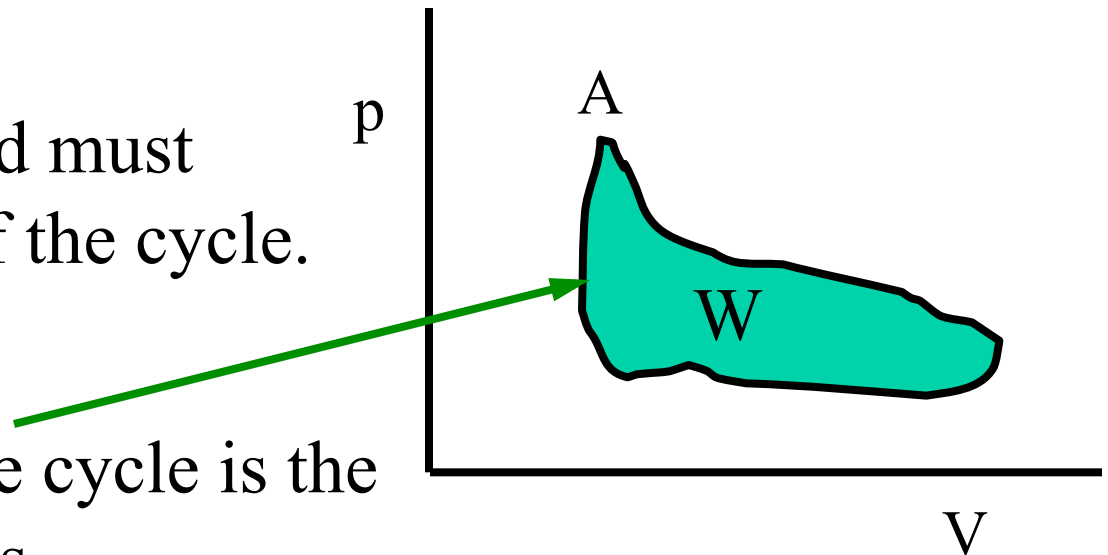
Engines

So..., What cycle will produce the maximum work (W) for the minimum cost (Q_H) and the minimum waste (Q_L)?
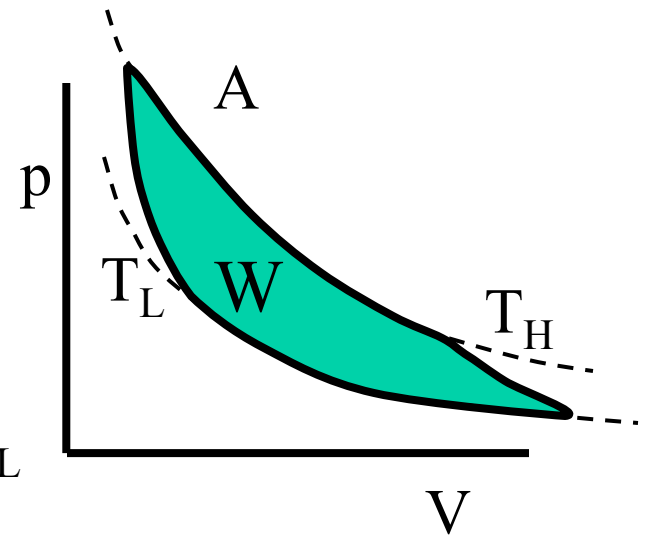

Note that T_H and T_L are fixed by external conditions such as the type of fuel used, surrounding environment, etc.
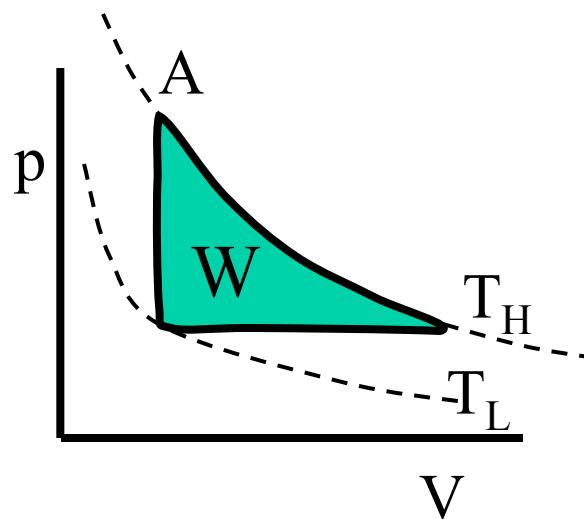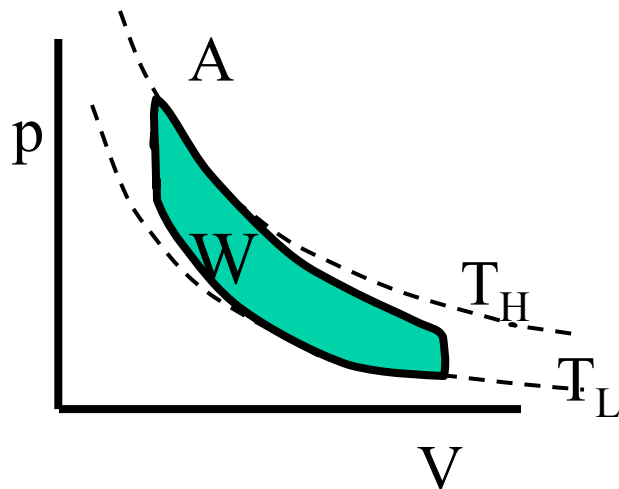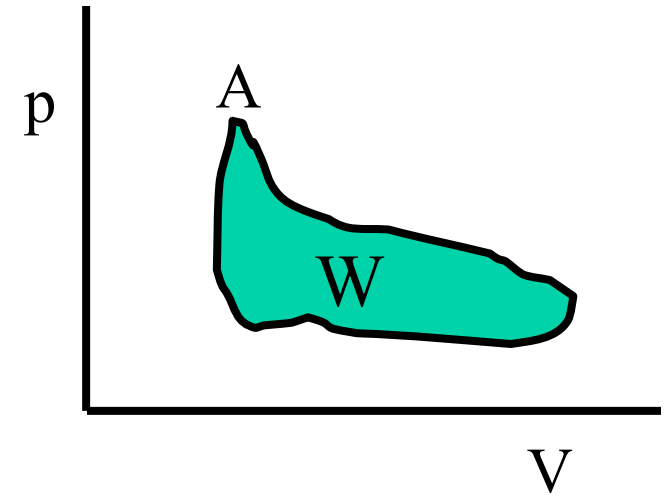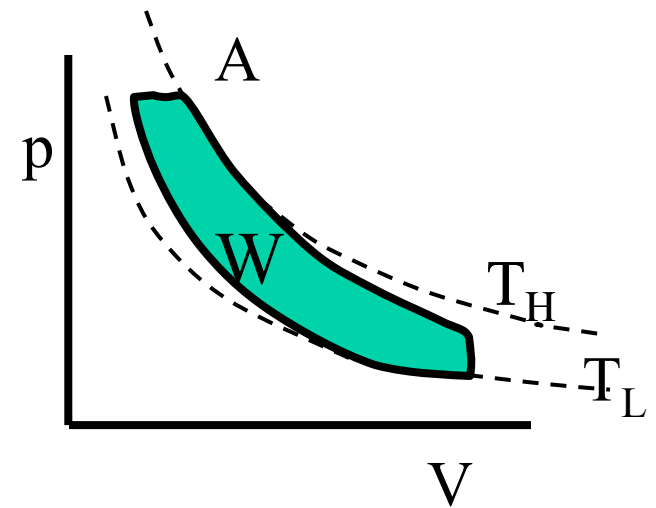

Test Problem

Stirling Cycle

Carnot Cycle

Engines

So..., What cycle will produce the maximum work (W) for the minimum cost (Q_H) and the minimum waste (Q_L)?

Note that T_H and T_L are fixed by external conditions such as the type of fuel used, surrounding environment, etc.

(Internal combustion engine) Otto Cycle   Diesel Cycle

Answer: The Carnot Cycle

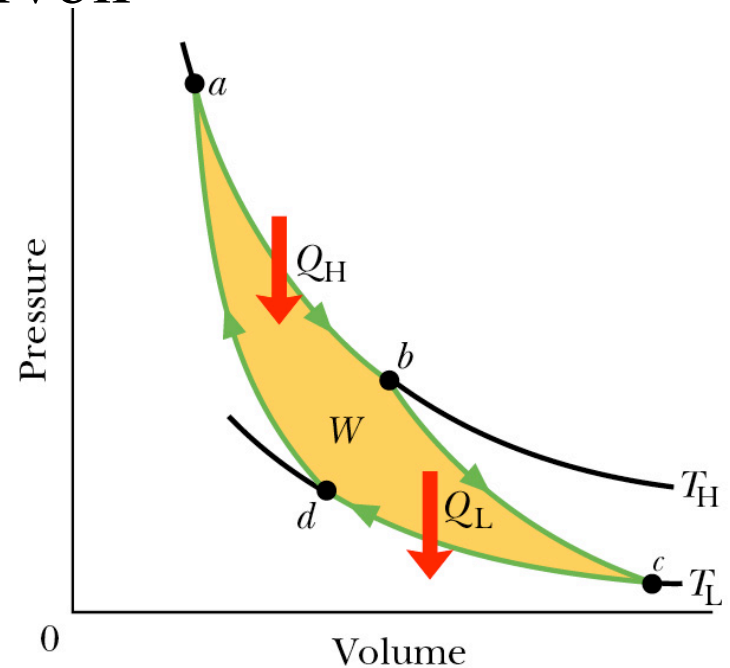**Carnot Engine**: The most efficient heat engine.

The Carnot cycle consists of four processes:

a-b: isothermal expansion, working substance gets heat Q_H from the high-temperature reservoir

b-c: adiabatic expansion. $Q = 0$

c-d: isothermal compression, working substance gives heat Q_L to the low temperature reservoir
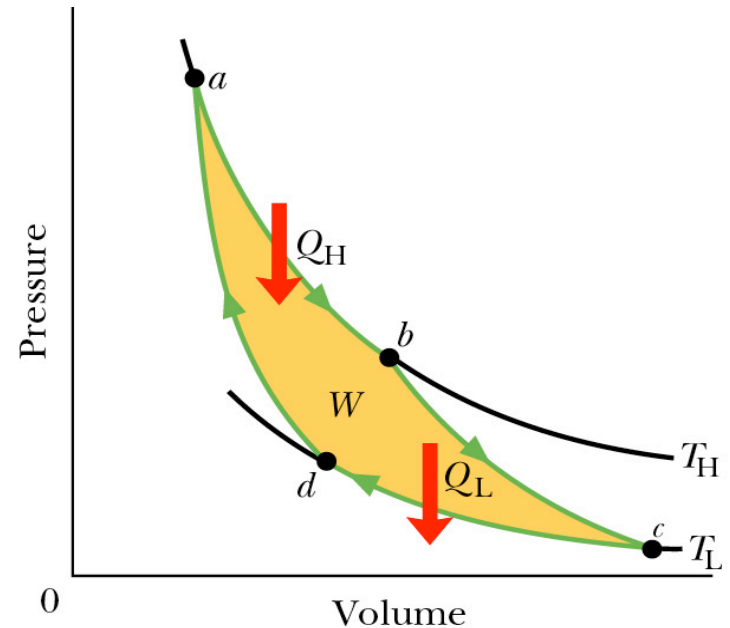
d-a: adiabatic compression. $Q = 0$

The work done by the gas:

a-b-c: positive work

c-d-a: negative work

Net work done in one cycle: area enclosed by cycle *abcda*.

For a complete cycle, $\Delta E_{int} = 0$ (since E_{int} is a state function) that is: $Q - W = 0$, since $Q = |Q_H| - |Q_L|$
Therefore: $W = Q = |Q_H| - |Q_L|$

For a complete cycle, $\Delta S = 0$ (since S is a state function.)

Thermal efficiency of an engine:

$$\varepsilon = \frac{\text{energy we get out}}{\text{energy we pay for}} = \frac{|W|}{|Q_H|} = \frac{|Q_H| - |Q_L|}{|Q_H|} = 1 - \frac{|Q_L|}{|Q_H|}$$
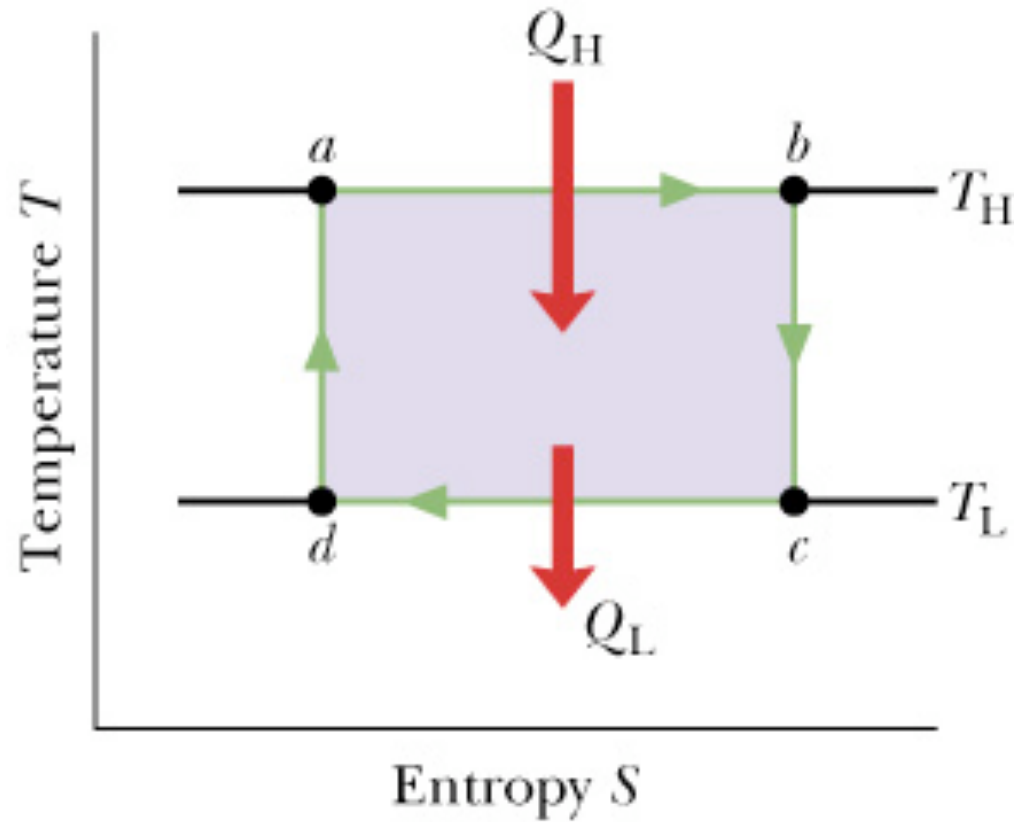
For Carnot engine: since the process is **reversible**, for the closed system (high-T reservoir + work substance + low-T reservoir), DS = 0 (2nd law of thermodynamics)

$$-\frac{|Q_H|}{T_H} + 0 + \frac{|Q_L|}{T_L} = 0 \qquad \frac{|Q_L|}{|Q_H|} = \frac{T_L}{T_H} \qquad \varepsilon = 1 - \frac{T_L}{T_H}$$

For real engine: since the process is **irreversible**, $\Delta S > 0$

$$-\frac{|Q_H|}{T_H} + 0 + \frac{|Q_L|}{T_L} > 0 \qquad \frac{|Q_L|}{|Q_H|} > \frac{T_L}{T_H} \qquad \varepsilon < (1 - \frac{T_L}{T_H})$$
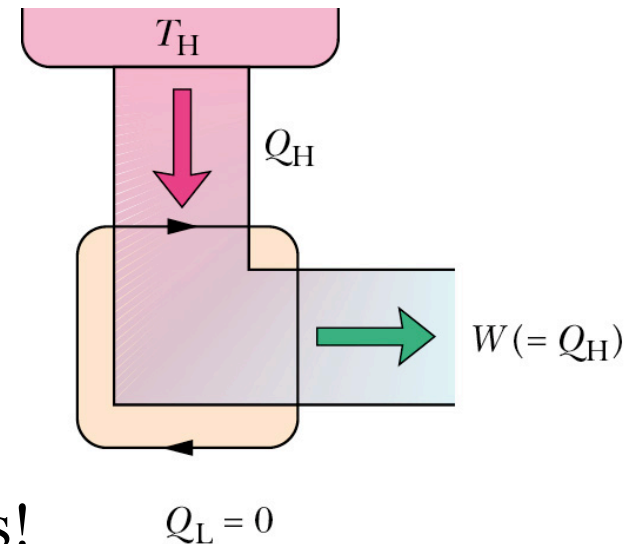
Temperature - Entropy Graph for the Carnot Engine

Is there a **perfect engine**, which converts all Q_H to work so that $Q_L = 0$ and $\varepsilon = 1$, possible?

The entropy change for the closed system:

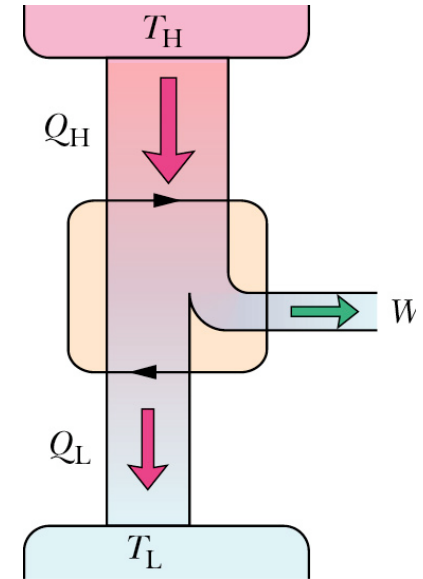$$\Delta S = -\frac{|Q_H|}{T_H} + 0 + 0 = -\frac{|Q_H|}{T_H} < 0$$

This violates the 2nd law of thermodynamics!

$$\varepsilon = 1 - \frac{T_L}{T_H}$$

Also, for $\varepsilon = 1$, we need $T_L = 0$ or T_H to be infinity, either of which is impossible.

Conclusion: Perpetual motion machines are impossible!!

A Carnot engine that operates between the temperatures $T_H = 850K$ and $T_L = 300\ K$, The engine performs 1200 J of work each cycle

(a) what is the efficiency of this engine?

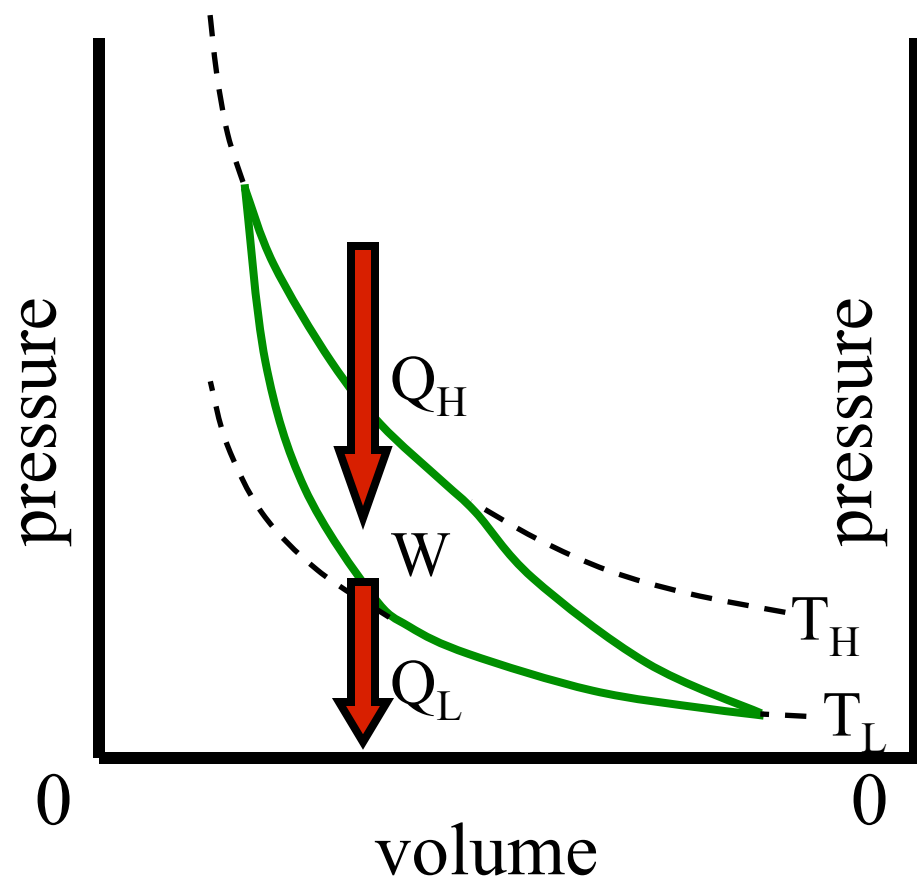$$\varepsilon = 1 - \frac{T_L}{T_H} = 1 - \frac{300}{850} = 0.647$$

(b) How much heat is extracted from the high-T reservoir each cycle?

$$\varepsilon = \frac{W}{Q_H} = 0.647 \Rightarrow Q_H = \frac{W}{\varepsilon} = \frac{1200J}{0.647} = 1854J$$

(c) How much heat is expelled into the low-T reservoir each cycle?

$$Q_L = Q_H - W = 1854J - 1200J = 654J$$

Carnot Engine

Carnot Refrigerator

pressure

volume

pressure

volume

Q_H

W

Q_L

T_H

T_L

Q_H

W

Q_L

T_H

T_L

0

0