Thermodynamics

A-Level Physics

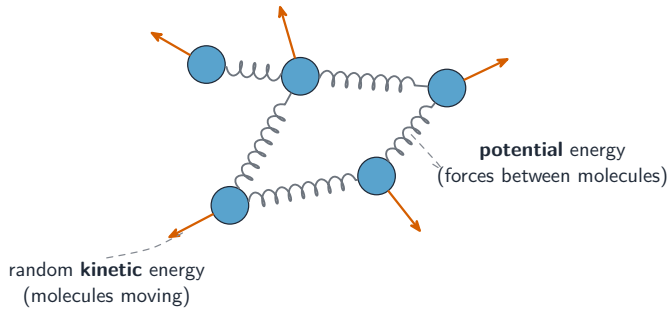
Internal energy

The **internal energy** 内能 U of a system is the sum of:

- the random **kinetic energies** 动能 of its **molecules** 分子 — they fly through space (**translational** 平动 motion), and unless they are single atoms they also spin (**rotational** 转动) and shake (**vibrational** 振动), and
- the **potential energies** from the forces between the molecules.

For a real solid, liquid or gas, both parts matter. In the **ideal-gas** 理想气体 model the **intermolecular** 分子间 forces are ignored, so the molecular potential energy is zero and the internal energy is purely kinetic.

The two-mark definition. *The internal energy of a system is the sum of the random distribution of the kinetic and potential energies of its molecules (or atoms).* Both marks need "sum of kinetic and potential energies" **and** "random" (or "of the molecules") — leaving out "random" describes the energy of a moving object, not its internal energy. For an ideal gas, "with reference to kinetic and potential energy": the internal energy is the total *kinetic* energy of the molecules only, because there are no intermolecular forces and therefore no potential energy.



Internal energy is the molecules' random kinetic energy (the arrows) plus the potential energy of the forces between them (the springs)

Two key points:

1. U **depends only on the state** of the system (its **temperature** 温度, **pressure** 压强, **volume** 体积, **amount of substance** 物质的量) — not on the path taken to get there.

2. U **is a sum over the molecules**, not the kinetic energy of the whole object moving. A moving train of gas has bulk kinetic energy, but that is separate from U — U is the energy of the *random* molecular motion.

Temperature and internal energy

Raising an object's temperature raises the random kinetic energy of its molecules, and so raises its internal energy.

For an ideal gas every molecule has average translational kinetic energy $\frac{3}{2}kT$ (Topic 15). With zero intermolecular potential energy, the total internal energy is

$$U = \tfrac{3}{2}NkT = \tfrac{3}{2}nRT.$$

So the internal energy of an ideal gas is directly proportional to the **thermodynamic temperature** 热力学温度. Doubling T doubles U. This is **only** exact for an ideal gas.

During a **phase change** 相变 (melting or boiling) of a real substance, U rises because the molecular potential energy rises (bonds breaking), even though the temperature stays constant.

Describing a change in internal energy — always name both energies. A three-mark "describe and explain, with reference to molecular kinetic and potential energies" answer says what happens to *each*:

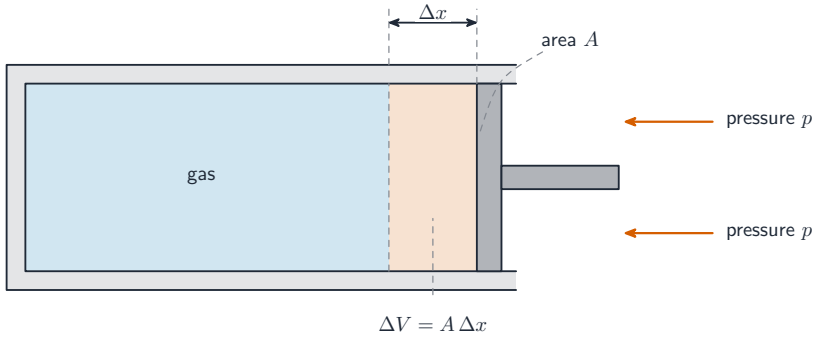
- **a gas heated at constant volume:** the kinetic energy of the molecules increases, because temperature is a measure of their mean kinetic energy; the potential energy is unchanged (no work is done, the molecules' separation does not change); so the internal energy increases.
- **a wire stretched within its elastic limit at constant temperature:** the kinetic energy of the atoms is unchanged (same temperature); the potential energy increases, because the atoms are pulled further apart against the interatomic forces; so the internal energy increases.
- **ice melting at 0 °C:** the kinetic energy is unchanged (constant temperature); the potential energy increases as the bonds between molecules are broken and the separation grows; so the internal energy increases by the latent heat supplied.

Worked example. A fixed mass of ideal gas is heated at constant pressure. Sketch the variation of its internal energy U with its volume V.

At constant pressure $V \propto T$ (Charles's law) and for an ideal gas $U \propto T$, so $U \propto V$: a **straight line through the origin**. The origin is on the line because at absolute zero both V (extrapolated) and U are zero.

Work done on or by a gas

A steam turbine does work as expanding steam pushes its blades around.



A gas pushing a piston of area A out by Δx does work $W = p\,\Delta V$ on the surroundings (swept volume $\Delta V = A\,\Delta x$)

When a gas changes volume against an outside pressure, mechanical work is done. At constant pressure p with a small volume change ΔV, the size of the work is

$$W = p\Delta V.$$

Worked example. A gas at a constant pressure of 1.0×10^5 Pa expands from 2.0×10^{-3} m^3 to 5.0×10^{-3} m^3. Find the work done by the gas.

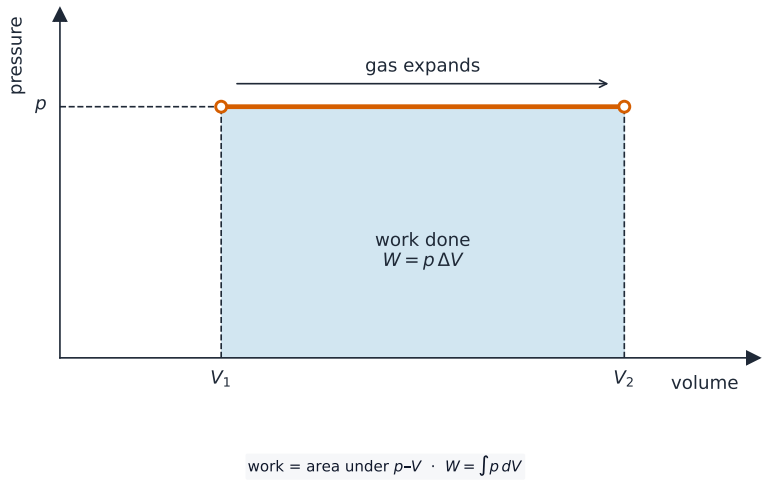
$$W = p\,\Delta V = (1.0 \times 10^5)(5.0 \times 10^{-3} - 2.0 \times 10^{-3}) = 300 \text{ J}.$$

Worked example. An ideal gas of mass 0.35 kg is heated at a constant pressure of 2.0×10^5 Pa; its internal energy rises by 7600 J and its volume increases by 1.2×10^{-2} m^3. Find the work done by the gas and the thermal energy supplied. The gas is then heated at constant *volume* until its internal energy rises by the same 7600 J; explain why less thermal energy is needed.

Work done *by* the gas $= p\Delta V = 2.0 \times 10^5 \times 1.2 \times 10^{-2} = 2400$ J, so the work done *on* it is $W = -2400$ J. First law: $q = \Delta U - W = 7600 - (-2400) = 1.0 \times 10^4$ J. At constant volume no work is done ($\Delta V = 0$, $W = 0$), so the whole of the thermal energy goes into internal energy: $q = \Delta U = 7600$ J. The extra 2400 J at constant pressure was the work the gas did pushing back the surroundings as it expanded.

Worked example. An aluminium block of volume 3.612×10^{-3} m^3 is heated from 0 °C to 40 °C; its volume increases by 1.0×10^{-5} m^3 against atmospheric pressure (1.0×10^5 Pa). Compare the work it does on the atmosphere with the thermal energy it receives ($m = 9.75$ kg, $c = 900$ J kg^{-1} K^{-1}).

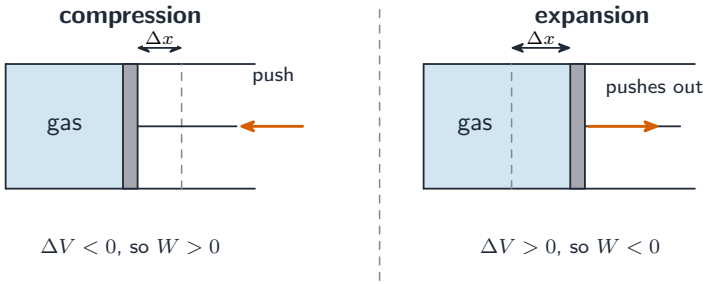
Work done by the block $= p\Delta V = 1.0 \times 10^5 \times 1.0 \times 10^{-5} = 1.0$ J; thermal energy $q = mc\Delta T = 9.75 \times 900 \times 40 = 3.5 \times 10^5$ J. The work is about 3×10^{-6} of the heating, so for a solid $\Delta U \approx q$: solids and liquids barely expand, and $p\Delta V$ only matters for a gas.



On a pressure–volume graph, the work done at constant pressure is the area under the line: $W = p\,\Delta V$

Sign convention in this syllabus

This syllabus writes the first law as $\Delta U = q + W$, where W is the work done **on** the gas and q is the energy put in **by heating**.



Work done on the gas: positive when it is compressed, negative when it expands

- when the gas is **compressed**, ΔV is negative and the work done **on** the gas is positive — the gas gains energy.
- when the gas **expands**, ΔV is positive and the work done **on** the gas is negative — the gas loses energy (it does work on the surroundings).

Watch which form a question wants:

- "work done **on** the gas" — positive when compressing.
- "work done **by** the gas" — the opposite sign, positive when expanding.

At constant volume ($\Delta V = 0$), no work is done.

First law of thermodynamics

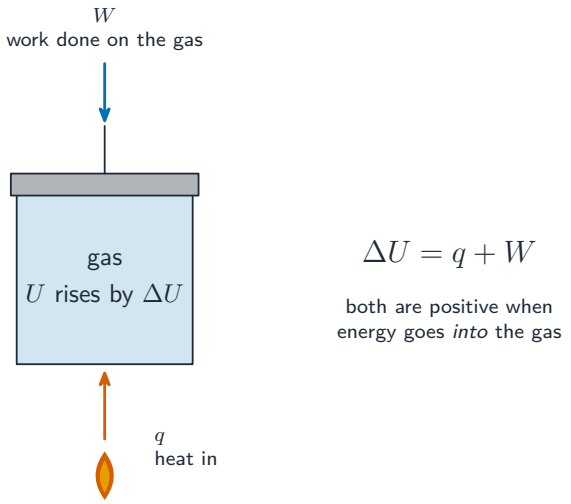
A power station is a heat engine: it converts heat into useful work.

The **first law of thermodynamics** 热力学第一定律 says that **energy is conserved when heat and work pass between a system and its surroundings**:

$$\Delta U = q + W,$$

where ΔU is the rise in internal energy, q is the energy added **by heating** (positive in, negative out), and W is the work done **on** the gas (positive when compressed). This is **conservation of energy** 能量守恒 for a gas.

As the exam asks it. "State the first law of thermodynamics, identifying any symbols" (2 marks): *the increase in internal energy of a system, ΔU, is equal to the sum of the thermal energy transferred to the system by heating, q, and the work done on the system, W*: $\Delta U = q + W$. Every symbol must be defined with its **direction** — "to the system" and "on the system" are what make the signs mean something. "State two ways in which the first law says the internal energy of a system may be changed": by *heating* (thermal energy transferred into or out of the system) and by *doing work* on or by the system.



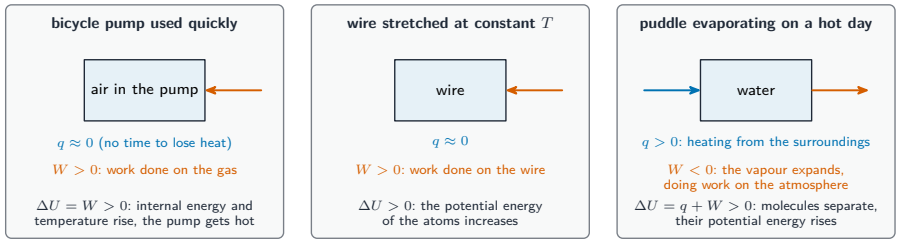
Both heating (q) and work done on the gas (W) put energy in, raising the internal energy by ΔU

Worked example. A gas absorbs 500 J of heat while it expands and does 200 J of work on its surroundings. Find the change in its internal energy.

The gas does work, so the work done *on* it is $W = -200$ J:

$$\Delta U = q + W = 500 + (-200) = 300 \text{ J}.$$

Explaining with the first law. A three-mark "use the first law to explain" answer has three steps: say what q is (and its sign), say what W is (and its sign), then combine them for ΔU — and, if asked, say what the change in internal energy means for the molecules.



The three classic first-law explanations: give q with its sign, W with its sign, then ΔU

- **Why a bicycle pump gets hot when used quickly:** the air is compressed, so work is done *on* it ($W > 0$); the compression is fast, so there is no time for thermal energy to leave ($q \approx 0$); therefore $\Delta U = W > 0$ — the internal energy, and so the temperature, of the air rises, and the pump warms up.
- **A spring stretched at constant temperature within its elastic limit:** work is done on the spring by the stretching force ($W > 0$); there is no thermal energy transfer ($q = 0$); so the internal energy increases — stored as the elastic potential energy of the atoms, which are pulled further apart.
- **Water evaporating from a puddle on a hot day:** thermal energy is transferred to the water from the surroundings ($q > 0$); the vapour formed occupies a far larger volume than the liquid, so the system does work on the atmosphere ($W < 0$); the internal energy still increases (q is larger than the work done), and the increase is potential energy — the molecules are separated against the attractive forces between them.

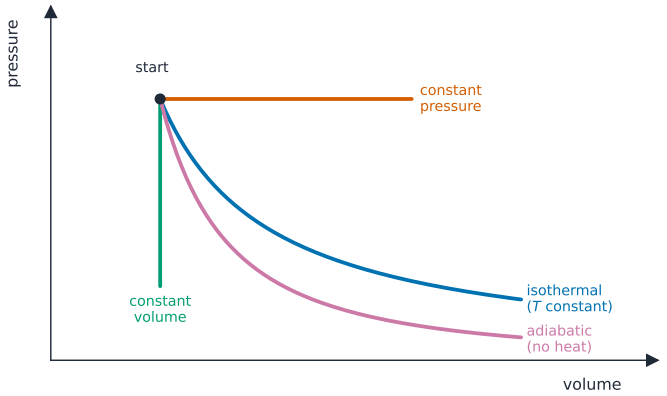
Reading the equation

ΔU is fixed by the change of state (for an ideal gas, by the change in temperature). The same ΔU can come from different mixes of q and W:

- all heat, no work: $\Delta U = q$ (constant-volume heating).
- all work, no heat: $\Delta U = W$ (insulated compression or expansion).

Standard processes

For an ideal gas, $\Delta U = \frac{3}{2}nR\Delta T$ — it depends only on ΔT.



isothermal, isobaric, isometric on p–V plane

The four standard processes, all starting from the same state

Process	What stays constant	ΔU	W (on gas)	q
Isothermal	T	0	W	$-W$
Constant volume	V	$\frac{3}{2}nR\Delta T$	0	ΔU
Constant pressure	p	$\frac{3}{2}nR\Delta T$	$-p\Delta V$	$\Delta U - W$
Adiabatic	(no heat)	varies	W	0

Read each row with the first law $\Delta U = q + W$:

- **Isothermal** 等温 (constant T): $\Delta T = 0$, so $\Delta U = 0$. Then $q = -W$ — any heat that goes in comes straight back out as work.
- **Adiabatic** 绝热 (no heat flow): $q = 0$, so $\Delta U = W$. The gas warms up only because work is done on it.
- **Constant volume** (sealed rigid container): no work is done ($\Delta V = 0$), so all the heat goes into internal energy: $q = \Delta U$.
- **Constant pressure** (gas pushing a **piston** 活塞): the gas does work as it expands, so the heat you supply does two jobs — it raises the internal energy *and* does the expansion work.

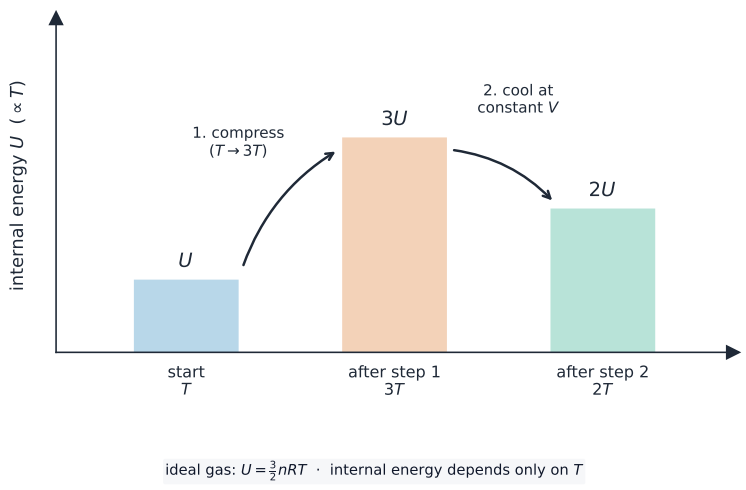
So for the **same rise in internal energy**, heating at constant pressure needs *more* thermal energy than heating at constant volume, by exactly the work $p\Delta V$ the gas does

while expanding — the constant-volume gas keeps every joule; the constant-pressure gas hands some back to the surroundings.

Worked example: two-step process

A sample of ideal gas at temperature T with internal energy U goes through:

1. **compression** to temperature $3T$; work W is done on the gas.
2. **cooling at constant volume** to temperature $2T$.



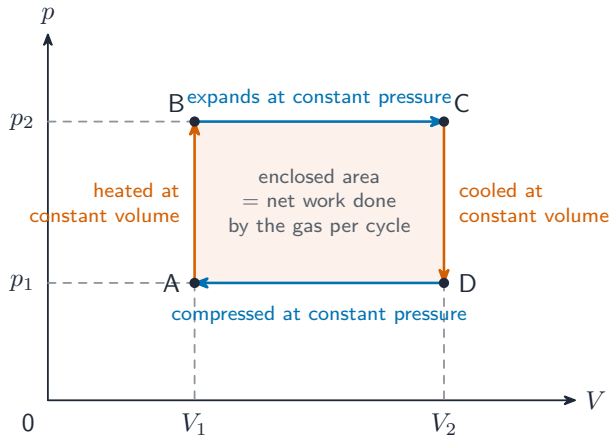
Internal energy tracks temperature: $U \to 3U$ on compressing to $3T$, then $3U \to 2U$ on cooling to $2T$

Step 1 ($T \to 3T$): $U = \frac{3}{2}nRT$, so $U \to 3U$, giving $\Delta U_1 = 2U$. $W_1 = +W$. So $q_1 = \Delta U_1 - W_1 = 2U - W$.

Step 2 ($3T \to 2T$, constant volume): $\Delta U_2 = -U$. $W_2 = 0$. So $q_2 = -U$ (heat flows out).

Check: total $\Delta U = 2U - U = U$, taking the gas from T to $2T$ ($U \to 2U$) — consistent.

Worked example: a cycle on a p–V diagram



A cycle: for each leg decide W from the volume change and ΔU from the temperature change, and q follows from the first law

A fixed mass of ideal gas is taken round the cycle ABCDA: A to B at constant volume V_1 (pressure $p_1 \to p_2$), B to C at constant pressure p_2 (volume $V_1 \to V_2$), C to D at constant volume, D to A at constant pressure p_1. Complete a table of the signs of q, W and ΔU for each leg, and explain the internal-energy change from B to C.

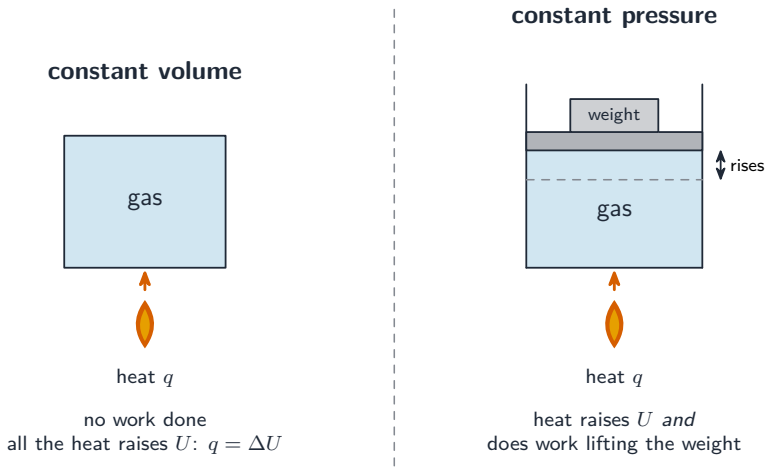
Leg	**Process**	W **(on gas)**	ΔU	q
A → B	constant volume, pressure rises	0 (no volume change)	+ (temperature rises, pV larger)	+ ($q = \Delta U$)
B → C	constant pressure, expands	− (gas does work $p_2(V_2 - V_1)$)	+ ($T \propto V$ at constant p)	+ (and larger than ΔU)
C → D	constant volume, pressure falls	0	−	− (thermal energy leaves)
D → A	constant pressure, compressed	+ (work done on the gas $p_1(V_2 - V_1)$)	−	− (larger in size than ΔU)

From B to C the gas expands at constant pressure, so its temperature rises (V/T constant) and its internal energy increases; it does work on the surroundings (W negative), so the thermal energy supplied must cover both: $q = \Delta U - W$, larger than the rise in internal energy. Round the whole cycle $\Delta U = 0$ (the gas returns to its starting state), so the net thermal energy in equals the net work done by the gas —

the area enclosed by the rectangle, $(p_2 - p_1)(V_2 - V_1)$.

Heat capacity at constant volume

For constant-volume heating of an ideal gas, $q = \Delta U = \frac{3}{2}nR\Delta T$. So the molar **heat capacity** 热容 at constant volume is $\frac{3}{2}R$ for a **monatomic** 单原子 ideal gas. (You are not required to use the symbol C_V, but the result $q = \frac{3}{2}nR\Delta T$ for constant-volume heating is.)



At constant volume all the heat raises U ($q = \Delta U$); at constant pressure the gas also does work

Heating without a temperature change

If heat is supplied during a phase change at constant pressure (e.g. boiling water), the temperature stays constant but the internal energy still rises (the **latent heat** 潜热 separates the molecules), and the gas does expansion work. The first law still holds: $\Delta U = q + W$.

Definitions the examiner accepts

A definition question is marked against fixed wording. Learn these exactly, and give one answer only.

Term	Definition
internal energy	the sum of the random distribution of the kinetic and potential energies of the molecules of a system
internal energy of an ideal gas	the total random kinetic energy of its molecules, since with no intermolecular forces there is no potential energy
first law of thermodynamics	the increase in internal energy of a system equals the thermal energy transferred to the system by heating plus the work done on the system: $\Delta U = q + W$
work done on a gas at constant pressure	$W = p\Delta V$ in size; positive when the gas is compressed, negative when it expands (the gas then does work on its surroundings)
thermal energy transfer (heating)	energy transferred to or from a system because of a temperature difference; q is positive when it enters
isothermal change	a change at constant temperature, so for an ideal gas $\Delta U = 0$ and $q = -W$
adiabatic change	a change with no thermal energy transfer, $q = 0$, so $\Delta U = W$

Exam tips

- **First law:** $\Delta U = q + W$ — define every symbol with its direction: q is energy transferred *to* the system by heating, W is work done *on* the system.
- For an ideal gas, **internal energy depends only on temperature** ($\Delta U \propto \Delta T$) and is kinetic energy only; for a solid or liquid the potential energy changes too.
- Work done by a gas at constant pressure $= p\Delta V$; read the sign from expansion (by) or compression (on), and remember that at constant volume $W = 0$.
- A "describe and explain" answer names both kinetic and potential energy and says what happens to each; an "explain using the first law" answer gives q, W and then ΔU, each with its sign.
- Round a complete cycle $\Delta U = 0$, so net heating equals net work done by the gas — the area enclosed on the p–V diagram.

Common mistakes

- Defining internal energy as "the total energy of the molecules" or forgetting "random" or "potential". The mark scheme wants the sum of random kinetic and potential energies.
- Using $W = p\Delta V$ with the wrong sign. When the gas expands the work done *on* it is negative.
- Saying the internal energy of an ideal gas rises when it is compressed isothermally. At constant temperature $\Delta U = 0$: the work done on it leaves again as heat.

- Treating a phase change as $\Delta U = 0$ because the temperature is constant. The potential energy rises; ΔU is the latent heat minus any expansion work.
- Forgetting that a gas heated at constant pressure does work, so it needs more heating than at constant volume for the same ΔU.
- Applying $\Delta U = \frac{3}{2}nR\Delta T$ to a real gas, a liquid or a solid. It is the ideal-gas result only.