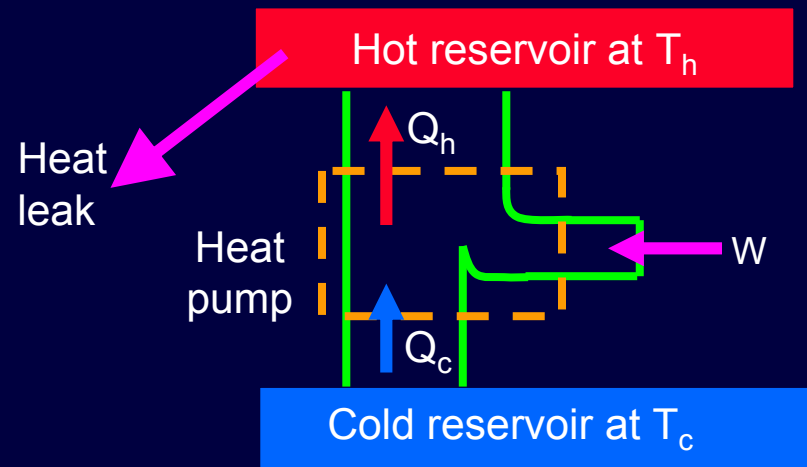
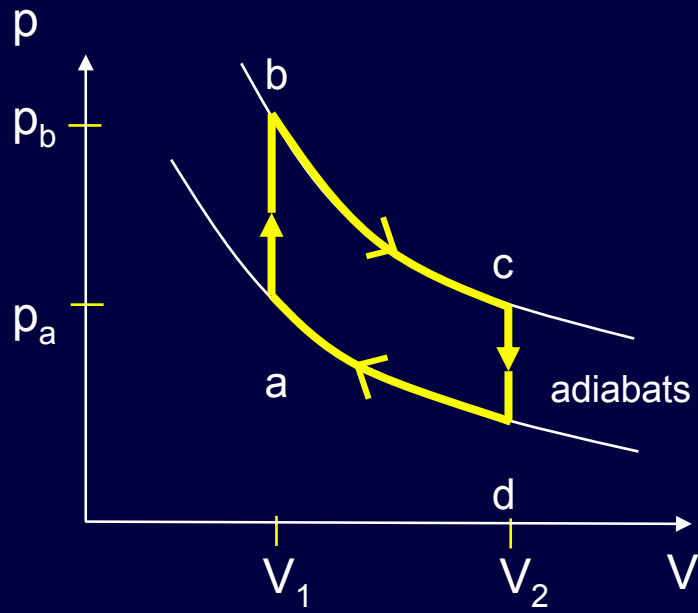


# Lecture 15

## Heat Engines

### Review & Examples



# Irreversible Processes

Entropy-increasing processes are irreversible, because the reverse processes would reduce entropy.

Examples:

- Free-expansion (actually, any particle flow between regions of different density)
- Heat flow between two systems with different temperatures.

Consider the four processes of interest here:

Isothermal: Heat flow but no T difference.

Reversible

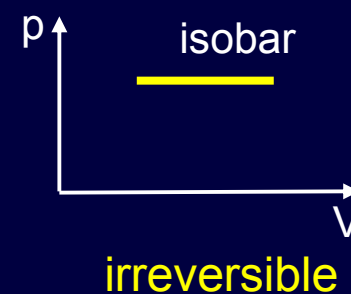
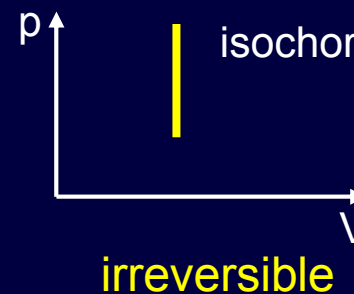
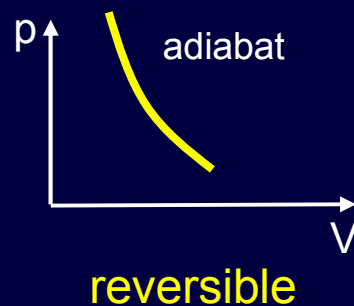
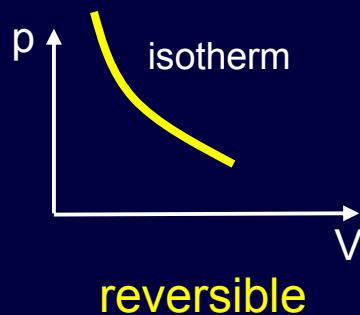
Adiabatic:  $Q = 0$ . No heat flow at all.

Reversible

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

Irreversible

(Assuming that there are only two reservoirs.)



# ACT 1

1) The entropy of a gas increases during a quasi-static isothermal expansion.

What happens to the entropy of the environment?

- 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?

- a)  $\Delta S_{\text{tot}} < 0$       b)  $\Delta S_{\text{tot}} = 0$       c)  $\Delta S_{\text{tot}} > 0$



Remove the barrier

# Solution

1) The entropy of a gas increases during a quasi-static isothermal expansion.

What happens to the entropy of the environment?

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

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

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

Energy (heat) leaves the environment, so its entropy decreases. In fact, since the environment and gas have the same  $T$ , the two entropy changes cancel:  $\Delta S_{\text{tot}} = 0$ . This is a reversible process.

2) Consider instead the 'free' expansion (*i.e.*, not quasi-static) of a gas.

What happens to the total entropy during this process?

a)  $\Delta S_{\text{tot}} < 0$

b)  $\Delta S_{\text{tot}} = 0$

c)  $\Delta S_{\text{tot}} > 0$



Remove the barrier

# Solution

1) The entropy of a gas increases during a quasi-static isothermal expansion.

What happens to the entropy of the environment?

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

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

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

Energy (heat) leaves the environment, so its entropy decreases. In fact, since the environment and gas have the same  $T$ , the two entropy changes cancel:  $\Delta S_{\text{tot}} = 0$ . This is a reversible process.

2) Consider instead the 'free' expansion (*i.e.*, not quasi-static) of a gas.

What happens to the total entropy during this process?

a)  $\Delta S_{\text{tot}} < 0$

b)  $\Delta S_{\text{tot}} = 0$

c)  $\Delta S_{\text{tot}} > 0$

There is no work or heat flow, so  $U_{\text{gas}}$  is constant.  $\Rightarrow T$  is constant. However, because the volume increases, so does the number of available states, and therefore  $S_{\text{gas}}$  increases. Nothing is happening to the environment. Therefore  $\Delta S_{\text{tot}} > 0$ . This is not a reversible process.

# Review

## Entropy in Macroscopic Systems

Traditional thermodynamic entropy:  $S = k \ln \Omega = k\sigma$

We want to calculate  $S$  from macrostate information ( $p, V, T, U, N, \text{etc.}$ )  
Start with the definition of temperature in terms of entropy:

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

The entropy changes when  $T$  changes: (We're keeping  $V$  and  $N$  fixed.)

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

If  $C_V$  is constant:  $= C_V \int_{T_1}^{T_2} \frac{dT}{T} = C_V \ln \left( \frac{T_2}{T_1} \right)$

# ACT 2

Two blocks, each with heat capacity\*  $C = 1 \text{ J/K}$  are initially at different temperatures,  $T_1 = 250 \text{ K}$ ,  $T_2 = 350 \text{ K}$ . They are then placed into contact, and eventually reach a final temperature of  $300 \text{ K}$ . (Why?) What can you say about the total change in entropy  $\Delta S_{\text{tot}}$ ?

a)  $\Delta S_{\text{tot}} < 0$

b)  $\Delta S_{\text{tot}} = 0$

c)  $\Delta S_{\text{tot}} > 0$

$$T_1$$

$$T_2$$

$$T_1 = 250 \text{ K}$$

$$T_2 = 350 \text{ K}$$

$$T_f \quad T_f$$

$$T_f = 300 \text{ K}$$

Two masses each  
with heat capacity  
 $C = 1 \text{ J/K}^*$

\*For a solid,  $C = C_V = C_p$ , to good approximation, since  $\Delta V \approx 0$ .

# Solution

Two blocks, each with heat capacity\*  $C = 1 \text{ J/K}$  are initially at different temperatures,  $T_1 = 250 \text{ K}$ ,  $T_2 = 350 \text{ K}$ . They are then placed into contact, and eventually reach a final temperature of  $300 \text{ K}$ . (Why?) What can you say about the total change in entropy  $\Delta S_{\text{tot}}$ ?

$$T_1$$

$$T_2$$

$$T_1 = 250 \text{ K}$$

$$T_2 = 350 \text{ K}$$

$$T_f \quad T_f$$

$$T_f = 300 \text{ K}$$

Two masses each with heat capacity  $C = 1 \text{ J/K}^*$

a)  $\Delta S_{\text{tot}} < 0$

b)  $\Delta S_{\text{tot}} = 0$

c)  $\Delta S_{\text{tot}} > 0$

This is an irreversible process, so there must be a net increase in entropy. Let's calculate  $\Delta S$ :

$$\Delta S_{\text{tot}} = C \ln \left( \frac{T_f}{T_1} \right) + C \ln \left( \frac{T_f}{T_2} \right)$$

$$= C \ln \left( \frac{300}{250} \right) + C \ln \left( \frac{300}{350} \right)$$

$$= C \ln \left( \frac{300^2}{250 \times 350} \right) = (0.028)C = 0.028 \text{ J/K}$$

The positive term is slightly bigger than the negative term.

\*For a solid,  $C = C_V = C_p$ , to good approximation, because  $\Delta V \approx 0$ .



# Example Process

To analyze heat engines, we need to be able to calculate  $\Delta U$ ,  $\Delta T$ ,  $W$ ,  $Q$ , *etc.* for the processes that they use.

How much heat is absorbed by 3 moles of helium when it expands from  $V_i = 10$  liters to  $V_f = 20$  liters and the temperature is kept at a constant 350 K?

What are the initial and final pressures?

# Solution

To analyze heat engines, we need to be able to calculate  $\Delta U$ ,  $\Delta T$ ,  $W$ ,  $Q$ , *etc.* for the processes that they use.

How much heat is absorbed by 3 moles of helium when it expands from  $V_i = 10$  liters to  $V_f = 20$  liters and the temperature is kept at a constant 350 K?

What are the initial and final pressures?

$$Q = W_{\text{by}}$$

The 1<sup>st</sup> law. For an ideal gas,  $\Delta T = 0 \rightarrow \Delta U = 0$ .  
Positive  $Q$  means heat flows into the gas.

$$W_{\text{by}} = nRT \ln(V_f/V_i) = 6048 \text{ J}$$

An expanding gas does work.

$$p_i = nRT/V_i = 8.72 \times 10^5 \text{ Pa}$$

Use the ideal gas law,  $pV = nRT$

$$p_f = p_i/2 = 4.36 \times 10^5 \text{ Pa}$$

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 (a “heat reservoir”) having that temperature. The reservoir supplies heat to the gas (or absorbs heat, if necessary) in order to keep the gas temperature constant.

Very often, we will not show the reservoir in the diagram. However, whenever we talk about a system being kept at a specific temperature, a reservoir is implied.

# Example Process (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  $V_i = 1$  liter,  $T_i = 300$  K. What are the final temperature and pressure?

# Solution

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  $V_i = 1$  liter,  $T_i = 300$  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  $p$  and  $V$  for adiabatic process in  $\alpha$ -ideal gas

$\gamma$  is the ratio of  $C_p/C_v$  for our diatomic gas ( $=(\alpha+1)/\alpha$ ).

Solve for  $p_f$ .

We need to express it in terms of things we know.

Use the ideal gas law to calculate the final temperature.

Alternative: Use the equation relating  $T$  and  $V$  for an adiabatic process to get the final temperature.  $\alpha = 5/2$

# Helpful Hints in Dealing with Engines and Fridges

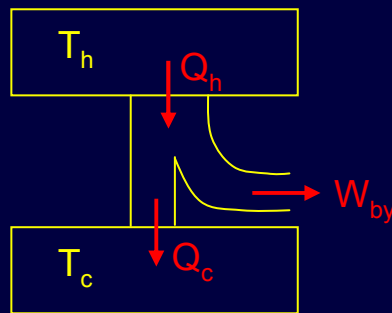
Sketch the process (see figures below).

Define  $Q_h$  and  $Q_c$  and  $W_{by}$  (or  $W_{on}$ ) as positive and show directions of flow.

Determine which  $Q$  is given.

Write the First Law of Thermodynamics (FLT).

We considered three configurations of Carnot cycles:



Engine:

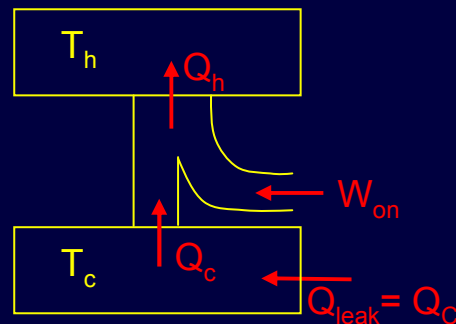
We pay for  $Q_h$ ,

we want  $W_{by}$ .

$$W_{by} = Q_h - Q_c = \varepsilon Q_h$$

$$\text{Carnot: } \varepsilon = 1 - T_c/T_h$$

This has large  $\varepsilon$   
when  $T_h - T_c$  is large.



Refrigerator:

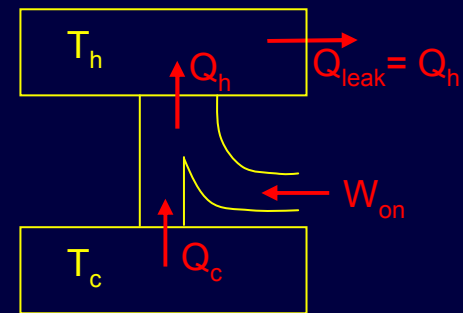
We pay for  $W_{on}$ ,

we want  $Q_c$ .

$$Q_c = Q_h - W_{on} = KW_{on}$$

$$\text{Carnot: } K = T_c/(T_h - T_c)$$

These both have large  $K$  when  $T_h - T_c$  is small.



Heat pump:

We pay for  $W_{on}$ ,

we want  $Q_h$ .

$$Q_h = Q_c + W_{on} = KW_{on}$$

$$\text{Carnot: } K = T_h/(T_h - T_c)$$

# ACT 3: Entropy Change in Heat Pump

Consider a Carnot heat pump.

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

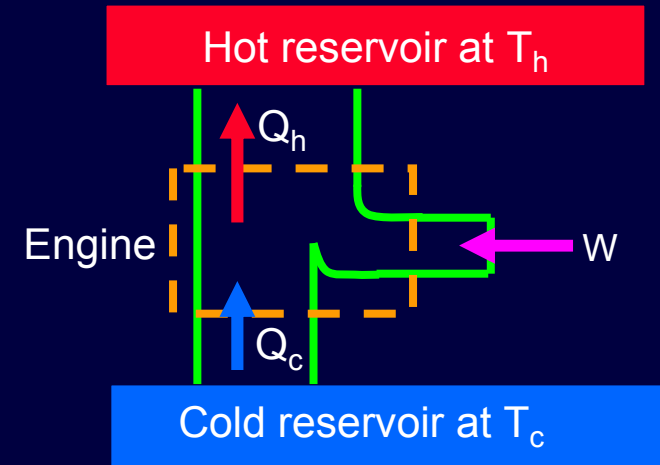
- a)  $\Delta S_h < 0$       b)  $\Delta S_h = 0$       c)  $\Delta S_h > 0$

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)  $|\Delta S_c| > |\Delta S_h|$



# Solution

Consider a Carnot heat pump.

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)  $\Delta S_h > 0$

Energy (heat) is entering the hot reservoir, so the number of available microstates is increasing.

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

a)  $\Delta S_c < 0$

b)  $\Delta S_c = 0$

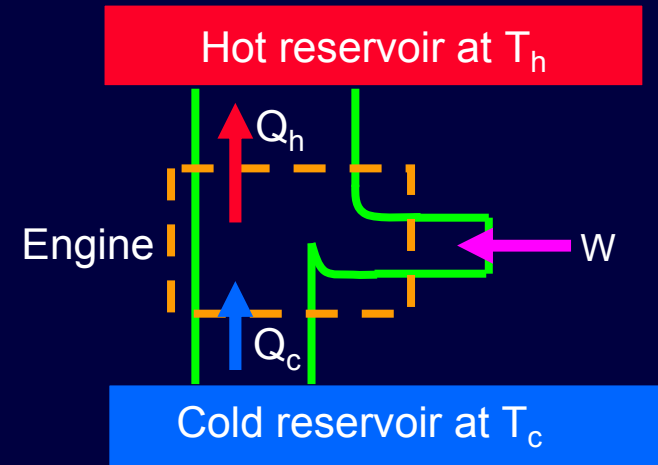
c)  $\Delta S_c > 0$

3) Compare the magnitudes of the two changes.

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

b)  $|\Delta S_c| = |\Delta S_h|$

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



# Solution

Consider a Carnot heat pump.

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)  $\Delta S_h > 0$

Energy (heat) is entering the hot reservoir, so the number of available microstates is increasing.

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

a)  $\Delta S_c < 0$

b)  $\Delta S_c = 0$

c)  $\Delta S_c > 0$

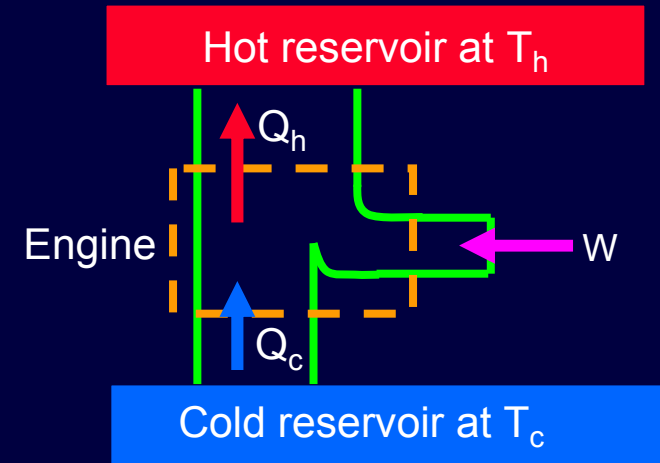
Energy (heat) is leaving the cold reservoir.

3) Compare the magnitudes of the two changes.

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

b)  $|\Delta S_c| = |\Delta S_h|$

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





# Solution

Consider a Carnot heat pump.

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)  $\Delta S_h > 0$

Energy (heat) is entering the hot reservoir, so the number of available microstates is increasing.

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

a)  $\Delta S_c < 0$

b)  $\Delta S_c = 0$

c)  $\Delta S_c > 0$

Energy (heat) is leaving the cold reservoir.

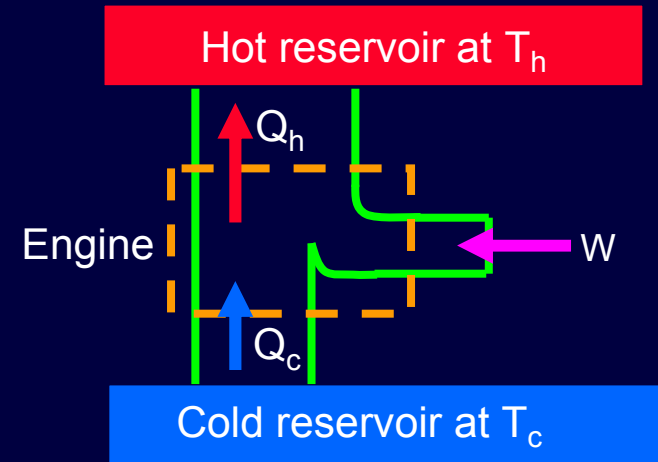
3) Compare the magnitudes of the two changes.

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

b)  $|\Delta S_c| = |\Delta S_h|$

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

It's a reversible cycle, so  $\Delta S_{\text{tot}} = 0$ . Therefore, the two entropy changes must cancel. Remember that the entropy of the "engine" itself does not change.

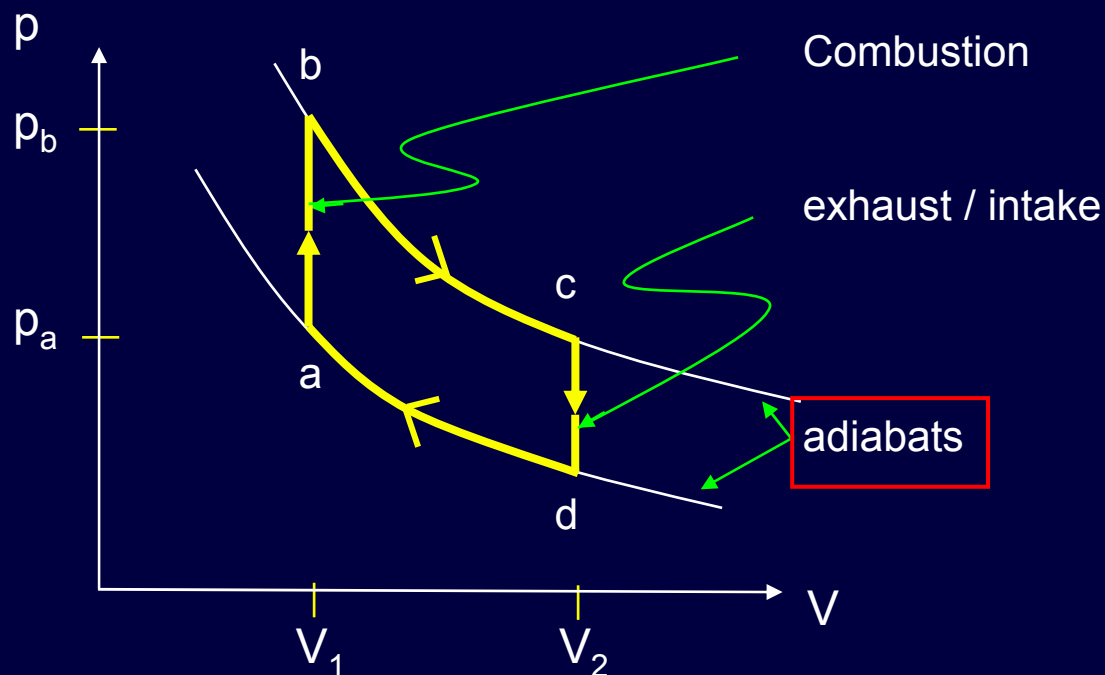


Note: We've neglected the heat leak OUT of the hot reservoir. In fact, this must equal  $Q_h$  (why?). If that heat leaks directly into the cold reservoir, this will be irreversible...

# Example: Gasoline Engine

It's not really a heat engine because the input energy is via fuel injected directly into the engine, not via heat flow. There is no obvious hot reservoir. However, one can still calculate work and energy input for particular gas types.

We can treat the gasoline engine as an Otto cycle:



$b \rightarrow c$  and  $d \rightarrow a$  are nearly adiabatic processes, because the pistons move too quickly for much heat to flow.

# Solution

Calculate the efficiency:

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

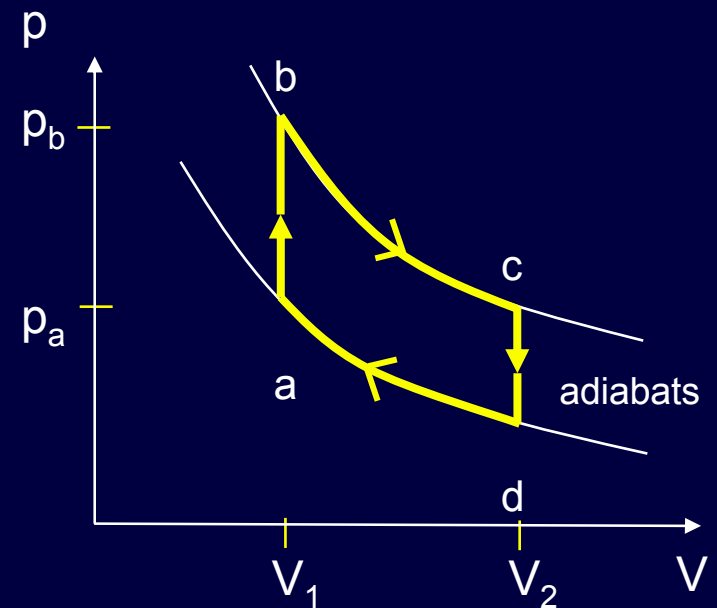
$$W_{by} = W_{b \rightarrow c} - W_{d \rightarrow a}$$

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

$$W_{d \rightarrow a} = U_d - U_a = C_v(T_d - T_a) \quad \text{because } Q_{d \rightarrow a} = 0$$

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

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



# Solution

Write it in terms of volume instead of temperature.  
We know the volume of the cylinders.

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

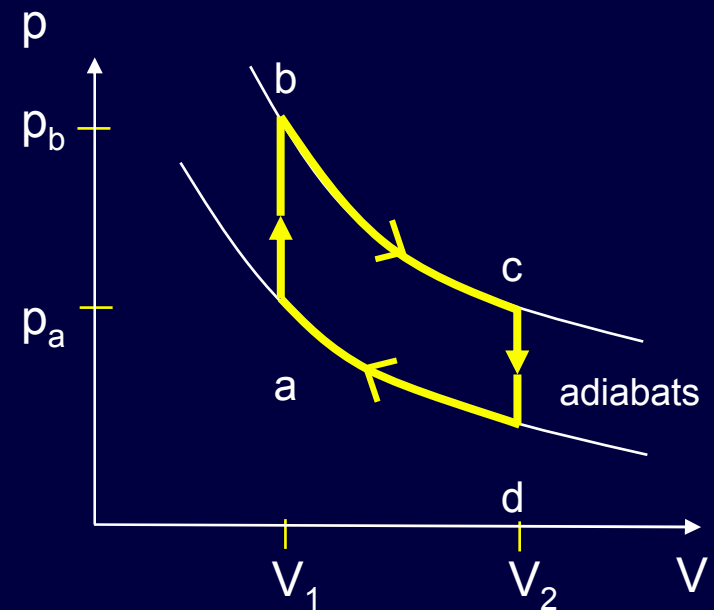
$$T_c^\alpha V_2 = T_b^\alpha V_1 \Rightarrow T_c = T_b (V_1/V_2)^{1/\alpha}$$

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

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

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

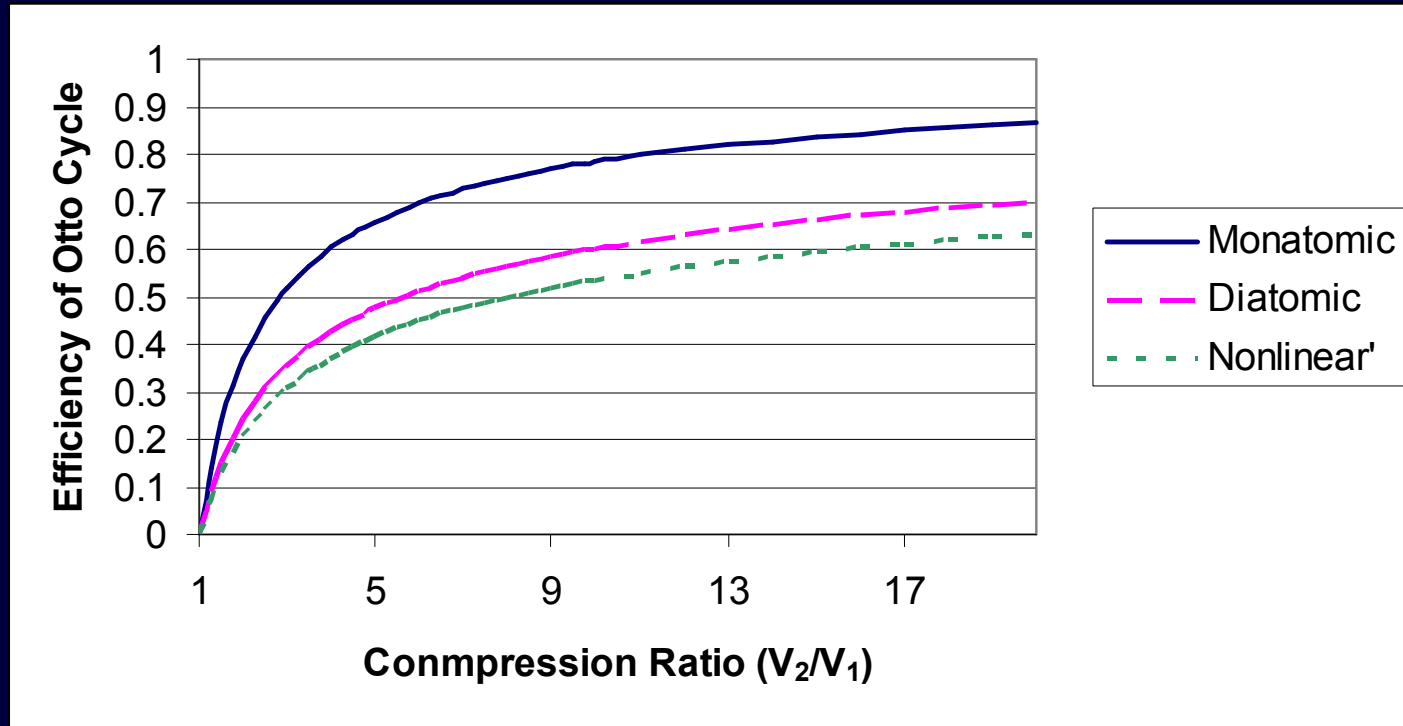
$$\varepsilon = 1 - \left(\frac{V_2}{V_1}\right)^{1-\gamma}$$



Compression ratio  $\equiv V_2/V_1 \approx 10$   
 $\gamma = 1.4$  (diatomic gas)  $\rightarrow \varepsilon = 60\%$

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

# Solution



Why not simply use a higher compression ratio?

- If  $V_2$  big, we need a huge, heavy engine (OK for fixed installations).
- If  $V_1$  small, the temperature gets too high, causing premature ignition. High compression engines need high octane gas, which has a higher combustion temperature.

# Free Energy Example

Suppose we have a liter of water at  $T = 100^\circ \text{C}$ .

What is its free energy, if the environment is  $T = 20^\circ \text{C}$ ?

Verify the result by calculating the amount of work we could obtain.

Remember that  $c_{\text{H}_2\text{O}} = 4186 \text{ J/kg}\cdot\text{K}$ .

# Solution

Suppose we have a liter of water at  $T = 100^\circ \text{C}$ .

What is its free energy, if the environment is  $T = 20^\circ \text{C}$ ?

Verify the result by calculating the amount of work we could obtain.

Remember that  $c_{\text{H}_2\text{O}} = 4186 \text{ J/kg}\cdot\text{K}$ .

$\Delta F = \Delta U - T\Delta S$ , where  $T$  is the temperature of the environment.

$$\Delta U = mc\Delta T = 1 \text{ kg} * 4186 \text{ J/kg}\cdot\text{K} * 80 \text{ K} = 3.349 \times 10^5 \text{ J.}$$

$$\Delta S = mc \ln(T_{\text{H}_2\text{O}}/T_{\text{env}}) = 1011 \text{ J/K}$$

$$\Delta F = 3.87 \times 10^4 \text{ J}$$

Remember to measure temperature in Kelvin.

Otherwise, you'll get the entropy wrong.

# Solution

Suppose we have a liter of water at  $T = 100^\circ \text{C}$ .

What is its free energy, if the environment is  $T = 20^\circ \text{C}$ ?

Verify the result by calculating the amount of work we could obtain.

Remember that  $c_{\text{H}_2\text{O}} = 4186 \text{ J/kg}\cdot\text{K}$ .

If we run a Carnot engine, the efficiency at a given water temperature is:

$\varepsilon = 1 - T_{\text{cold}}/T_{\text{hot}}$ . So, for each small decrease in water temperature, we get this much work out of the engine:

$$dW = \varepsilon Q = -\varepsilon mc dT$$

Thus, the total work obtained as  $T$  drops from  $100^\circ \text{C}$  to  $20^\circ \text{C}$  is:

$$\begin{aligned} W &= -mc \int_{373}^{293} \left(1 - \frac{293}{T}\right) dT \\ &= (4186 \text{ J/K}) \left[ T - (293 \text{ K}) \ln\left(\frac{373}{293}\right) \right]_{293}^{373} \\ &= 3.87 \times 10^4 \text{ J} \end{aligned}$$