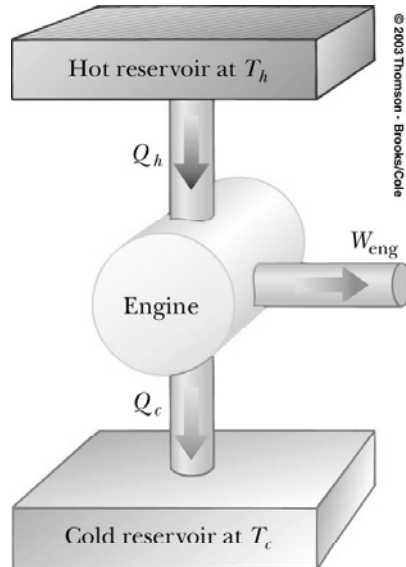


Chapter 12: The laws of Thermodynamics



Work in thermodynamic processes

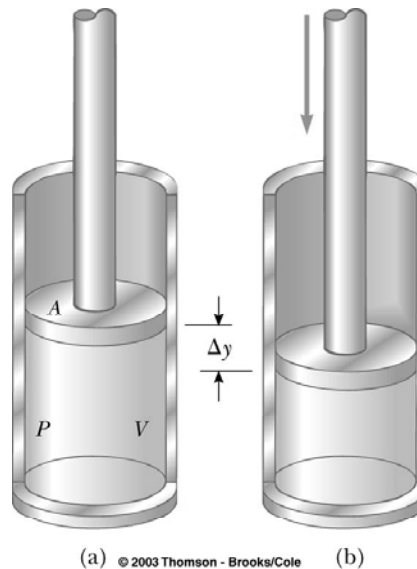
The work done on a gas in a cylinder is directly proportional to the force and the displacement.

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

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

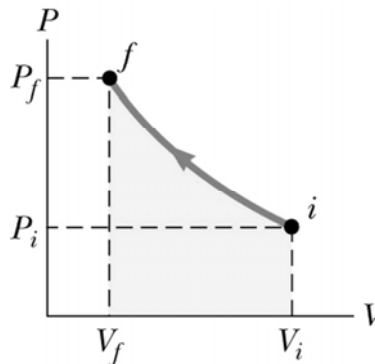


Work: questions

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 $4V$.

- 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 .

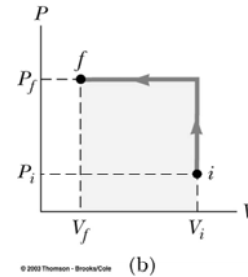
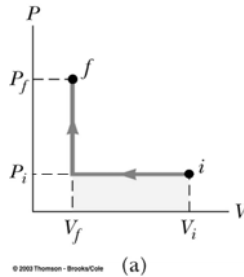
PV diagrams



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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.

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

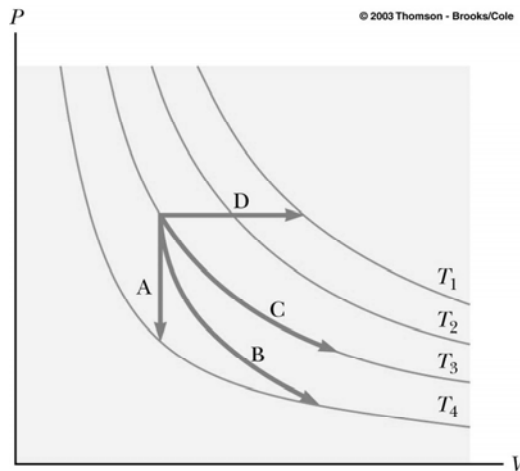
$$U = \frac{3}{2}nRT \mapsto U_f = U_i \rightarrow W = -Q$$

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

Adiabatic processes: if the energy transferred by heat in a process is zero then

$$\Delta U = W$$

First law of thermodynamics: question

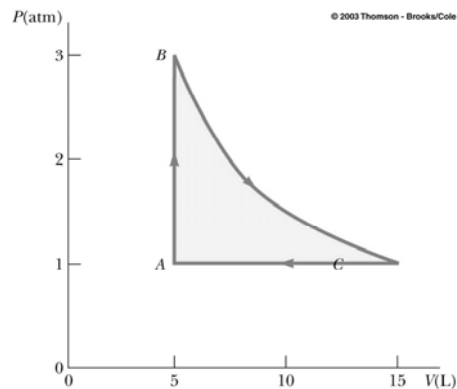


Which of the following processes correspond to

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

First law of thermodynamics: example

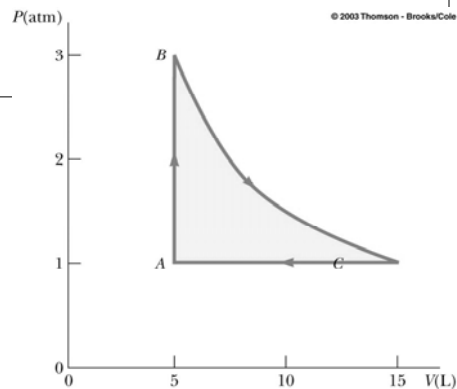
An ideal mono-atomic gas is confined in a cylinder by a movable piston. The gas starts at $P=1.00\text{atm}$, $V=5.00\text{L}$ and $T=300\text{K}$. An isovolumetric process raises the pressure to 3atm . Then an isothermal expansion brings the system back to 1atm . Finally an isobaric compression at 1atm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



- 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, 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 ΔU for each transition
- 5) Tabulate W,Q and ΔU for each transition and calculate the net effect of each.

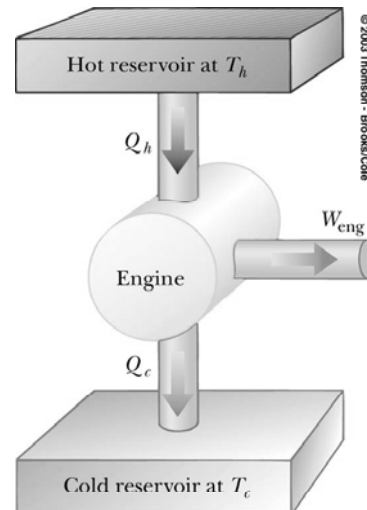


Heat engines

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



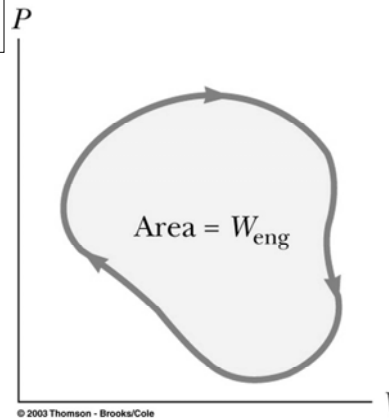
Heat engines

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

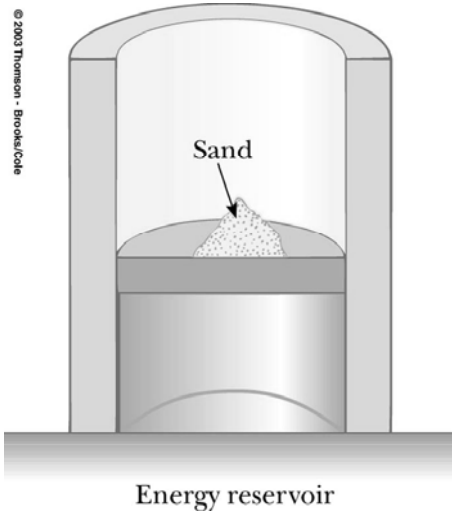
Thermal efficiency of the heat engine is the ratio of the work done by the engine to the energy absorbed from the hot reservoir in a cycle

$$\mathcal{E} = \frac{W_{eng}}{|Q_{hot}|}$$

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

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

Reversible and Irreversible processes

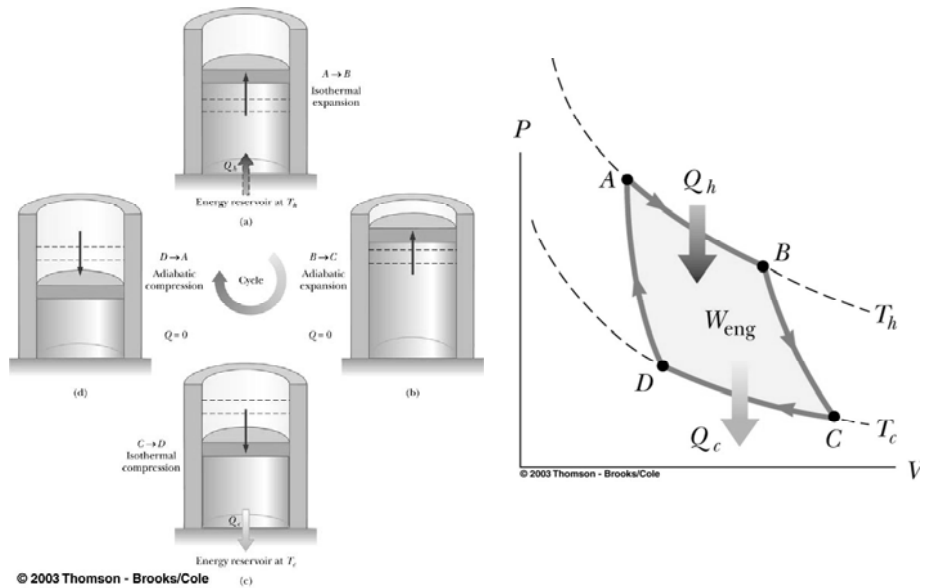


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Reversible process: the system is taken through a path of states in equilibrium and can be returned to the original state along the same path.

Most natural processes are **Irreversible!**

Carnot engine



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

$$\varepsilon = 1 - \frac{T_{cold}}{T_{hot}}$$

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.

- Before tune-up the efficiency is 25%. Calculate, per cycle, the heat absorbed from combustion of fuel and the energy lost by the engine
- 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.

Human metabolism

The metabolic rate is proportional to the consumption of oxygen by volume

$$\frac{\Delta U}{\Delta t} = 4.8 \frac{\Delta V_{O_2}}{\Delta t}$$

TABLE 12.1 Oxygen Consumption and Metabolic Rates for Various Activities

Activity	O ₂ use (mL/min)	Metabolic rate (kcal/h)	Metabolic rate (W)
Sleeping	3.5	70	80
Light activity (dormitory, slow walking)	10	200	230
Moderate activity (walking briskly)	20	400	465
Heavy activity (basketball, fast breast stroke)	35	700	810
Extreme activity (bicycle racing)	70	1 400	1 600

^a Source: *A Companion to Medical Studies*, 2/e, R. Passmore, Philadelphia, F. A. Davis, 1968.
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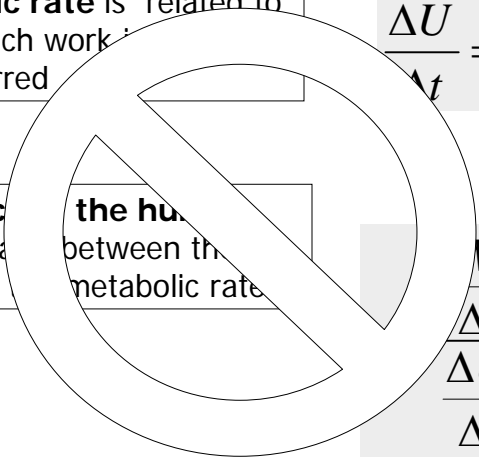
Efficiency Human body as a machine

The metabolic rate is related to the rate at which work is done and heat if transferred

$$\frac{\Delta U}{\Delta t} = \frac{Q}{\Delta t} + \frac{W}{\Delta t}$$

The efficiency of the human body is the ratio between the work rate and the metabolic rate

$$e = \frac{\frac{W}{\Delta t}}{\frac{\Delta U}{\Delta t}}$$

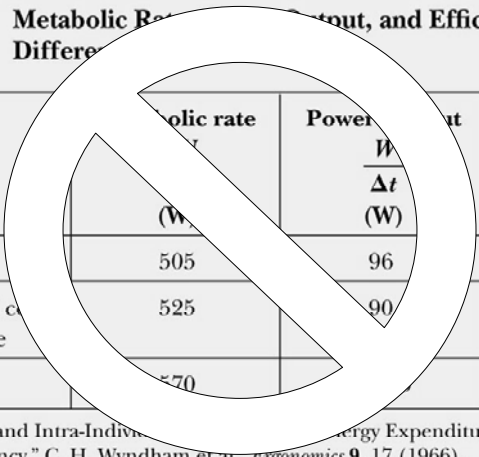


Efficiency Human body as a machine

TABLE 12.3 Metabolic Rate, Power Output, and Efficiency for Different Activities

Activity	Metabolic rate (W)	Power output (W)	Efficiency e
Cycling	505	96	0.19
Pushing loaded cars in a mine	525	90	0.17
Shoveling	570	18	0.03

^a Source: "Inter- and Intra-Individual Variability in Energy Expenditure and Mechanical Efficiency," C. H. Wyndham et al., *Ergonomics* 9, 17 (1966).
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Entropy

Entropy (S) is a measure of the state of disorder of a system

The change in entropy (ΔS) of a system between two equilibrium states is given by the energy transferred in a reversible path divided by the absolute temperature T of the system in this interval

$$\Delta S = \frac{Q_{rev}}{T}$$

Second law of thermodynamics: the entropy of the universe increases in all natural processes.

Entropy: question time

Which of the following statements is true for a reversible, adiabatic path:

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

Two gases A and B are initially in contact with a hot source at temperature T . Heat exchange occurs. A receives the heat transferred to B. What can you conclude about their change in entropy ΔS ? What can you say about their absolute state of disorder?

Second law of thermodynamics

A disorderly arrangement is more probable than an orderly one if the laws of physics are allowed to act without interference

Isolated systems tend toward greater disorder
Entropy is a measure of disorder

Boltzmann's definition of Entropy

$$S = k_B \ln W$$

W is a number proportional to the probability that the system has a particular configuration

Second law of Thermodynamics: example

The surface of the Sun is at 5700 K, and the temperature of the Earth's surface is approximately 290 K. What entropy change occurs when 10 J of energy is transferred from the Sun to the Earth?

What is the change in entropy of 1 kg of liquid water at 100°C as it changes to steam at 100°C?