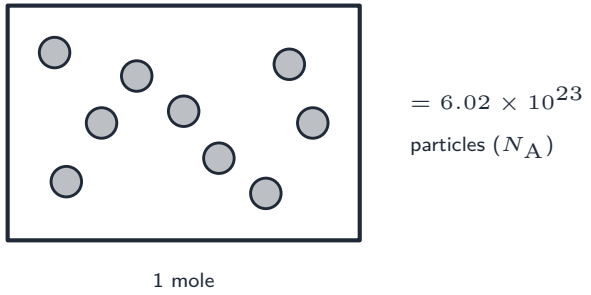
Ideal gases

A-Level Physics

The mole

Amount of substance 物质的量 is an SI base quantity. Its unit is the **mole** 摩尔 (mol) — one of the seven SI base units, with the kilogram, metre, second, ampere and **kelvin** 开尔文 from Topic 1.



One mole contains the Avogadro number of particles

One mole of any substance has a number of particles equal to the **Avogadro constant** 阿伏伽德罗常量:

$$N_{\mathrm{A}} = 6.02 \times 10^{23}\ \mathrm{mol}^{-1}.$$

A "particle" means whatever you are counting — **atoms** 原子 for a **monatomic** 单原子 element like helium, **molecules** 分子 for O_2 or H_2O. Always say what you are counting.

For n moles, the number of particles is $N = nN_{\mathrm{A}}$.

The **molar mass** 摩尔质量 M_{m} is the mass of one mole (kg mol^{-1} or g mol^{-1}). Mass of n moles is $M = nM_{\mathrm{m}}$. Mass of one particle is $m_0 = M_{\mathrm{m}}/N_{\mathrm{A}}$.

The examiner's wording. *The Avogadro constant is the number of atoms (or molecules) in one mole of a substance* — one mark; adding "in 0.012 kg of carbon-12" is accepted but not needed. Asked for "the relationship between N_{A}, R and k", write $k = R/N_{\mathrm{A}}$ (or $R = N_{\mathrm{A}}k$).

Worked example. Oxygen has a molar mass of 32 g mol^{-1}. Find the mass of one oxygen molecule, and the number of molecules in 8.0 g of oxygen.

$m_0 = \dfrac{M_{\mathrm{m}}}{N_{\mathrm{A}}} = \dfrac{0.032}{6.02 \times 10^{23}} = 5.3 \times 10^{-26}$ kg. 8.0 g is $n = 8.0/32 = 0.25$ mol, so $N = nN_{\mathrm{A}} = 1.5 \times 10^{23}$ molecules. Keep molar masses in kg mol^{-1} when the answer is in kilograms — the factor of 1000 is the usual slip.

Equation of state of an ideal gas

Compressed gas cylinders store a fixed mass of gas at high pressure.

An **ideal gas** 理想气体 obeys $pV \propto T$ exactly, where T is the **thermodynamic temperature** 热力学温度.

The **equation of state** 状态方程 can be written two equal ways:

$$pV = nRT \qquad \text{or} \qquad pV = NkT.$$

Here:

- p — **pressure** 压强 (Pa).
- V — **volume** 体积 (m^3).
- T — thermodynamic temperature in kelvin (never °C).
- n — number of moles; N — number of molecules.
- R — **molar gas constant** 摩尔气体常量, $R = 8.31$ J mol^{-1} K^{-1}.
- k — **Boltzmann constant** 玻尔兹曼常量, $k = 1.38 \times 10^{-23}$ J K^{-1}.

Since $N = nN_A$, we get $k = R/N_A$: k is the gas constant **per molecule**, as R is per mole.

The two-mark definition. *An ideal gas is one that obeys $pV = nRT$ (or $pV \propto T$, with T the thermodynamic temperature) at all values of pressure, volume and temperature.* Both marks need the equation (or the proportionality with T named as thermodynamic) **and** "at all values" or "for all p, V and T". Asked to "state the meaning of each symbol in $pV = NkT$": p is the pressure, V the volume, N the **number of molecules**, k the Boltzmann constant and T the thermodynamic temperature — a real gas is nearly ideal at low pressure and high temperature, where its molecules are far apart.

Using the equation of state

List the variables you have, find the unknown, and choose the form that matches your "amount" (moles → nRT; molecules → NkT). Always use SI units: Pa, m^3, K.

Worked example. A cylinder of volume 0.020 m^3 holds gas at 27 °C and a pressure of 2.0×10^5 Pa. How many moles of gas are there? ($R = 8.31$ J mol^{-1} K^{-1}.)

Convert to kelvin: $T = 27 + 273 = 300$ K. Then from $pV = nRT$,

$$n = \frac{pV}{RT} = \frac{(2.0 \times 10^5)(0.020)}{8.31 \times 300} \approx 1.6 \text{ mol}.$$

If a fixed amount of gas changes from state 1 to state 2:

$$\frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2}.$$

Worked example. A fixed mass of gas at 300 K occupies 0.50 m^3. It is heated to 450 K at constant pressure. Find the new volume.

At constant pressure V/T is constant, so

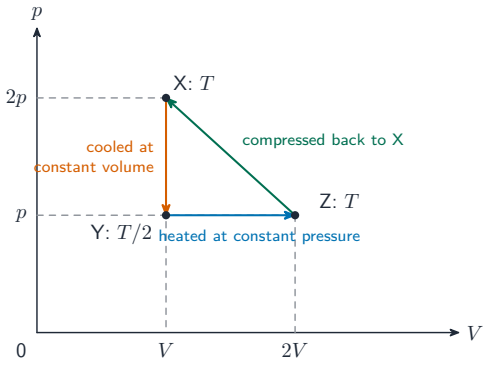
$$V_2 = V_1 \frac{T_2}{T_1} = 0.50 \times \frac{450}{300} = 0.75 \text{ m}^3.$$

Worked example. A sealed vessel of volume 0.0500 m^3 contains 0.0424 kg of an ideal gas at 227 °C and 1.37×10^5 Pa. Find the amount of gas, the mass of one molecule, and the mean-square speed of its molecules.

$T = 227 + 273 = 500$ K. $n = \dfrac{pV}{RT} = \dfrac{1.37 \times 10^5 \times 0.0500}{8.31 \times 500} = 1.65$ mol. The molar mass is $0.0424/1.65 = 0.0257$ kg mol^{-1}, so one molecule has mass $0.0257/(6.02 \times 10^{23}) = 4.3 \times 10^{-26}$ kg. From $\frac{1}{2}m\langle c^2\rangle = \frac{3}{2}kT$, $\langle c^2\rangle = \dfrac{3kT}{m} = \dfrac{3 \times 1.38 \times 10^{-23} \times 500}{4.27 \times 10^{-26}} = 4.8 \times 10^5$ m^2 s^{-2} (an r.m.s. speed of about 700 m s^{-1}).

Worked example. Cylinder X (volume 0.0260 m^3, 0.740 mol) and cylinder Y (volume 0.0180 m^3, 0.320 mol) contain ideal gas and are in thermal equilibrium with each other at 290 K. Find the pressure in each, and explain what happens to the number of molecules in each cylinder if a tap joining them is opened.

$p_X = \dfrac{nRT}{V} = \dfrac{0.740 \times 8.31 \times 290}{0.0260} = 6.86 \times 10^4$ Pa and $p_Y = \dfrac{0.320 \times 8.31 \times 290}{0.0180} = 4.28 \times 10^4$ Pa. Gas flows from the higher pressure (X) to the lower (Y) until the pressures are equal; the temperature is unchanged, so the final pressure is $p = \dfrac{(n_X + n_Y)RT}{V_X + V_Y} = 5.8 \times 10^4$ Pa, and X ends with $n_X = pV_X/RT = 0.63$ mol — it loses about 0.11 mol to Y.



A cycle on a p–V diagram: a vertical line is constant volume, a horizontal line constant pressure, and pV/T is the same at every state

Worked example. A fixed amount of ideal gas at temperature T is in state X, with pressure $2p$ and volume V. It is cooled at constant volume to state Y, where its pressure is p; then heated at constant pressure to state Z, where its volume is $2V$; then returned to X. Find the temperatures at Y and Z, and describe how the internal energy changes round the cycle.

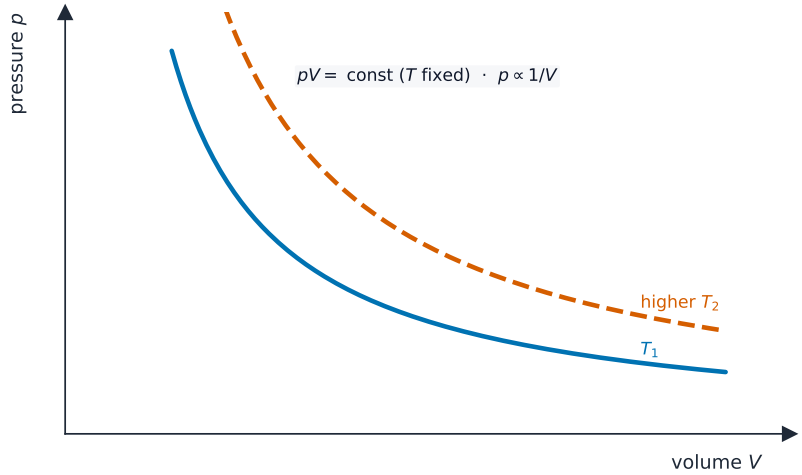
X to Y is at constant volume, so p/T is constant: halving the pressure halves the temperature, $T_Y = T/2$. Y to Z is at constant pressure, so V/T is constant: doubling the volume doubles the temperature, $T_Z = T$. The internal energy of an ideal gas depends only on temperature, so it falls from X to Y (by $\frac{3}{2}nR \cdot T/2$), rises by the same amount from Y to Z, and is unchanged from Z back to X. Read each leg off the diagram before writing an equation: vertical means constant V, horizontal means

constant p.

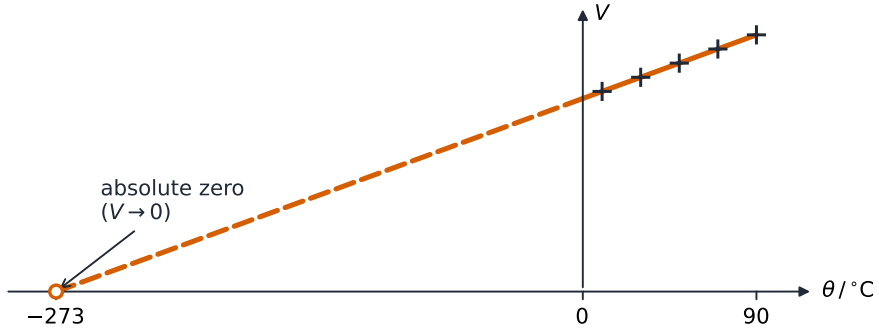
Special cases:

- **constant temperature** (**Boyle's law** 玻意耳定律): $p_1V_1 = p_2V_2$.
- **constant pressure** (**Charles's law** 查理定律): $V/T = \text{constant}$.
- **constant volume** (**pressure law** 气体压强定律): $p/T = \text{constant}$.

A common mistake is using °C instead of K — $pV \propto T$ only holds with T in kelvin.



Boyle's law: at constant temperature pV is constant, so a p–V graph is a hyperbola



$V \propto T$ · Charles: extrapolates to absolute zero

At constant pressure the volume of a gas rises linearly with temperature, reaching zero at absolute zero (Charles's law)

Kinetic theory of gases

A scuba diver breathes compressed gas; its pressure, volume and temperature are all linked.

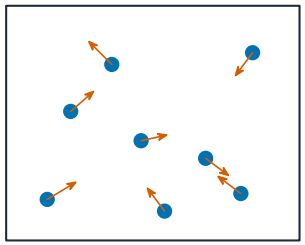
The **kinetic theory** 分子动理论 explains a gas's large-scale behaviour from the **random motion** 无规则运动 of its molecules.

Assumptions

For an ideal gas:

1. a **large number** of identical molecules in continuous random motion.
2. the molecules' own volume is too small to matter compared with the container.

3. the time of each collision is too short to matter compared with the time between collisions.
4. **intermolecular** 分子间 forces are ignored except during collisions (molecules go in straight lines between them).
5. collisions (with the walls and with each other) are **elastic** — an **elastic collision** 弹性碰撞 loses no kinetic energy, so the gas does not cool down by itself.
6. Newton's laws apply.



1. many identical molecules, in continuous **random motion**
2. their own volume is **tiny** next to the container
3. straight lines between hits - intermolecular forces **ignored**
4. collisions are **elastic**: no kinetic energy is lost

poor at very high pressure (volume matters) or very low temperature (forces matter)

The key assumptions of the kinetic theory of an ideal gas

These assumptions become poor at very high pressure (molecular volume matters) or very low temperature (intermolecular forces matter).

As the exam asks it. "State two (or three) basic assumptions of the kinetic theory": choose from *the molecules are in continuous random motion*; *the volume of the molecules is negligible compared with the volume of the gas*; *there are no forces between the molecules except during collisions*; *the collisions are perfectly elastic*; *the time of a collision is negligible compared with the time between collisions*. "State what is meant by an elastic collision": *one in which the total kinetic energy is conserved* (as well as momentum). "Use the assumptions to suggest why the gas at the surface of a star, at very high pressure, is not ideal": the molecules are so close together that their own volume is not negligible compared with the gas volume, and intermolecular forces act between them — the two assumptions that fail when a gas is compressed.

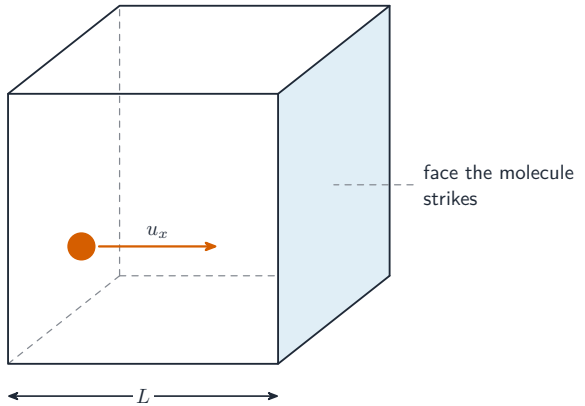
Worked example. A balloon contains 0.40 mol of hydrogen ($m = 3.34 \times 10^{-27}$ kg per molecule) in 9.8×10^{-3} m^3. Estimate the average separation of the molecules, the gravitational force between neighbouring molecules, and comment on the kinetic-theory assumption this tests.

$N = 0.40 \times 6.02 \times 10^{23} = 2.4 \times 10^{23}$ molecules, so each occupies $V/N = 4.1 \times 10^{-26}$ m^3 and the average separation is $d = (V/N)^{1/3} = 3.4 \times 10^{-9}$ m. The gravitational force between two molecules is $F = \dfrac{Gm^2}{d^2} = \dfrac{6.67 \times 10^{-11} \times (3.34 \times 10^{-27})^2}{(3.4 \times 10^{-9})^2} = 6 \times 10^{-47}$ N

— some 10^{20} times smaller than a molecule's own weight ($mg = 3.3 \times 10^{-26}$ N). Forces between molecules really are negligible except during collisions, as the theory assumes.

Pressure of a gas — outline of the derivation

Take a cubic box of side L with N molecules, each of mass m. Look at one molecule moving along the x-axis with velocity u_1.



The pressure derivation considers one molecule's velocity component u_x normal to a face of a cube of gas

- **one collision with the right wall**: velocity reverses to $-u_1$, change in **momentum** 动量 $\Delta p_x = -2mu_1$. By Newton's third law the wall gets an **impulse** 冲量 of $+2mu_1$.
- **time between hits on that wall**: travel $2L$ there and back, so $\Delta t = 2L/u_1$.
- **average force from this molecule**: $F_1 = \Delta p/\Delta t = mu_1^2/L$.
- **add over all molecules**: $F = (Nm/L)\langle u_x^2 \rangle$, where $\langle u_x^2 \rangle$ is the **mean square** 均方 of the x-velocity.
- **pressure**: $p = F/L^2 = Nm\langle u_x^2 \rangle / V$.

In 3-D, by symmetry $\langle u_x^2 \rangle = \frac{1}{3}\langle c^2 \rangle$, where $\langle c^2 \rangle$ is the **mean-square speed** 均方速率. So

$$pV = \tfrac{1}{3} Nm\langle c^2 \rangle .$$

"Explain how molecular movement causes the pressure exerted by a gas" (3 marks). The molecules move randomly and collide with the walls of the container; at each collision a molecule's momentum changes (it rebounds), so by Newton's second

law the wall exerts a force on it, and by the third law it exerts an equal force on the wall; the very many collisions each second produce a steady total force on the wall, and the pressure is that force per unit area. The syllabus phrase "a simple model considering one-dimensional collisions" means the derivation above: it is sufficient to follow one molecule bouncing between two opposite faces and then average.

The density form. Since Nm is the total mass of the gas and Nm/V is its density ρ, the same result reads $p = \frac{1}{3}\rho\langle c^2\rangle$ — the version to use when a question gives a density instead of N and m.

Worked example. An ideal gas at a pressure of 1.6×10^5 Pa has a density of 1.9 kg m^{-3}. Show that the r.m.s. speed of its molecules is about 500 m s^{-1}.

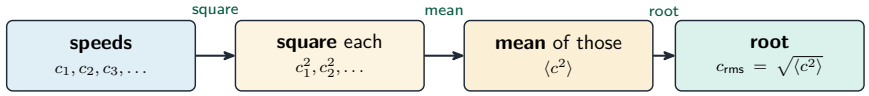
$\langle c^2\rangle = \dfrac{3p}{\rho} = \dfrac{3 \times 1.6 \times 10^5}{1.9} = 2.53 \times 10^5$ m^2 s^{-2}, so $c_{\text{r.m.s.}} = \sqrt{2.53 \times 10^5} = 503$ m s$^{-1} \approx$ 500 m s^{-1}. In a "show that", keep an extra figure (503) before comparing with the value given.

Root-mean-square speed

The square root of $\langle c^2\rangle$ is the **root-mean-square** 均方根 (r.m.s.) speed:

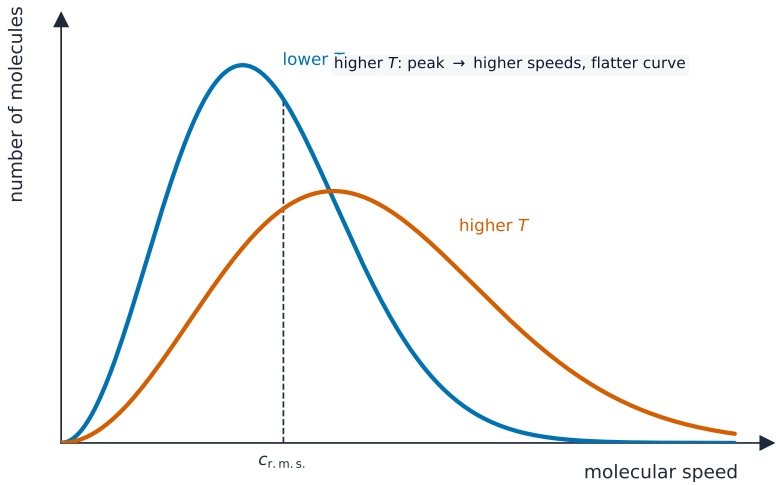
$$c_{\text{r.m.s.}} = \sqrt{\langle c^2\rangle}.$$

It is a useful single measure of how fast the molecules move, slightly larger than the mean speed (squaring weights fast molecules more).

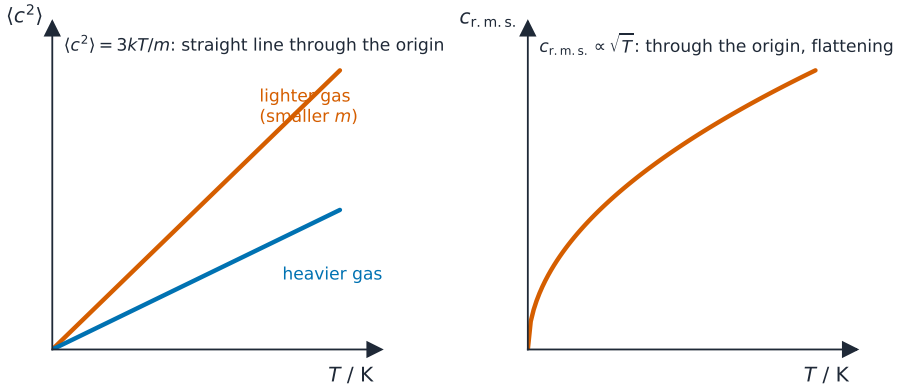


read the name **backwards**: **r**oot of the **m**ean of the **s**quares - squaring weights fast molecules more, so c_{rms} is slightly above the mean speed

Root-mean-square speed: square each speed, take the mean, then the square root



The spread of molecular speeds: a higher temperature broadens the curve and shifts it to faster speeds



The two graphs the exam asks you to sketch: $\langle c^2\rangle \propto T$ is a straight line through the origin, so $c_{r.m.s.}$ rises as $\sqrt{T}$

Average translational kinetic energy

Compare the two expressions for pV:

$$pV = NkT \quad \text{and} \quad pV = \tfrac{1}{3}Nm\langle c^2\rangle.$$

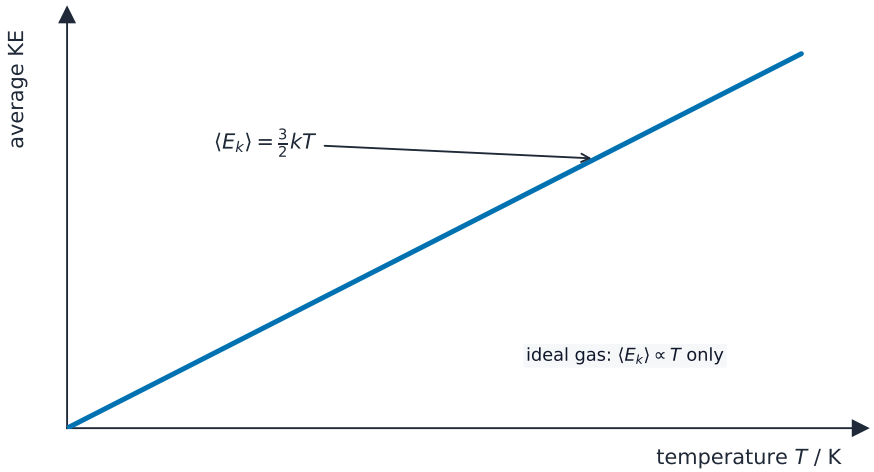
Set them equal, cancel N, and multiply by $\frac{3}{2}$:

$$\tfrac{3}{2}kT = \tfrac{1}{2}m\langle c^2\rangle.$$

The right side is the **average translational kinetic energy** 平动动能 $\langle E_\text{k}\rangle$ of one molecule. So

$$\langle E_\text{k}\rangle = \tfrac{1}{2}m\langle c^2\rangle = \tfrac{3}{2}kT.$$

This is a key result: **the average translational kinetic energy of an ideal-gas molecule depends only on the thermodynamic temperature**, not on the type of gas or its pressure.



Average molecular KE is proportional to thermodynamic temperature: $\langle E_k\rangle = \frac{3}{2}kT$

Worked example. Find the root-mean-square speed of oxygen molecules at 300 K. (Mass of one O_2 molecule $= 5.3\times10^{-26}$ kg, $k = 1.38\times10^{-23}$ J K^{-1}.)

From $\frac{1}{2}m\langle c^2\rangle = \frac{3}{2}kT$, the mean-square speed is $\langle c^2\rangle = 3kT/m$:

$$c_\text{r.m.s.} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3(1.38\times10^{-23})(300)}{5.3\times10^{-26}}} \approx 480 \text{ m s}^{-1}.$$

Worked example. The surface of the Moon reaches about 400 K in sunlight. Calculate the r.m.s. speed of hydrogen molecules ($m = 3.34\times10^{-27}$ kg) at this temperature,

and use the Moon's escape speed of 2.4 km s^{-1} to suggest why the Moon has no hydrogen atmosphere.

$c_\text{r.m.s.} = \sqrt{\dfrac{3kT}{m}} = \sqrt{\dfrac{3\times1.38\times10^{-23}\times400}{3.34\times10^{-27}}} = 2.2\times10^3$ m s^{-1}. This r.m.s. speed is close to the escape speed, and the speeds are spread widely about it, so a large fraction of the molecules move faster than 2.4 km s^{-1} at any moment and escape; over time the hydrogen is lost.

Worked example. The gas at the surface of a star is mainly hydrogen atoms ($m = 1.67\times10^{-27}$ kg) with an r.m.s. speed of 9300 m s^{-1}. Find the temperature of the surface.

$$T = \frac{m\langle c^2\rangle}{3k} = \frac{1.67\times10^{-27}\times9300^2}{3\times1.38\times10^{-23}} = 3.5\times10^3 \text{ K}.$$

Worked example. For a fixed sample of gas, a graph of pV against kT is a straight line through the origin of gradient 7.2×10^{22}. When $pV = 270$ J the r.m.s. speed of the molecules is 1900 m s^{-1}. Find the number of molecules and the mass of one molecule in u.

From $pV = NkT$ the gradient is $N = 7.2\times10^{22}$. From $pV = \frac{1}{3}Nm\langle c^2\rangle$: $m = \dfrac{3pV}{N\langle c^2\rangle} = \dfrac{3\times270}{7.2\times10^{22}\times1900^2} = 3.1\times10^{-27}$ kg $= \dfrac{3.1\times10^{-27}}{1.66\times10^{-27}} = 1.9$ u — hydrogen molecules, within the rounding.

Comparing gases and samples. At the same temperature every gas has the same average kinetic energy per molecule, so $\langle c^2\rangle \propto 1/m$: hydrogen ($M_\text{m} = 2$) and oxygen ($M_\text{m} = 32$) have $\dfrac{c_\text{H}}{c_\text{O}} = \sqrt{\dfrac{32}{2}} = 4$. Two samples at the same T — X with N molecules of mass m in volume V, Y with $2N$ molecules of mass $2m$ in volume $2V$ — have the *same pressure* ($p = NkT/V$ and both N and V double), the same average kinetic energy per molecule, but Y's molecules have half the mean-square speed ($3kT/2m$) and Y has twice the internal energy (twice as many molecules).

Consequences

- **doubling the absolute temperature doubles the average KE** of each molecule, so $\langle c^2\rangle$ doubles and $c_\text{r.m.s.}$ grows by $\sqrt{2}$.
- for **two gases at the same temperature**, the lighter gas has a larger $\langle c^2\rangle$. Hydrogen molecules move faster on average than oxygen molecules in the same room.
- **total translational KE** of N molecules: $\frac{3}{2}NkT = \frac{3}{2}nRT$.

Internal energy of an ideal gas

For an ideal gas the molecules are point particles with no intermolecular potential energy and (in this simple model) no rotation or vibration. So the **internal energy** 内能 is just the total **kinetic energy** 动能:

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

So the internal energy of an ideal gas is proportional to the thermodynamic temperature — doubling T doubles U.

As the exam asks it. "Use one of the basic assumptions to explain what can be deduced about the potential energy of the molecules": there are *no forces between the molecules* (except in collisions), so there is *no potential energy* associated with their separation — the random-motion energy is entirely kinetic. "Explain why the internal energy of an ideal gas is directly proportional to thermodynamic temperature" (2 marks): the internal energy is the sum of the kinetic and potential energies of the molecules; the potential energy is zero (no intermolecular forces), and the average kinetic energy of a molecule is $\frac{3}{2}kT$, proportional to T; so the total, $U = \frac{3}{2}NkT$, is proportional to T. "Derive $\frac{3}{2}kT$" (2 marks): equate $pV = NkT$ with $pV = \frac{1}{3}Nm\langle c^2\rangle$, cancel N, and rearrange to $\frac{1}{2}m\langle c^2\rangle = \frac{3}{2}kT$ — show the cancelling and the factor of $\frac{3}{2}$.

Worked example. A sample of 0.26 m^3 of an ideal gas is at 2.0×10^5 Pa and 290 K. Find the number of molecules, the average translational kinetic energy of a molecule, and the internal energy of the gas.

$N = \dfrac{pV}{kT} = \dfrac{2.0 \times 10^5 \times 0.26}{1.38 \times 10^{-23} \times 290} = 1.3 \times 10^{25}$. $\langle E_\mathrm{k}\rangle = \frac{3}{2}kT = 1.5 \times 1.38 \times 10^{-23} \times 290 = 6.0 \times 10^{-21}$ J. $U = N\langle E_\mathrm{k}\rangle = 1.3 \times 10^{25} \times 6.0 \times 10^{-21} = 7.8 \times 10^4$ J — or directly $U = \frac{3}{2}pV = 7.8 \times 10^4$ J, a neat check.

Changing pressure at fixed temperature

Doubling p at fixed T (by squeezing the gas to half its volume) does **not** change $\langle E_\mathrm{k}\rangle$ — that depends only on T. There are more wall collisions per second, but each molecule has the same average kinetic energy.

Definitions the examiner accepts

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

Term	Definition
mole	the amount of substance containing a number of particles equal to the Avogadro constant
Avogadro constant	the number of atoms or molecules in one mole of a substance, 6.02×10^{23} mol^{-1}
ideal gas	a gas that obeys $pV = nRT$ (equivalently $pV \propto T$, T thermodynamic) at all values of p, V and T
Boltzmann constant	the gas constant per molecule, $k = R/N_\mathrm{A}$
elastic collision	a collision in which the total kinetic energy is conserved
mean-square speed	the mean of the squares of the speeds of the molecules, $\langle c^2\rangle$
root-mean-square speed	the square root of the mean-square speed, $c_\mathrm{r.m.s.} = \sqrt{\langle c^2\rangle}$
average translational kinetic energy of a molecule	$\frac{1}{2}m\langle c^2\rangle = \frac{3}{2}kT$, depending only on thermodynamic temperature
internal energy of an ideal gas	the total kinetic energy of its molecules, $\frac{3}{2}NkT$, since there is no potential energy

Exam tips

- Use $pV = nRT$ (n in mol) or $pV = NkT$ (N molecules), with temperature in **kelvin** and volume in m^3 (1 cm^3 = 10^{-6} m^3).
- Learn the **kinetic-theory assumptions** word for word (random motion, negligible molecular volume, no intermolecular forces except in collisions, elastic collisions, negligible collision time), and know which two fail at high pressure.
- Mean translational KE = $\frac{3}{2}kT$ — it depends **only on temperature**; at the same T a lighter molecule is faster, $\langle c^2\rangle \propto 1/m$.
- For a "show that" about pressure, give the chain: collisions with the wall, change of momentum, force (Newton's second and third laws), force per unit area.
- $p = \frac{1}{3}\rho\langle c^2\rangle$ when a density is given; $U = \frac{3}{2}NkT = \frac{3}{2}pV$ when the internal energy is asked.

Common mistakes

- Using °C in $pV = nRT$ or in $\langle E_\mathrm{k}\rangle = \frac{3}{2}kT$. Convert first; a temperature *ratio* only works in kelvin.
- Defining an ideal gas by "obeys $pV = nRT$" alone. Add "at all values of p, V and T".
- Confusing n (moles) with N (molecules), or R with k. $N = nN_\mathrm{A}$ and $k = R/N_\mathrm{A}$.

- Giving "molecules move randomly" as the reason for pressure. The mark is for the change of momentum at the wall and the resulting force per unit area.
- Sketching $c_{\text{r.m.s.}}$ against T as a straight line. $\langle c^2 \rangle$ is linear in T; $c_{\text{r.m.s.}}$ rises as $\sqrt{T}$.
- Saying a molecule's kinetic energy changes when the pressure is doubled at constant temperature. Only the number of collisions per second changes.