

15.3.1 Deriving $pV = \text{one third } Nm \text{ mean-square speed, and what it says about temperature}$

Name: _____ Class: _____ Date: _____

Total: 31 marks

KEY WORDS root-mean-square 均方根 • kinetic energy 动能
 • translational kinetic energy 平动动能 • kinetic theory 分子动理论
 • kinetic theory of gases 气体分子运动论

Objective

Sheet 15.3 quoted $pV = \frac{1}{3}Nm\langle c^2 \rangle$ and substituted into it. This sheet is the part the exam sets its longest questions on: **deriving** that equation from one molecule bouncing in a box, **deducing** from it that the mean translational **kinetic energy** of a molecule is $\frac{3}{2}kT$, and using that result to compare **root-mean-square speeds** 均方根速率 between gases and between temperatures. This sheet covers syllabus 15.3.

You must be able to:

- state the basic **assumptions** 假设 of the **kinetic theory of gases** 气体分子运动论
- explain how molecular movement causes the pressure of a gas, and **derive** and use $pV = \frac{1}{3}Nm\langle c^2 \rangle$
- understand that the root-mean-square speed is $c_{\text{r.m.s.}} = \sqrt{\langle c^2 \rangle}$
- compare $pV = \frac{1}{3}Nm\langle c^2 \rangle$ with $pV = NkT$ to deduce that the mean translational kinetic energy of a molecule is $\frac{3}{2}kT$, and use that expression

1 Worked examples

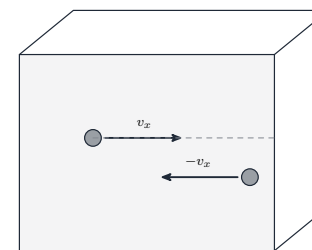
Study these first. Each one shows a **method** that a question later on this sheet needs.

- The assumptions, and what each one is for

assumption	why the derivation needs it
the gas contains a large number of molecules in random motion	so that averages are meaningful and no direction is special
the volume of the molecules is negligible compared with the volume of the container	so the molecules travel the full distance L between walls
collisions are perfectly elastic	so the speed is unchanged and the momentum change is exactly $2mv_x$
the time of a collision is negligible compared with the time between collisions	so the force can be averaged over the round trip
there are no forces between molecules except during collisions	so a molecule travels in a straight line at constant velocity between walls

- Quote them as **properties of the model**, not of a real gas. The exam wants the assumptions, not a description of a gas.

■ The derivation, five steps



side L , so volume $V = L^3$

1 one collision with this wall reverses v_x , so the molecule's momentum changes by $2mv_x$, and by Newton's third law the wall receives $2mv_x$

2 it next hits the same wall after travelling $2L$, so the time between collisions is $\Delta t = \frac{2L}{v_x}$

3 so the average force on the wall is $F = \frac{2mv_x}{2L/v_x} = \frac{mv_x^2}{L}$

4 Pressure is F/L^2 , so one molecule contributes $\frac{mv_x^2}{L^3}$; adding N molecules gives $p = \frac{Nm\langle v_x^2 \rangle}{V}$. 5 No direction is special, so $\langle v_x^2 \rangle = \frac{1}{3}\langle c^2 \rangle$, and therefore $pV = \frac{1}{3}Nm\langle c^2 \rangle$.

- One collision reverses v_x , so the molecule's momentum changes from $+mv_x$ to $-mv_x$: a change of $2mv_x$. By Newton's third law the wall receives the same.
- The molecule crosses the box and comes back before hitting the same wall again, a distance $2L$, so the time between collisions is $\Delta t = \frac{2L}{v_x}$.
- Force is rate of change of momentum:

$$F = \frac{2mv_x}{2L/v_x} = \frac{mv_x^2}{L}$$

- Pressure is force per unit area, and the wall has area L^2 , so one molecule con-

tributes $\frac{mv_x^2}{L^3}$. For N molecules, using the **mean** of v_x^2 .

$$p = \frac{Nm\langle v_x^2 \rangle}{V}$$

5. The motion is **random**, so no direction is special and $\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle$. Since $c^2 = v_x^2 + v_y^2 + v_z^2$, this gives $\langle v_x^2 \rangle = \frac{1}{3}\langle c^2 \rangle$, and so

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

- $\langle c^2 \rangle$ is the **mean-square speed** – square every molecule's speed, then average. The **root-mean-square speed** is $c_{\text{r.m.s.}} = \sqrt{\langle c^2 \rangle}$, and it is *not* the mean speed.

■ From the equation to the temperature

Compare the derived result with the ideal-gas equation written per molecule:

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

so $\frac{1}{3}Nm\langle c^2 \rangle = NkT$, and multiplying both sides by $\frac{3}{2N}$:

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

- The left side is the **mean translational kinetic energy** of one molecule. So **thermodynamic temperature is a measure of the mean translational kinetic energy of the molecules** – that sentence is the point of the whole topic.
- It contains **no reference to the gas**: at the same temperature, every ideal gas has the same mean molecular kinetic energy, whatever the molecules are made of.

■ Three consequences worth having ready

$$\langle c^2 \rangle = \frac{3kT}{m} \quad \Rightarrow \quad c_{\text{r.m.s.}} = \sqrt{\frac{3kT}{m}}$$

question	answer
two gases at the same temperature	same mean kinetic energy, so $c_{\text{r.m.s.}} \propto \frac{1}{\sqrt{m}}$: the lighter molecule is faster
the same gas at double the temperature	$c_{\text{r.m.s.}} \propto \sqrt{T}$, so the speed rises by a factor of $\sqrt{2}$, not 2
heating at constant volume	the molecules move faster, so they hit the walls more often and with a larger momentum change each time; the average force, and so the pressure, rises

- Both halves of that last answer are needed. “They move faster so they hit harder” is worth one mark of two.

2 Practice

Now use the methods above.

2.1 State **three** assumptions of the kinetic theory of gases. [3]

2.2 Explain why the momentum change of a molecule rebounding from a wall is $2mv_x$ and not mv_x . [2]

2.3 Show that the time between successive collisions of one molecule with the **same** wall of a cubical box of side L is $\frac{2L}{v_x}$. [2]

2.4 State what is meant by the **mean-square speed** and by the **root-mean-square speed**. [2]

2.5 Explain why $\langle v_x^2 \rangle = \frac{1}{3}\langle c^2 \rangle$. [2]

3 Exam-style questions

3.1 The thermodynamic temperature of an ideal gas is doubled. The root-mean-square speed of its molecules is multiplied by [1]

- | | |
|---|----------------------|
| A | $\sqrt{2}$ |
| B | 2 |
| C | 4 |
| D | $\frac{1}{\sqrt{2}}$ |

3.2 The kinetic theory gives $pV = \frac{1}{3}Nm\langle c^2 \rangle$, and the ideal-gas equation gives $pV = NkT$.

(a) Use these to show that the mean translational kinetic energy of a molecule is $\frac{3}{2}kT$. [3]

(b) Calculate the mean translational kinetic energy of a molecule at 27 °C. Take $k = 1.38 \times 10^{-23} \text{ J K}^{-1}$. [2]

(c) State what this result shows about the meaning of thermodynamic temperature. [1]

3.3 Helium, of molar mass 4.0 g mol^{-1} , and oxygen, of molar mass 32 g mol^{-1} , are both held at 300 K. Take $N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$ and $k = 1.38 \times 10^{-23} \text{ J K}^{-1}$.

(a) Calculate the mass of one helium atom. [2]

(b) Calculate the root-mean-square speed of a helium atom at 300 K. [3]

(c) Without calculating it exactly, state and explain how the root-mean-square speed of an oxygen molecule at the same temperature compares with that of a helium atom. [3]

(d) The helium is now heated to 600 K. State and explain the effect on the root-mean-square speed of its atoms. [2]

(e) Use the kinetic theory to explain why the pressure of a fixed mass of gas increases when it is heated at constant volume. [3]

Solutions

Each answer shows the steps, then the **result**.

2.1

- any **three** of: a large number of molecules in **random** motion; the **volume of the molecules** is negligible compared with the volume of the container; collisions are **perfectly elastic**; the duration of a collision is negligible compared with the time between collisions; there are **no forces** between molecules except during collisions

2.2

- momentum is a **vector**: the molecule arrives with $+mv_x$ and leaves with $-mv_x$
- the **change** is $(-mv_x) - (+mv_x) = -2mv_x$, so its magnitude is $2mv_x$

2.3

- after rebounding, the molecule must cross the box and return before it can hit the same wall again, a distance of $2L$
- its component of velocity in that direction is v_x and is unchanged in magnitude, so

$$\Delta t = \frac{\text{distance}}{\text{speed}} = \frac{2L}{v_x}$$

2.4

- the **mean-square speed** $\langle c^2 \rangle$ is the average of the squares of the speeds of all the molecules
- the **root-mean-square speed** is the square root of that, $c_{\text{r.m.s.}} = \sqrt{\langle c^2 \rangle}$

2.5

- the motion is **random**, so no direction is preferred and $\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle$
- since $c^2 = v_x^2 + v_y^2 + v_z^2$, taking means gives $\langle c^2 \rangle = 3\langle v_x^2 \rangle$, so $\langle v_x^2 \rangle = \frac{1}{3}\langle c^2 \rangle$

3.1 A

- $c_{\text{r.m.s.}} = \sqrt{\frac{3kT}{m}}$, so $c_{\text{r.m.s.}} \propto \sqrt{T}$
- doubling T multiplies the speed by $\sqrt{2}$. **B** is the standard error – it is the mean *kinetic energy* that doubles, not the speed

3.2

(a)

- both expressions equal pV , so set them equal

$$\frac{1}{3}Nm\langle c^2 \rangle = NkT$$

- the N cancels

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

- multiply both sides by $\frac{3}{2}$

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

(b)

- convert the temperature to kelvin, $T = 300 \text{ K}$

$$E = \frac{3}{2}kT = 1.5 \times 1.38 \times 10^{-23} \text{ J K}^{-1} \times 300 \text{ K} = \mathbf{6.2 \times 10^{-21} \text{ J}}$$

(c)

- thermodynamic temperature is a measure of the **mean translational kinetic energy** of the molecules, and it is the same for every ideal gas at that temperature

3.3

(a)

- one mole contains N_A atoms

$$m = \frac{4.0 \times 10^{-3} \text{ kg mol}^{-1}}{6.02 \times 10^{23} \text{ mol}^{-1}} = \mathbf{6.6 \times 10^{-27} \text{ kg}}$$

(b)

- rearrange $\frac{1}{2}m\langle c^2 \rangle = \frac{3}{2}kT$

$$\langle c^2 \rangle = \frac{3kT}{m} = \frac{3 \times 1.38 \times 10^{-23} \text{ J K}^{-1} \times 300 \text{ K}}{6.6 \times 10^{-27} \text{ kg}} = 1.87 \times 10^6 \text{ m}^2 \text{ s}^{-2}$$

$$c_{\text{r.m.s.}} = \sqrt{1.87 \times 10^6 \text{ m}^2 \text{ s}^{-2}} = \mathbf{1.4 \times 10^3 \text{ m s}^{-1}}$$

(c)

- at the same temperature both gases have the **same mean translational kinetic energy**, $\frac{3}{2}kT$
- so $\frac{1}{2}m\langle c^2 \rangle$ is the same for both, and $c_{\text{r.m.s.}} \propto \frac{1}{\sqrt{m}}$
- an oxygen molecule has **eight times** the mass, so its r.m.s. speed is $\frac{1}{\sqrt{8}}$ of the helium value – about **2.8 times smaller**, roughly 480 m s^{-1}

(d)

- the r.m.s. speed **increases by a factor of $\sqrt{2}$** , to about $1.9 \times 10^3 \text{ m s}^{-1}$
- because $c_{\text{r.m.s.}} \propto \sqrt{T}$, and the thermodynamic temperature has doubled

(e)

- heating raises the mean translational kinetic energy, so the molecules move **faster** on average
- they therefore hit the walls **more frequently**
- and each collision produces a **greater change of momentum**; both effects raise the average force on the walls, and with the area unchanged the pressure rises