Thermodynamics

B.4 · AHL

Why can't a power station use all its fuel energy?

> The first law counts energy; the second law says which way it can flow.

- Invented model: 1300 MW of fuel energy gives 500 MW of electricity.
- A cold drink never freezes on its own while warming the room.
- The whole unit is additional higher level.

The first law of thermodynamics

- Q is heat to the system; W is work done by the system.
- 300 J in, 120 J of work out, so $\Delta U = 180$ J.

$$Q = \Delta U + W$$

Work done on the gas is negative.

Closed and isolated systems

Closed

No mass in or out.

Energy crosses as heat or work.

Isolated

No mass in or out.

No energy in or out.

Work and internal energy

- For a slow equilibrium piston path, the area under the actual P–V curve gives boundary work.
- ΔU depends only on ΔT, in any process.

$$W = P\Delta V \qquad \Delta U = \tfrac{3}{2} nR\Delta T$$

For a monatomic ideal gas.

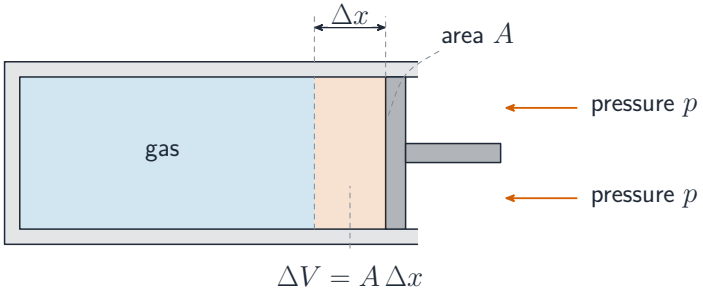
Worked example: heating at constant pressure

1. **Known.** 0.50 mol helium at constant 100 kPa warms from 300 to 400 K; use R = 8.31 J/(mol K).
2. **Work.** $\Delta V = nR\Delta T/P = 4.2 \times 10^{-3}$ m^3, so $W = 415.5$ J.
3. **Internal energy.** $\Delta U = 1.5 \times 0.50 \times 8.31 \times 100 = 623.25$ J.

Decision

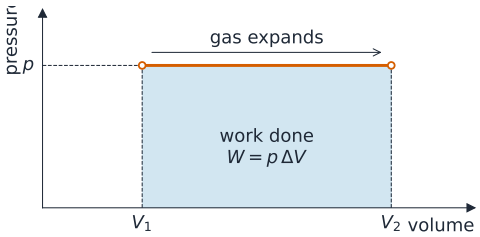
$Q = 623.25 + 415.5 = 1038.75$ J, about 1.04 kJ

Work done by an expanding gas



The gas does work on the surroundings

Work is the area under p–V



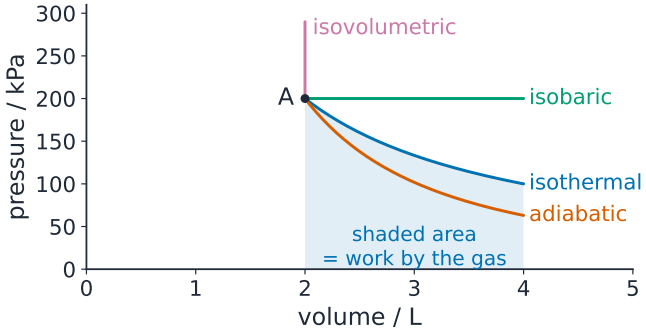
work = area under p–V · $W = \int p\,dV$

For any path, work is the area under the curve

Four processes

Process	**Fixed**	**First law**
isovolumetric	V	$Q = \Delta U$
isobaric	P	$Q = \Delta U + P\Delta V$
isothermal	T	$Q = W$
adiabatic	$Q = 0$	$\Delta U = -W$

The processes on a P–V diagram



- The shaded area is the work done in the isothermal expansion.
- The adiabatic gas cools as it does work, so its pressure falls faster.

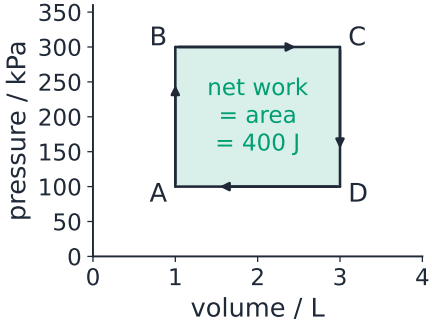
Adiabatic compression

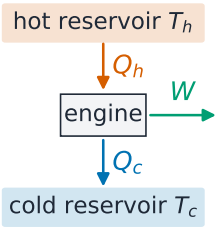
- Invented reversible monatomic model: 100 kPa, 300 K compressed to one eighth of its volume.
- $P_2 = 3200$ kPa and $T_2 = 1200$ K. Rapid alone does not imply reversible.

$$PV^{5/3} = \text{constant}$$

For a reversible adiabatic change of a monatomic ideal gas.

Heat engines and cycles





- Over a **cycle** $\Delta U = 0$, so $W = Q_h - Q_c$.
- A clockwise loop on a P–V diagram is an engine.

Efficiency of the rectangular cycle

1. **Given.** Monatomic ideal-gas **cycle**: 300 J absorbed on A $\rightarrow$ B, 1500 J on B $\rightarrow$ C; 1400 J rejected on the other legs.
2. **Heat input.** $Q_h = 300 + 1500 = 1800$ J: add only absorbed heat.
3. **Net work.** $W = Q_h - Q_c = 1800 - 1400 = 400$ J, matching $600 - 200 = 400$ J from the P–V area.

Decision

$\eta = W/Q_h = 400/1800 = 0.22$

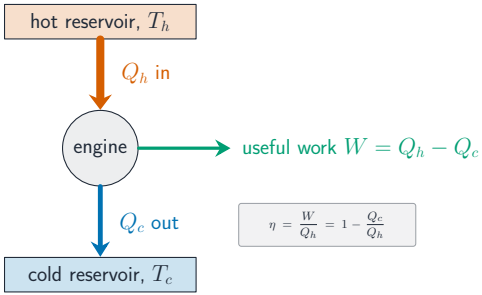
The Carnot limit

- Invented reservoirs at 800 K and 300 K give at most 0.625; irreversible engines have lower **efficiency**.
- Two isothermal and two adiabatic processes, all reversible.

$$\eta_{\text{Carnot}} = 1 - \frac{T_c}{T_h}$$

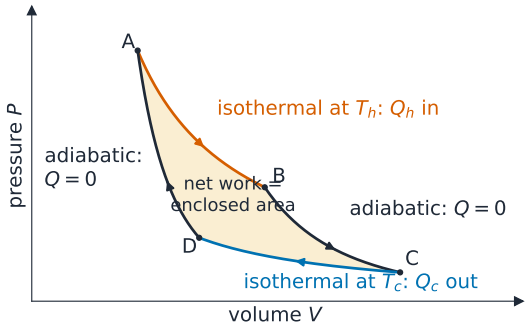
Temperatures in kelvin; only $T_c = 0$ K would give 100%.

A heat engine



$\eta = W/Q_h$, always less than 1

The Carnot cycle



The enclosed area is the net work

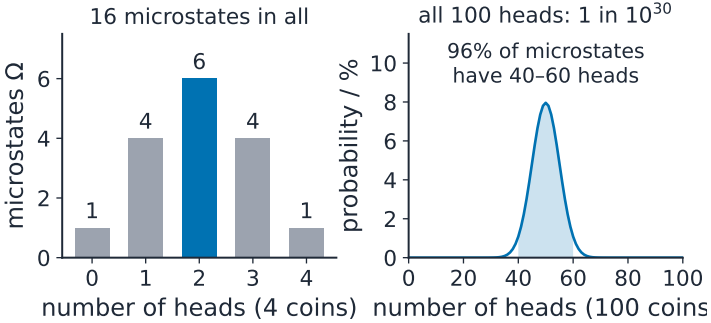
Entropy

- 1.0 kg of ice melting at 273 K gains 1.2×10^3 J K^{-1}.
- Four coins, two heads: $\Omega = 6$.

$$\Delta S = \frac{\Delta Q}{T} \qquad S = k_B \ln \Omega$$

Entropy is a state property related to accessible microstates; use reversible heat at constant T in the ratio.

Microstates



- For independent fair flips, all coin sequences are equally likely.
- With 100 coins, all heads is 1 in 10^{30}.

The second law

> The total **entropy** of an **isolated system** never decreases.

- Clausius: heat never flows spontaneously from cold to hot.
- Kelvin: no cyclic engine turns heat from one reservoir fully into work.

Check: heat flows from hot to cold

Your turn

1,000 J flows between large reservoirs maintained at 400 K and 300 K. What is their total entropy change?

A. $-0.8\ \text{J K}^{-1}$

B. 0

C. $+0.8\ \text{J K}^{-1}$

D. $+5.8\ \text{J K}^{-1}$

Local decreases in entropy

A subsystem can lose **entropy**; the isolated combination cannot.

- A subsystem can lose entropy.
- Include energy and any matter transfers; the surroundings must compensate for its decrease.

Exam tips

> Write the first law with signs before substituting.

- Q to the system, W by the system.
- $\Delta U = \frac{3}{2} nR\Delta T$ in every process.
- Isothermal means $\Delta U = 0$; adiabatic means $Q = 0$.

Check yourself

Try these

A gas absorbs 500 J while 200 J of work is done on it. Find ΔU.

A monatomic ideal gas at 200 kPa and 3.0 L expands reversibly and adiabatically to 6.0 L. Find final pressure.

Find the total entropy change when 600 J flows between reservoirs held at 500 K and 300 K.