Thermodynamics

Internal energy as the sum of random kinetic and potential energies, why a temperature rise means more internal energy, work done when a gas changes volume, and the first law of thermodynamics.

16.1 Internal energy

The **internal energy** of a system is the sum of the **random distribution of kinetic and potential energies** of its molecules. It is determined by the **state** of the system: its temperature, volume and phase.

- The kinetic part depends on **temperature**.
- The potential part depends on the **separation** of the molecules, so it changes when a substance melts or boils.

A rise in temperature means a rise in the mean kinetic energy of the molecules, which means a rise in internal energy.

During melting or boiling, the temperature is constant, so the kinetic energy is unchanged, but the potential energy rises, so the internal energy still rises.

> **An ideal gas has no forces between molecules, so its molecules have no potential energy. Its internal energy is entirely kinetic, so it depends only on the temperature. If an ideal gas's temperature is unchanged, $\Delta U = 0$.**

16.2 The first law of thermodynamics

Work done by a gas

When a gas expands at constant pressure p, pushing a piston of area A through a distance d, the work it does is $F\,d = pAd$:

$$W = p\Delta V$$

- When a gas **expands**, it does work on the surroundings. Work done **on** the gas is negative.
- When a gas is **compressed**, work is done on it. Work done **on** the gas is positive.

On a pressure–volume graph, the work done is the **area under the line**, which still applies when the pressure varies.

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The first law

$\Delta U = q + W$

Symbol	Meaning	Positive when
ΔU	increase in internal energy	internal energy rises
q	energy transferred **to** the system by heating	the system is heated
W	work done **on** the system	the gas is compressed

NOTE

Exam tip: check which sign convention your course uses; this chapter takes W as work done **on** the gas. Many mistakes come from treating W as work done **by** the gas. For an expansion at constant pressure, $W = -p\Delta V$.

TRY IT

A gas at a constant 1.0×10^5 Pa expands by 2.0×10^{-3} m³ and receives 500 J of heating. Find the change in internal energy. Work done on the gas: $W = -1.0 \times 10^5 \times 2.0 \times 10^{-3} = -200$ J. $\Delta U = 500 - 200 = +300$ J, so the gas gets hotter.

Common processes

Process	Condition	Consequence for an ideal gas
Constant volume	$\Delta V = 0$, so $W = 0$	$\Delta U = q$
Constant temperature	$\Delta T = 0$	$\Delta U = 0$, so $q = -W$
Thermally insulated (or very fast)	$q = 0$	$\Delta U = W$: compressing warms the gas
Complete cycle	returns to its start	$\Delta U = 0$, so net $q =$ − net W

A bicycle pump warms up because you do work on the gas quickly, leaving little time for heat to escape, so $q \approx 0$ and $\Delta U \approx W$.

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