



MEGA
LECTURE

IB DP PHYSICS

Theme B: The Particulate Nature of Matter

B.4 Thermodynamics

Revision Notes · Higher Level only

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What the syllabus requires

B.4 Thermodynamics is Higher Level only. By the end of B.4 you should be able to work confidently with each of the following. Use this list as a final checklist before the exam.

Understanding	You should be able to...
First law of thermodynamics	Apply $Q = \Delta U + W$ as a statement of energy conservation for a gas, with the correct sign convention for each term.
Work done by a gas	Calculate $W = P\Delta V$ at constant pressure and interpret work as the area under a P–V curve in general.
Internal energy of an ideal gas	Use $\Delta U = (3/2)nR\Delta T$ for a monatomic ideal gas; recognise U as a state function.
The four processes	Describe isobaric, isovolumetric, isothermal and adiabatic changes on P–V diagrams and do the first-law bookkeeping for each, including $PV^{5/3} = \text{constant}$ for adiabatic changes of a monatomic gas.
Cyclic processes and heat engines	Find net work as the enclosed area of a cycle; draw the energy-flow diagram of an engine; calculate efficiency $\eta = W / Q_H$.
Carnot cycle	Describe the four strokes of the Carnot cycle and use $\eta_{\text{Carnot}} = 1 - T_C / T_H$ as the maximum possible efficiency.
Second law of thermodynamics	State the Kelvin and Clausius forms, explain their equivalence, and link the law to irreversibility and the arrow of time.
Entropy	Use $\Delta S = \Delta Q / T$ and $S = k_B \ln \Omega$; explain why the entropy of an isolated system (and of the universe) never decreases, in terms of microstates.

Exam note: B.4 appears only in **Higher Level** papers. It is examined together with B.1–B.3 (thermal energy transfer, gas laws, kinetic theory), so keep $PV = nRT$ and $U = (3/2)nRT$ at your fingertips throughout this topic.

1. Systems, surroundings and internal energy

Thermodynamics tracks energy as it moves between a **system** (for us, almost always a fixed mass of ideal gas in a cylinder with a piston) and its **surroundings** (everything else: the piston, the walls, the room). Only two kinds of energy transfer cross the boundary:

- **Heat Q** — energy transferred because of a temperature difference (through the walls).
- **Work W** — energy transferred mechanically, by the gas pushing the piston (or the piston pushing the gas).

The energy stored inside the system is its **internal energy U** : for an ideal gas, the total random kinetic energy of its molecules (there is no intermolecular potential energy in an ideal gas). U is a **state function**: it depends only on the current state (n , T) of the gas, not on the history of how the gas got there. In contrast, Q and W are **path functions** — they describe transfers, and their values depend on the route taken on the P–V diagram.

Sign conventions (learn these cold)

Quantity	Positive means...	Negative means...
Q	heat flows into the gas	heat flows out of the gas
W	work done by the gas on the surroundings (gas expands)	work done on the gas (gas is compressed)
ΔU	internal energy rises (temperature rises, for an ideal gas)	internal energy falls (temperature falls)

Warning: IB Physics writes the first law as $Q = \Delta U + W$ with W the work done **by** the gas. Chemistry (and many textbooks) use $\Delta U = Q + W$ with W done **on** the gas. Mixing the two conventions is the single most common source of sign errors in this topic — commit to the IB form and state your signs explicitly.

2. Work done by a gas

When a gas at pressure P pushes a piston of area A outward through a small distance d , the force is $F = PA$ and the work done by the gas is $W = Fd = PAd = P\Delta V$. So at **constant pressure**:

$$W = P\Delta V \text{ (constant pressure only)}$$

- Expansion: $\Delta V > 0$, so $W > 0$ — the gas does work on the surroundings.
- Compression: $\Delta V < 0$, so $W < 0$ — the surroundings do work on the gas.
- No volume change: $W = 0$, however much the pressure changes. A gas does no work unless its volume changes.

If the pressure varies during the change, the same argument applied to each small step gives the general result:

$$W = \text{area under the } P\text{--}V \text{ curve between the initial and final volumes}$$

This is why the P – V diagram is the natural picture for thermodynamics: different paths between the same two states enclose different areas, so the work done — and, by the first law, the heat exchanged — depends on the path, even though ΔU does not.

Worked example 1 — work and the first law at constant pressure

A gas held at a constant pressure of 2.0×10^5 Pa expands from $3.0 \times 10^{-3} \text{ m}^3$ to $5.0 \times 10^{-3} \text{ m}^3$ while 1000 J of heat is supplied. Find (a) the work done by the gas, (b) the change in its internal energy.

(a) $W = P\Delta V = 2.0 \times 10^5 \times (5.0 - 3.0) \times 10^{-3} = \textbf{+400 J}$.

(b) First law: $\Delta U = Q - W = 1000 - 400 = \textbf{+600 J}$. The gas warms up: of the 1000 J supplied, 400 J leaves again as work on the piston and 600 J is stored as molecular kinetic energy.

3. The first law of thermodynamics

The first law is conservation of energy written for a gas: the heat supplied to a gas either raises its internal energy or is passed on as work done by the gas.

$$Q = \Delta U + W$$

Every term is in joules and every term carries its own sign from the table in Section 1. A reliable routine: (1) decide the sign of W from whether the volume grows or shrinks; (2) decide the sign of ΔU from whether the temperature rises or falls; (3) let the first law tell you Q — do not guess the direction of heat flow from intuition.

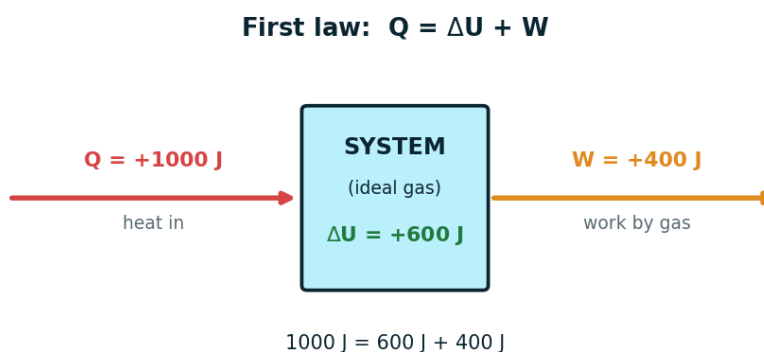


Figure 2. The first law as energy bookkeeping for a gas. Heat $Q = +1000 \text{ J}$ flowing in splits into a rise in internal energy $\Delta U = +600 \text{ J}$ and work $W = +400 \text{ J}$ done by the gas: $Q = \Delta U + W$, i.e. $1000 = 600 + 400 \text{ J}$.

Internal energy of a monatomic ideal gas

From kinetic theory (B.3), the average kinetic energy per molecule is $(3/2)k_B T$, so for n moles:

$$U = (3/2) nRT \quad \Delta U = (3/2) nR\Delta T = (3/2) Nk_B \Delta T$$

Because U depends only on T (for a fixed amount of ideal gas), $\Delta U = 0$ whenever $\Delta T = 0$ — the key fact behind isothermal processes. Using $PV = nRT$, you can also write $U = (3/2)PV$, which is often the fastest route in P – V diagram problems.

Worked example 2 — heating at constant volume

0.50 mol of a monatomic ideal gas is heated in a rigid, sealed container from 300 K to 400 K. Find the work done by the gas, the change in internal energy, and the heat supplied.

Rigid container: $\Delta V = 0$, so $W = 0$.

$$\Delta U = (3/2)nR\Delta T = 1.5 \times 0.50 \times 8.31 \times 100 = \mathbf{+620 \text{ J}}$$
 (623 J unrounded).

First law: $Q = \Delta U + W = 623 + 0 = \mathbf{+620 \text{ J}}$. At constant volume, every joule of heat goes into internal energy.

4. The four processes

Exam questions build almost everything from four idealised processes. For each one, know (i) what is constant, (ii) the shape on a P – V diagram, and (iii) how the first law simplifies.

Process	Constant	P – V shape	First-law bookkeeping	Key relation
Isobaric	pressure	horizontal line	$Q = \Delta U + P\Delta V$ (all three terms non-zero)	$V / T = \text{const}$

Process	Constant	P–V shape	First-law bookkeeping	Key relation
Isovolumetric (isochoric)	volume	vertical line	$W = 0$, so $Q = \Delta U$	$P / T = \text{const}$
Isothermal	temperature	hyperbola (isotherm)	$\Delta U = 0$, so $Q = W$	$PV = \text{const}$
Adiabatic	no heat exchanged	steeper-than-isoth erm curve	$Q = 0$, so $\Delta U = -W$	$PV^{5/3} = \text{const}$ (monatomic)

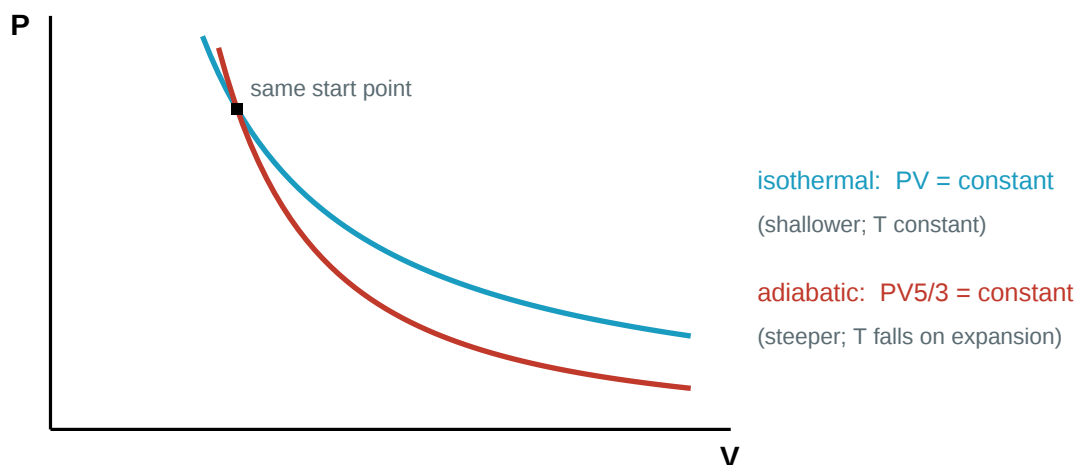
Isothermal changes in practice

To stay at constant temperature the change must be **slow**, in a thin-walled container in good thermal contact with a constant-temperature bath, so heat can leak in or out and keep T fixed. In an isothermal **expansion** the gas does work while $\Delta U = 0$, so an equal amount of heat must flow **in** ($Q = W > 0$); in an isothermal compression the same amount of heat flows out.

Adiabatic changes in practice

Adiabatic means **no heat is exchanged** ($Q = 0$): the change is **fast** (no time for heat flow) and/or the container is well insulated. The gas is thrown back on its own resources: in an adiabatic **expansion** the work done by the gas comes entirely from internal energy, so the gas **cools** ($\Delta U = -W < 0$); an adiabatic **compression heats** the gas — this is why a bicycle pump warms up. For a monatomic ideal gas the path obeys $PV^{5/3} = \text{constant}$ (the exponent $\gamma = 5/3$ applies to monatomic gases only).

Why adiabats are steeper than isotherms



Starting from the same state and expanding by the same amount, the isothermal gas keeps its temperature (heat flows in to replace the energy lost as work), but the adiabatic gas cools. At the same final volume the adiabatic gas is colder, so by $PV = nRT$ its pressure is lower: the adiabat drops away more steeply. Mathematically, $PV = \text{constant}$ falls like $1/V$ while $PV^{5/3} = \text{constant}$ falls like $1/V^{5/3}$.

Worked example 3 — isothermal expansion

An ideal gas expands isothermally at 300 K to twice its original volume, doing 500 J of work in the process. State ΔU , find Q , and describe what happens to the pressure.

Isothermal, ideal gas: $\Delta T = 0$, so $\Delta U = 0$.

First law: $Q = \Delta U + W = 0 + 500 = \mathbf{+500\text{ J}}$ — heat flows into the gas at exactly the rate energy leaves as work.

$PV = \text{constant}$ and V doubles, so the pressure **halves**.

Worked example 4 — adiabatic compression (monatomic)

A monatomic ideal gas at $1.0 \times 10^5 \text{ Pa}$, 300 K, volume $4.0 \times 10^{-3} \text{ m}^3$, is compressed rapidly (adiabatically) to $1.0 \times 10^{-3} \text{ m}^3$. Find the new pressure and temperature.

$$P_1 V_1^{5/3} = P_2 V_2^{5/3}, \text{ so } P_2 = P_1 (V_1/V_2)^{5/3} = 1.0 \times 10^5 \times 4^{5/3} = 1.0 \times 10^5 \times 10.1 \approx \mathbf{1.0 \times 10^6 \text{ Pa}}.$$

Ideal gas law across the change: $T_2 = T_1 \times (P_2 V_2)/(P_1 V_1) = 300 \times (10.1 \times 0.25) = \mathbf{760 \text{ K}}$ (756 K unrounded).

Check with the first law: $Q = 0$, the surroundings do work on the gas ($W < 0$), so $\Delta U = -W > 0$ and the temperature must rise. It does — by a factor of about 2.5.

Exam technique: “Rapid” or “well insulated” in a question means adiabatic ($Q = 0$). “Slow, in thermal contact with surroundings at constant temperature” means isothermal ($\Delta U = 0$). “Rigid container” means isovolumetric ($W = 0$). Translate the words into the zero term first.

5. Cyclic processes

In a **cycle** the gas returns to its starting state, so every state function returns to its starting value. In particular, over one complete cycle:

$$\Delta U_{\text{cycle}} = 0, \text{ so } Q_{\text{net}} = W_{\text{net}} = \text{area enclosed by the loop}$$

- **Clockwise** loop on a P – V diagram: the expansion happens at higher pressure than the compression, so positive work outweighs negative work — net work is done **by** the gas. This is a **heat engine**.
- **Anticlockwise** loop: net work is done **on** the gas, which pumps heat from cold to hot — a refrigerator or heat pump.

Worked example 5 — full bookkeeping for a rectangular cycle

A monatomic ideal gas is taken clockwise around the rectangular cycle $A \rightarrow B \rightarrow C \rightarrow D \rightarrow A$: $A (4.0 \times 10^5 \text{ Pa}, 1.0 \times 10^{-3} \text{ m}^3) \rightarrow B (4.0 \times 10^5 \text{ Pa}, 3.0 \times 10^{-3} \text{ m}^3) \rightarrow C (1.0 \times 10^5 \text{ Pa}, 3.0 \times 10^{-3} \text{ m}^3) \rightarrow D (1.0 \times 10^5 \text{ Pa}, 1.0 \times 10^{-3} \text{ m}^3) \rightarrow \text{back to } A$. Complete the energy table and find the efficiency of the cycle.

Use $U = (3/2)PV$ at each corner: $U_A = 600 \text{ J}$, $U_B = 1800 \text{ J}$, $U_C = 450 \text{ J}$, $U_D = 150 \text{ J}$.

Leg	Type	$W = P\Delta V / \text{J}$	$\Delta U / \text{J}$	$Q = \Delta U + W / \text{J}$
$A \rightarrow B$	isobaric expansion	+800	+1200	+2000
$B \rightarrow C$	isovolumetric cooling	0	-1350	-1350
$C \rightarrow D$	isobaric compression	-200	-300	-500
$D \rightarrow A$	isovolumetric heating	0	+450	+450
Cycle total		+600	0	+600

Checks: ΔU sums to zero (state function); net work +600 J equals the enclosed area $(3.0 \times 10^5 \text{ Pa}) \times (2.0 \times 10^{-3} \text{ m}^3) = 600 \text{ J}$; and $Q_{\text{net}} = W_{\text{net}}$.

Heat is absorbed on legs $D \rightarrow A$ and $A \rightarrow B$: $Q_{\text{in}} = 450 + 2000 = 2450 \text{ J}$. Efficiency $\eta = W_{\text{net}} / Q_{\text{in}} = 600 / 2450 = \mathbf{0.24 (24\%)}$.

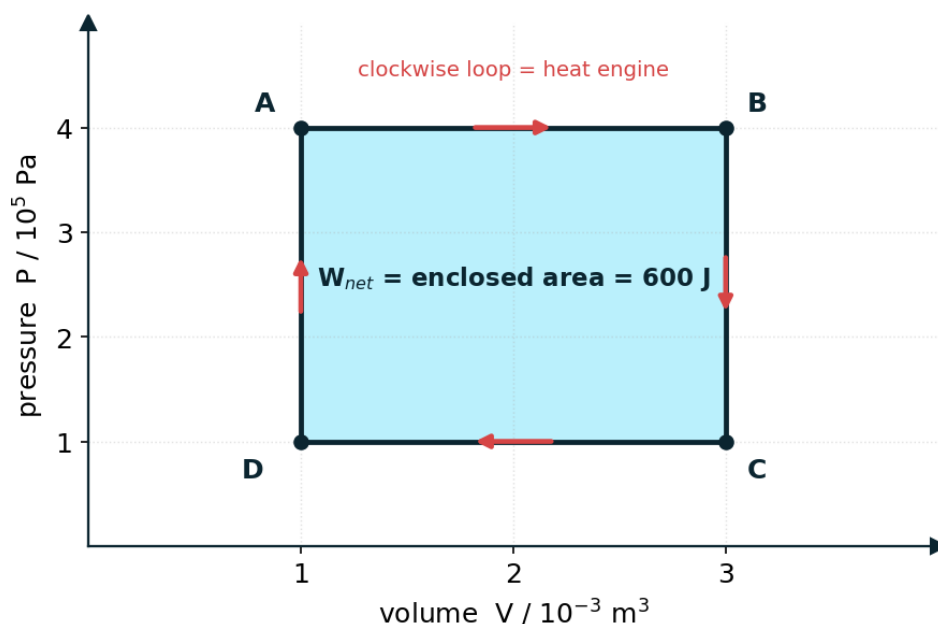
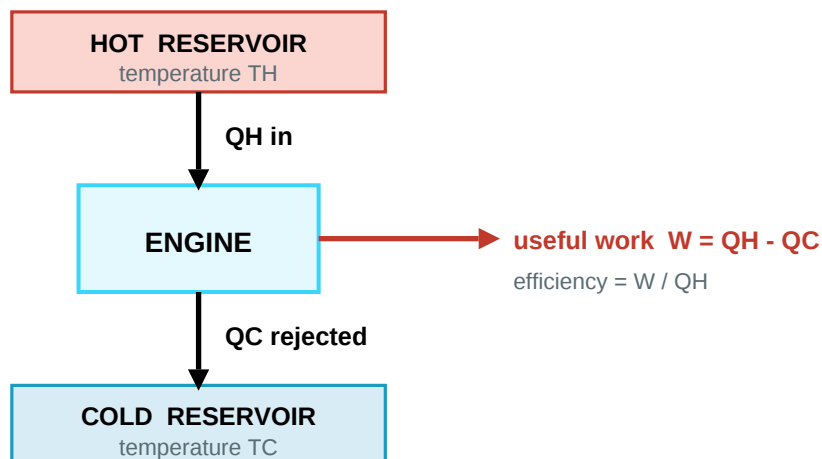


Figure 1. The rectangular cycle $A \rightarrow B \rightarrow C \rightarrow D$ of Worked example 5, traversed clockwise. Net work done by the gas equals the enclosed area, $(3.0 \times 10^5 \text{ Pa})(2.0 \times 10^{-3} \text{ m}^3) = 600 \text{ J}$, which also equals Q_{net} since $\Delta U_{\text{cycle}} = 0$.

Exam technique: In any cycle table, three checks must all pass: each row obeys $Q = \Delta U + W$; the ΔU column sums to zero; and the W and Q columns sum to the same number (the enclosed area). Examiners deliberately leave gaps that only these checks can fill.

6. Heat engines

A heat engine is any device that runs a gas around a cycle to convert heat into useful work: petrol and diesel engines, jet engines, steam turbines in power stations. Every engine has the same energy-flow architecture:



Per cycle, the engine takes heat Q_H from the hot reservoir, delivers useful work W , and — unavoidably — dumps waste heat Q_C into the cold reservoir. Energy conservation gives $W = Q_H - Q_C$, and the **thermal efficiency** is the fraction of the input heat converted to work:

$$\eta = W / Q_H = (Q_H - Q_C) / Q_H = 1 - Q_C / Q_H$$

Because some heat must always be rejected (Section 8), $Q_C > 0$ and $\eta < 1$ for every real engine. Typical values: petrol engine ≈ 0.25 – 0.30 , diesel ≈ 0.35 – 0.40 , combined-cycle power station ≈ 0.60 .

Worked example 6 — engine bookkeeping and power

In each cycle an engine absorbs 500 J from its hot reservoir and rejects 350 J to its cold reservoir. It completes 20 cycles per second. Find the efficiency and the output power.

$$W = Q_H - Q_C = 500 - 350 = 150 \text{ J per cycle.}$$

$$\eta = W / Q_H = 150 / 500 = \mathbf{0.30 \text{ (30\%)}}.$$

$$\text{Power} = 150 \text{ J} \times 20 \text{ s}^{-1} = \mathbf{3.0 \text{ kW.}}$$

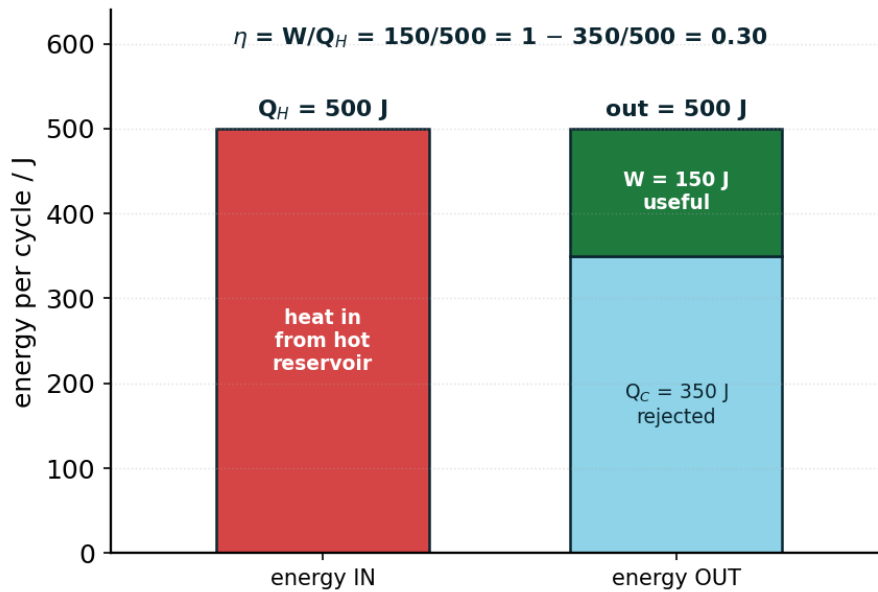


Figure 3. Energy accounting for the engine of Worked example 6. Of $Q_H = 500 \text{ J}$ drawn from the hot reservoir each cycle, $W = 150 \text{ J}$ becomes useful work and $Q_C = 350 \text{ J}$ is rejected to the cold reservoir. The efficiency is $\eta = W/Q_H = 1 - Q_C/Q_H = 0.30$ (30%).

7. The Carnot cycle — the best any engine can do

The **Carnot cycle** is the idealised, reversible cycle of an engine working between just two temperatures, T_H and T_C . Its four strokes alternate isothermal and adiabatic processes:

Stroke	Process	What happens
1	Isothermal expansion at T_H	Gas absorbs Q_H from the hot reservoir and does work; T constant, so $\Delta U = 0$.
2	Adiabatic expansion	No heat flows; the gas keeps doing work at the expense of internal energy and cools from T_H to T_C .
3	Isothermal compression at T_C	Work is done on the gas; it rejects Q_C to the cold reservoir; $\Delta U = 0$.
4	Adiabatic compression	No heat flows; work done on the gas warms it from T_C back to T_H , closing the loop.

Because every step is carried out reversibly (infinitesimally slowly, with no friction and no heat flow across a finite temperature difference), the Carnot cycle wastes nothing that the second law does not force it to waste. **No engine operating between the same two reservoirs can beat it**; any real engine, with its friction and its rapid, irreversible strokes, does worse. For the Carnot cycle the heat ratio equals the temperature ratio ($Q_C/Q_H = T_C/T_H$), so:

$$\eta_{\text{Carnot}} = 1 - T_C / T_H \text{ (temperatures in kelvin!)}$$

Read the formula like an engineer: efficiency improves by running the hot reservoir **hotter** or the cold reservoir **colder**. It reaches 1 only if $T_C = 0 \text{ K}$ (unattainable) — so even a perfect engine cannot convert heat entirely into work.

Worked example 7 — real vs Carnot efficiency

A coal-fired power station runs its turbines with steam at 800 K and rejects heat to a river at 300 K. Its measured overall efficiency is 0.36. (a) Find the Carnot efficiency. (b) What fraction of the theoretical maximum does the plant achieve? (c) A student uses Celsius temperatures (527 °C and 27 °C) directly in the Carnot formula — show why the result is absurd.

(a) $\eta_{\text{Carnot}} = 1 - 300/800 = \mathbf{0.625}$.

(b) $0.36 / 0.625 = \mathbf{0.58}$ — the plant achieves about 58% of the Carnot limit; the rest is lost to friction, turbulence and heat transfer across finite temperature differences.

(c) $1 - 27/527 = 0.95$, which would claim near-perfect conversion of heat to work — and the formula would give a different answer again in Fahrenheit. Only the kelvin scale starts at absolute zero, so **only kelvin temperatures may be used**.

Common pitfall: Using Celsius in $\eta_{\text{Carnot}} = 1 - T_{\text{C}}/T_{\text{H}}$ is the classic B.4 error. Convert to kelvin first (add 273), every single time. Also note the Carnot efficiency uses **reservoir temperatures**, not heats — for a real engine you may only use $\eta = W/Q_{\text{H}}$.

8. The second law of thermodynamics

The first law forbids energy from appearing or disappearing, but it would happily allow a ship to power itself by cooling the ocean, or heat to flow from ice into your warm hand. The **second law** rules out these never-observed processes by giving energy flow a direction. Two equivalent statements are required:

Statement	In words
Kelvin (Kelvin–Planck) form	No process is possible whose sole result is the complete conversion of heat into work. (Every engine must reject waste heat to a cold reservoir: $\eta < 1$.)
Clausius form	No process is possible whose sole result is the transfer of heat from a colder body to a hotter body. (Refrigerators need a work input.)
Entropy form	The entropy of an isolated system — and of the universe as a whole — never decreases: $\Delta S \geq 0$. Real processes increase it.

Why the two statements are equivalent

Violate one and you can violate the other. If a Kelvin-violating engine existed (turning heat entirely into work), its work output could drive an ordinary refrigerator, and the combined machine would move heat from cold to hot with no outside help — violating Clausius. Conversely, a Clausius-violating device could quietly return an engine's waste heat back to the hot reservoir, leaving a machine whose only net effect is turning heat into work — violating Kelvin. Each statement stands or falls with the other.

Irreversibility and the arrow of time

Macroscopic processes are **irreversible**: gases mix but never unmix, hot coffee cools but never reheats itself, a dropped egg never reassembles. Nothing in Newton's laws forbids the reversed motion of every molecule — what forbids it in practice is statistics: the reversed process would take the system from overwhelmingly probable arrangements to fantastically improbable ones. The relentless increase of entropy

is what distinguishes past from future — the thermodynamic **arrow of time**.

9. Entropy

Entropy S is the state function that makes the second law quantitative. It has two faces, and the syllabus requires both.

Macroscopic (thermodynamic) definition

When heat ΔQ enters a system **reversibly** at constant kelvin temperature T , the system's entropy changes by:

$$\Delta S = \Delta Q / T \text{ (unit: J K}^{-1}\text{)}$$

Heat in: $\Delta S > 0$. Heat out: $\Delta S < 0$. The same joule of heat carries more entropy at low temperature than at high temperature — which is exactly why heat flowing from hot to cold **raises** total entropy: the cold body gains more entropy (Q/T_C) than the hot body loses (Q/T_H).

Microscopic (statistical) definition

A **macrostate** is what you can measure from outside (P , V , T). A **microstate** is one complete microscopic arrangement — the position and velocity of every molecule — consistent with that macrostate. If a macrostate can be realised in Ω ways, Boltzmann's formula gives its entropy:

$$S = k_B \ln \Omega$$

Systems drift toward the macrostate with the most microstates simply because there are overwhelmingly more ways to be there. Toss 4 labelled coins: there is only $\Omega = 1$ way to get four heads, but $\Omega = 6$ ways to get two heads and two tails. With 10^{23} molecules instead of 4 coins, the most probable macrostate is not just favoured — departures from it are never observed. A gas released into a doubled volume spreads out because the spread-out macrostate has vastly more microstates, not because any force pushes it.

The entropy of the universe never decreases

For any real (irreversible) process, $\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$; only for a perfectly reversible process is the total change zero. Entropy of a **subsystem** can fall — a freezer turns water into low-entropy ice — but only by exporting more than the difference: the compressor dumps enough heat into the kitchen that the entropy of (food + kitchen) rises. Local order is always paid for with greater disorder elsewhere.

Free expansion — entropy rise without heat

A gas bursts through a valve into an insulated vacuum: no heat enters ($Q = 0$) and the gas pushes against nothing ($W = 0$), so $\Delta U = 0$ and, for an ideal gas, T is unchanged. Yet the process is violently irreversible and entropy **increases**: each molecule now has twice the volume available, so Ω is enormously larger. To calculate ΔS you must use $\Delta Q/T$ along an imaginary **reversible** isothermal path between the same two states — never $\Delta Q/T$ with the actual $Q = 0$.

Worked example 8 — melting ice raises the entropy of the universe

A 2.0 kg block of ice at 0 °C (273 K) melts in a room held at 290 K. Specific latent heat of fusion of ice $L = 3.34 \times 10^5 \text{ J kg}^{-1}$. Find the entropy change of (a) the ice, (b) the room, (c) the universe.

Heat absorbed by ice: $Q = mL = 2.0 \times 3.34 \times 10^5 = 6.68 \times 10^5 \text{ J}$, transferred at the constant melting temperature 273 K.

(a) $\Delta S_{\text{ice}} = +6.68 \times 10^5 / 273 = \mathbf{+2450 \text{ J K}^{-1}}$.

(b) The room loses the same heat at 290 K: $\Delta S_{\text{room}} = -6.68 \times 10^5 / 290 = \mathbf{-2300 \text{ J K}^{-1}}$.

(c) $\Delta S_{\text{universe}} = 2450 - 2300 = \mathbf{+150 \text{ J K}^{-1}} > 0$, as the second law demands. The transfer is irreversible because it crosses a finite temperature gap (290 K $\rightarrow$ 273 K); the closer the two temperatures, the closer the total change is to zero.

Link: $S = k_B \ln \Omega$ explains $\Delta S = \Delta Q/T$: adding heat increases the molecules' kinetic energy spread, multiplying the number of available microstates. The same ΔQ multiplies Ω by a bigger factor when the gas is cold than when it is already hot.

10. Common pitfalls

- Writing the first law with the wrong convention. In IB physics W is work done **by** the gas: $Q = \Delta U + W$. If the gas is compressed, W is negative.
- Using Celsius temperatures in $\eta_{\text{Carnot}} = 1 - T_C/T_H$ or in $\Delta S = \Delta Q/T$. Both demand kelvin.
- Claiming $\Delta U = 0$ for an adiabatic process. Adiabatic means $Q = 0$; it is the **isothermal** process that has $\Delta U = 0$.
- Using $W = P\Delta V$ when the pressure is changing — it only holds for isobaric steps. Otherwise use the area under the curve.
- Using $\Delta U = (3/2)nR\Delta T$ for a diatomic gas, or $PV^{5/3} = \text{constant}$ for a non-monatomic gas. Both are monatomic-only results.
- Forgetting that efficiency uses only the heat **absorbed**: $\eta = W_{\text{net}}/Q_{\text{in}}$, not W_{net} divided by the total heat moved.
- Saying entropy of a system can never decrease. It can (freezer); it is the entropy of the **universe** (system + surroundings) that cannot.
- Applying $\Delta S = \Delta Q/T$ to a free expansion with $Q = 0$ and concluding $\Delta S = 0$. The formula needs a reversible path.

11. Quick reference

Result	Statement
First law	$Q = \Delta U + W$ (Q into gas positive; W by gas positive)
Work (constant P)	$W = P\Delta V$; in general $W = \text{area under the } P\text{--}V \text{ curve}$
Internal energy (monatomic)	$U = (3/2)nRT = (3/2)Nk_B T = (3/2)PV$; $\Delta U = (3/2)nR\Delta T$

Result	Statement
Isobaric / isovolumetric	$W = P\Delta V$ / $W = 0$ so $Q = \Delta U$
Isothermal	$\Delta U = 0$, $Q = W$, $PV = \text{constant}$
Adiabatic (monatomic)	$Q = 0$, $\Delta U = -W$, $PV^{5/3} = \text{constant}$; adiabats steeper than isotherms
Cycle	$\Delta U = 0$; $W_{\text{net}} = Q_{\text{net}}$ = enclosed area; clockwise = engine
Engine efficiency	$\eta = W/Q_H = 1 - Q_C/Q_H$
Carnot limit	$\eta_{\text{Carnot}} = 1 - T_C/T_H$ (kelvin only; maximum possible)
Second law	Kelvin: heat cannot be converted wholly into work. Clausius: heat cannot flow from cold to hot unaided. Entropy: $\Delta S_{\text{universe}} \geq 0$
Entropy	$\Delta S = \Delta Q/T$ (reversible, T in kelvin); $S = k_B \ln \Omega$

12. Test yourself

Attempt these without notes; full answers below.

1. A gas at a constant pressure of 2.5×10^5 Pa is compressed from $6.0 \times 10^{-3} \text{ m}^3$ to $2.0 \times 10^{-3} \text{ m}^3$ while releasing 1500 J of heat. Find the work done by the gas and the change in internal energy.
2. 1.2 mol of a monatomic ideal gas in a rigid container cools from 350 K to 290 K. Find W , ΔU and Q .
3. During a slow isothermal expansion a gas does 240 J of work. State ΔU and find Q , explaining the direction of heat flow.
4. A monatomic ideal gas at 6.4×10^5 Pa and 400 K expands adiabatically to twice its volume. Find the new pressure and the new temperature.
5. An engine of efficiency 0.28 absorbs 900 J from its hot reservoir each cycle. Find the work output and the heat rejected per cycle.
6. An inventor claims an engine operating between 600 K and 300 K with an efficiency of 0.55. Assess the claim.
7. An engine must achieve an efficiency of 0.40 while rejecting heat at 290 K. Find the minimum possible hot-reservoir temperature.
8. 0.50 kg of water is boiled away at 373 K ($L_v = 2.26 \times 10^6 \text{ J kg}^{-1}$). Find the entropy change of the water.
9. A freezer turns water at 0°C into ice at 0°C , decreasing the water's entropy. Explain why this does not violate the second law.
10. An insulated container is divided in two; one half holds an ideal gas, the other is a vacuum. The partition is removed. State Q , W , ΔU and ΔT , and explain — using microstates — why the entropy nevertheless increases.

Answers

1. $W = P\Delta V = 2.5 \times 10^5 \times (2.0 - 6.0) \times 10^{-3} = \mathbf{-1000 \text{ J}}$ (work done on the gas). $Q = -1500 \text{ J}$ (heat released). $\Delta U = Q - W = -1500 - (-1000) = \mathbf{-500 \text{ J}}$: the gas cools despite being compressed, because it loses more heat than it gains as work.

2. Rigid: $W = 0$. $\Delta U = (3/2)nR\Delta T = 1.5 \times 1.2 \times 8.31 \times (-60) = \mathbf{-900 \text{ J}}$ (-898 J unrounded). $Q = \Delta U = \mathbf{-900 \text{ J}}$ (heat flows out).
3. Isothermal ideal gas: $\Delta U = 0$, so $Q = W = \mathbf{+240 \text{ J}}$. Heat flows into the gas: it must absorb energy to keep its temperature (and internal energy) constant while doing work.
4. $P_2 = P_1/2^{5/3} = 6.4 \times 10^5 / 3.17 = \mathbf{2.0 \times 10^5 \text{ Pa}}$. Then $T_2 = T_1(P_2V_2)/(P_1V_1) = 400 \times (2.0/6.4) \times 2 = \mathbf{250 \text{ K}}$ (252 K unrounded) — adiabatic expansion cools the gas.
5. $W = \eta Q_H = 0.28 \times 900 = \mathbf{252 \text{ J}}$; $Q_C = Q_H - W = 900 - 252 = \mathbf{648 \text{ J}}$.
6. $\eta_{\text{Carnot}} = 1 - 300/600 = 0.50$. The claimed 0.55 exceeds the Carnot limit for these reservoirs, so the claim **violates the second law** and must be rejected.
7. $0.40 = 1 - 290/T_H$ gives $T_H = 290/0.60 = \mathbf{480 \text{ K}}$ (483 K unrounded). Any real engine would need T_H hotter still, since it cannot reach the Carnot limit.
8. $Q = mL_v = 0.50 \times 2.26 \times 10^6 = 1.13 \times 10^6 \text{ J}$ at constant 373 K, so $\Delta S = 1.13 \times 10^6 / 373 = \mathbf{+3.0 \times 10^3 \text{ J K}^{-1}}$.
9. The freezer is not isolated. Its compressor does work and ejects heat (the extracted latent heat plus the electrical work) into the warmer room; the room's entropy gain exceeds the water's entropy loss, so $\Delta S_{\text{universe}} > 0$. Local entropy decreases are always allowed when paid for elsewhere.
10. $Q = 0$ (insulated), $W = 0$ (expansion into vacuum — nothing to push against), so $\Delta U = 0$ and, for an ideal gas, $\Delta T = 0$. But each molecule can now be in twice as many places, so the number of microstates Ω rises enormously and $S = k_B \ln \Omega$ increases. The reverse — all molecules spontaneously gathering in one half — is not impossible, merely so improbable that it never happens.