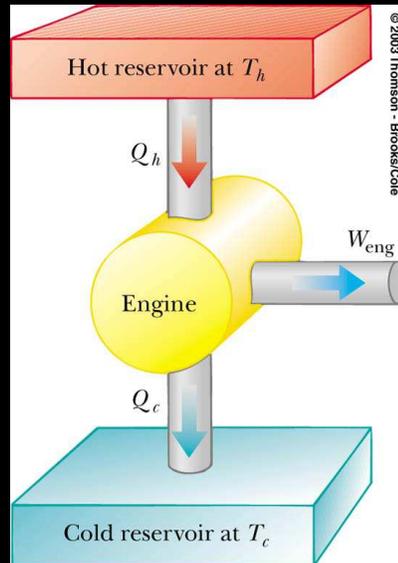


## The laws of Thermodynamics



## Work in thermodynamic processes

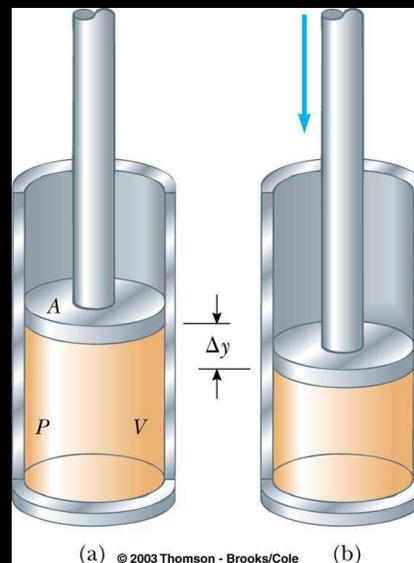
The work done on a gas in a cylinder is directly proportional to the force and the displacement.

$$W = -F\Delta y = -PA\Delta y$$

It can be also expressed in terms of the pressure exerted by the piston and the variation in volume.

$$W = -P\Delta V$$

Compression: work is positive  
Expansion: work is negative

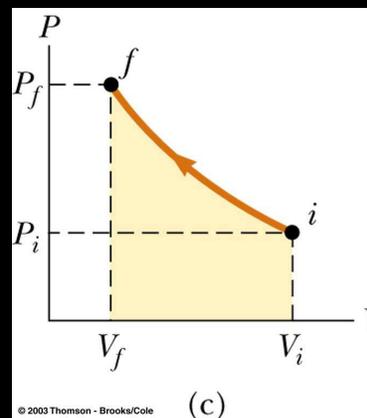


## Work: questions

A monoatomic gas is expanded from an initial state with volume  $V=1$  L to a final state  $4V$ . This process happens at constant pressure  $P=1$  atm. Next, the pressure on the gas is increased at constant volume  $4V$  to 2 atm.

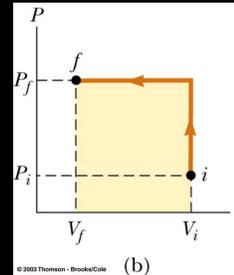
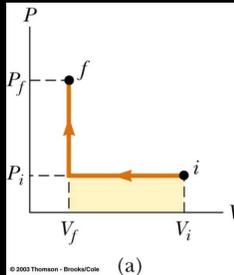
- 1) The work done during the first process is:
  - a) positive, b) negative c) zero
- 2) The work done during the second process is:
  - a) positive, b) negative c) zero
- 3) What is the net work and sketch the processes in a graph of  $P$  versus  $V$ .

## PV diagrams



The work done on a gas when taking it from an initial thermodynamic state (I) to a final thermodynamic state (f) can be determined by the area below the PV diagram.

## PV diagrams

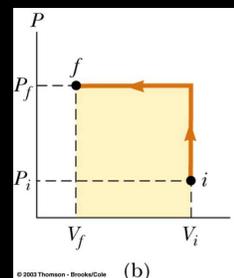
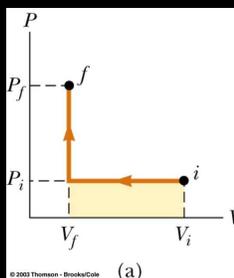


**Isobaric process:** constant pressure

**Isovolumetric process:** constant volume

The work depends not only on the initial and final state but also on the path taken.

## PV diagrams: question time



In which case if there more work done on the system:

- A
- B
- Both the same

## First law of thermodynamics

The change in internal energy of the system is the sum of the heat transferred to the system and the work done on the system

$$\Delta U \equiv U_f - U_i = Q + W$$

## First law of Thermodynamics

**Isolated systems:**  $W=0$  and  $Q=0$   $U_f = U_i$

**Cyclic processes:** if the process ends up in the same thermodynamics state as it started there will be no change in its internal energy

$$U_f = U_i \rightarrow W = -Q$$

## First law of Thermodynamics

**Isothermal processes:** if the temperature is constant over the process

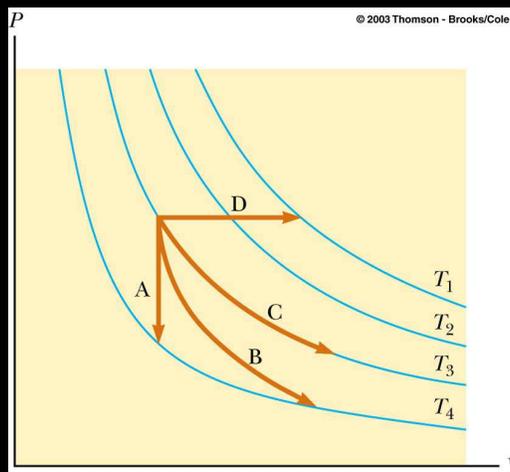
$$U = \frac{3}{2}nRT \mapsto U_f = U_i \rightarrow W = -Q$$

$$W_{env} = nRT \ln \frac{V_f}{V_i}$$

**Adiabatic processes (Q=0):** if the energy transferred by heat in a process is zero then

$$\Delta U = W$$

## First law of thermodynamics: question

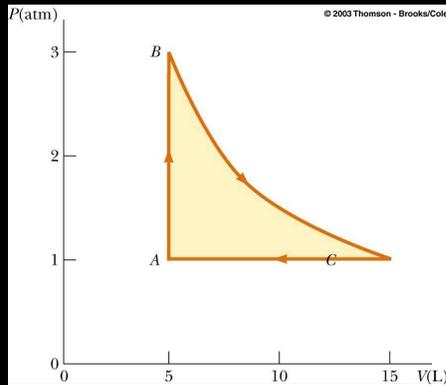


Which of the following processes correspond to

1. Isobaric
2. Isothermal
3. Isovolumetric
4. Adiabatic

## First law of thermodynamics: example

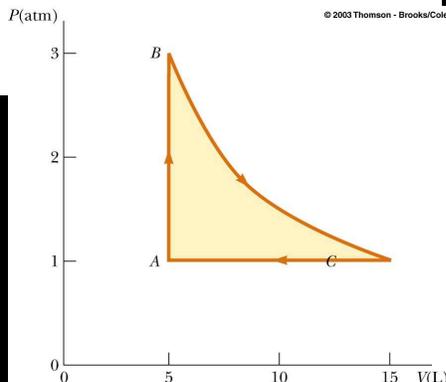
An ideal mono-atomic gas is confined in a cylinder by a movable piston. The gas starts at  $P=1.00\text{atm}$ ,  $V=5.00\text{L}$  and  $T=300\text{K}$ . An isovolumetric process raises the pressure to 3 atm. Then an isothermal expansion brings the system back to 1atm. Finally an isobaric compression at 1atm completes the cycle and return the gas to its original state.  
( $R=8.31\text{ J/mol/K}=0.0821\text{ atm L/mol/K}$ )



- 1) Find the number of moles, the temperature B, and the volume of the gas at C.

## First law of Thermodynamics: example

- 2) Find the internal energy of the gas (in kJ), at A, B, and C. List  $P, V, T, U$  for the points A, B and C.
- 3) Consider the process A to B, B to C and C to A. For each case determine the sign of  $W$  and  $Q$ .
- 4) Calculate  $Q, W$  and  $\Delta U$  for each transition
- 5) Tabulate  $W, Q$  and  $\Delta U$  for each transition and calculate the net effect of each.

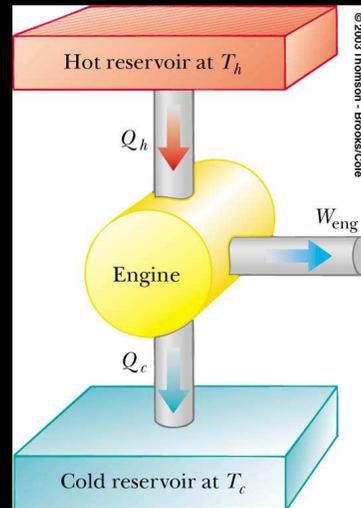


## Heat engines

**The heat engine** is a device that converts internal energy into other useful forms of energy (electrical, mechanical, etc)

In general, it carries a working substance (ex: water) through cycles:

- 1) Energy is transferred from a hot reservoir
- 2) Work is done by the engine
- 3) Energy is expelled into a cold reservoir



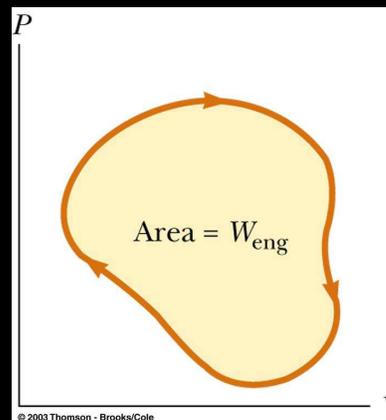
## Heat engines

Because the substance goes through a cycle its initial internal energy is the same as the final:

$$W_{engine} = -Q_{net}$$

$$W_{engine} = |Q_{hot}| - |Q_{cold}|$$

The work done by an engine for a cyclic process is the area enclosed in the curve of a PV diagram



## Thermal efficiency of Heat engines

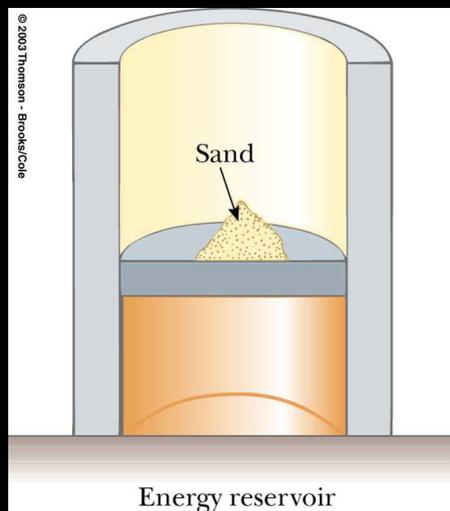
**Thermal efficiency** of the heat engine is the ratio of the work done by the engine to the energy absorbed from the hot reservoir in a cycle

$$\varepsilon = \frac{W_{eng}}{|Q_{hot}|}$$

$$\varepsilon = \frac{|Q_{hot}| - |Q_{cold}|}{|Q_{hot}|} = 1 - \frac{|Q_{cold}|}{|Q_{hot}|}$$

**Second law of thermodynamics: It is impossible to construct a heat engine with 100% efficiency!**

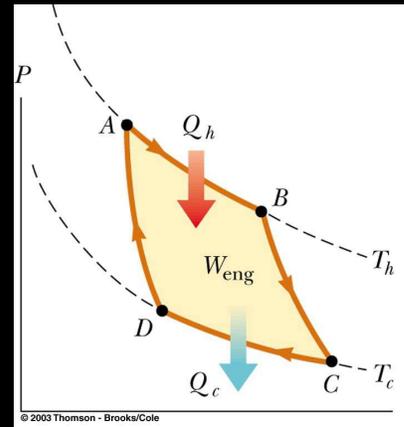
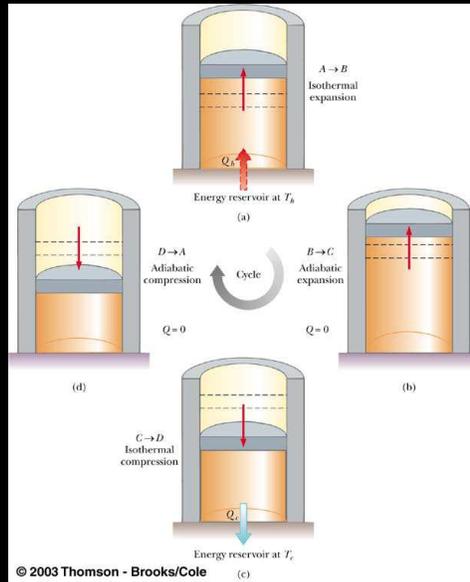
## Reversible and Irreversible processes



**Reversible process:** the system is taken through a path of states in equilibrium and can be returned to the original state along the same path.

Most natural processes are **Irreversible!**

## Carnot engine



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## Carnot's theorem

**No real engine operating between two energy reservoirs can be made more efficient than a Carnot engine operating between the same reservoirs**

$$\mathcal{E} = 1 - \frac{T_{cold}}{T_{hot}}$$

All real engines operate irreversibly (friction and cycles are short)

## Carnot engine: question time

Three engines operate between reservoirs separated in temperature by 300 K. The reservoir temperatures are:

Engine A operates between 1000K and 700K

Engine B operates between 800K and 500K

Engine C operates between 600K and 300K

- 1) Which one has the highest efficiency?
- 2) Which one has the lowest efficiency?

## Heat engines: example

A car engine delivers 8.2 KJ of work per cycle.

- a) Before tune-up the efficiency is 25%. Calculate, per cycle, the heat absorbed from combustion of fuel and the energy lost by the engine
- b) After a tune-up the efficiency is 31%. What are the new values of the quantities calculated in a) when 8.2 KJ of work is delivered per cycle.