



energy bookkeeping for a reaction: what's spent, what's released, what decides direction



System, surroundings, and the three kinds of system

- the **system** is the part of the universe under study; everything else is the **surroundings**, and the two exchange matter and/or energy across a boundary
- open system: exchanges both matter and energy with the surroundings, e.g. hot tea in an open cup
- closed system: exchanges energy but not matter, e.g. a sealed flask being heated
- isolated system: exchanges neither, e.g. a substance in an ideal thermos flask

State functions and thermodynamic processes



- a **state function** depends only on the initial and final state, never on the path taken to get there: internal energy, enthalpy, entropy, Gibbs energy
- path functions**, by contrast, depend on the route: heat (q) and work (w) are not state functions, only their sum ΔU is
- isothermal: temperature constant throughout ($\Delta T=0$); adiabatic: no heat exchange with surroundings ($q=0$)
- isochoric: volume constant ($\Delta V=0$), so no pressure-volume work is done; isobaric: pressure constant throughout

The first law of thermodynamics

internal energy change = heat absorbed plus work done ON the system

$$\Delta U = q + w$$

pressure-volume work done ON the system during a volume change

$$w = -p_{\text{ext}} \Delta V$$

the first law is just energy conservation: energy can move between the system and surroundings as heat or work, but the total is never created or destroyed. sign convention here: heat absorbed BY the system and work done ON the system are both positive

Sign convention, read carefully

$$q > 0$$

heat absorbed by the system (endothermic)

$$q < 0$$

heat released by the system (exothermic)

$$w > 0$$

work done ON the system, e.g. the surroundings compress it

$$w < 0$$

work done BY the system, e.g. a gas expands and pushes back

ΔU doesn't care how you got there; q and w individually do, and only their sum is guaranteed to match at the end

