20. a. Explain how the kinetic molecular model of an ideal gas accounts for the relation between the temperature of a gas and the average kinetic energy of its molecules.
    b. A gas is kept in a container. Its pressure is reduced by pumping some of the gas out. Does the temperature of the gas fall?
    c. The density of helium at STP is 0.1785 kg/m³. Find the rms speed of helium atoms at 30 °C. (STP pressure 1.01×10^5 Pa.)

21. A given mass of gas has a volume of 640 cm³ at 47 °C and a pressure of 75 cm of mercury. At what temperature will its pressure be doubled, if it is heated at constant volume?

22. Find the number of moles and the number of molecules in one cubic meter of air at STP. ($R = 8.31$ J/(mol K), $N_A = 6.02 \times 10^{23}$ mol^{-1}, STP 273 K and 1.01×10^5 Pa.)

23. Helium gas of volume 2.60 L, at a pressure of 1.30 atm and a temperature of 41.0 °C, is warmed until both its pressure and its volume are doubled.
    a. What is its final temperature?
    b. How many grams of helium are there? (Molar mass of helium 4.00 g/mol, $R = 8.314$ J/(mol K), 1 atm = 1.01×10^5 Pa.)

24. A partly filled balloon holds 500 m³ of helium at 27 °C and 1 atm. It rises, and its volume grows to 900 m³ at a height where the temperature is −3 °C. What is the pressure of the helium there?

25. Find the density of methane at 20 °C and a pressure of 5 atm. (Molar mass of methane 16 g/mol, $R = 8.314$ J/(mol K), 1 atm = 1.013×10^5 Pa.)

26. A chamber of volume 1×10^{-3} m³ contains 1×10^{25} molecules of a gas. Each molecule has a mass of 2.7×10^{-28} kg, and their rms speed is 400 m/s. Find the pressure of the gas.



Figure 13.6 *A weather balloon being filled before its launch. It leaves the ground far from fully stretched; as it rises into thinner air, the gas inside expands until the balloon is several times wider and bursts, high in the stratosphere.*
Photo: Photouploadforscience, CC BY 4.0

A companion to your textbook, not a replacement for it: study from the book your school uses, and where the two differ, follow your teacher. Found a mistake? Please tell us.

Unit 13

Ideal Gas

This unit online, with its interactives:
science-playground.com/s/11f13

Pump up a bicycle tyre in Pokhara and ride it over the pass to Kathmandu; seal a packet of biscuits in the Tarai and open it at Namche, and it has swollen like a pillow. A gas changes its volume, its pressure and its temperature all together, and very simply: one short equation connects the three for every gas there is. Why every gas, whatever its molecules are made of?

This unit answers that question twice. First from the outside, from measurements: the gas laws join into the **ideal gas equation**, $PV = nRT$. Then from the inside: picture a gas as a swarm of tiny molecules flying about and bouncing off the walls, apply Newton's laws to one of them, and out comes the pressure of the gas, how fast its molecules move, and what temperature really is.

13.1 Introduction

A STORY FROM SCIENCE

Robert Boyle and his "spring of the air"

Robert Boyle (1627–1691) was born at Lismore Castle in Ireland, the fourteenth child of the Earl of Cork, one of the richest men in the British Isles. His wealth let him spend his life on experiments. With his assistant Robert Hooke he built one of the first good air pumps, and with it showed that sound doesn't cross a vacuum, that a candle goes out and a mouse dies without air, and that air has weight.

In 1662 he published the experiment that made his name. He trapped air in the short, closed arm of a J-shaped glass tube with mercury, poured in more and more mercury, and measured how the trapped air shrank. Double the pressure on it, and its volume halved: pressure and volume are inversely proportional, at a fixed temperature. He called it the "spring of the air"; we call it **Boyle's law**. Boyle insisted that experiments, not old authorities, must decide what is true, and he described his so carefully that others could repeat them. He is often called the first modern chemist.

Heat a solid or a liquid and it expands a little (Unit 10); its pressure hardly matters. Heat a gas, and its **temperature**, **volume** and **pressure** can all change, and by large amounts. These three, with the amount of gas, are **macroscopic** properties: they describe the gas as a whole and are measured with ordinary instruments (a thermometer, a measuring cylinder, a pressure gauge). The mass, velocity and kinetic energy of each **molecule** are **microscopic** properties: no one can measure them molecule by molecule.

The **gas laws** (Boyle's law, Charles's law, the pressure law, Dalton's law and others) connect the macroscopic properties of a gas. Combined, they give one equation, the **ideal gas equation**, which describes the state of a gas at equilibrium. The **kinetic molecular theory** then explains the macroscopic properties from the microscopic ones: the molecules hit the walls of the container, and the momentum they give the walls is the pressure of the gas.



Figure 13.1 *Robert Boyle (1627–1691), in a portrait painted near the end of his life.*
Photo: Johann Kerseboom, Public domain

13.2 Volume coefficient and pressure coefficient

When a gas is heated, its pressure and its volume can both change at once, which is hard to study. So a gas is studied in two simpler ways: heated at **constant pressure** (and its volume measured) or at **constant volume** (and its pressure measured). That gives a gas two coefficients of expansion.

Volume coefficient

The **volume coefficient** γ_P of a gas is the increase in volume of a given mass of gas, **per unit of its volume at 0 °C**, for each degree rise in temperature, at **constant pressure**:

$$\gamma_P = \frac{V_\theta - V_0}{V_0\,\theta}$$

where V_0 is the volume at 0 °C and V_θ the volume at θ °C. Its unit is $\mathrm{K^{-1}}$ (or $\mathrm{°C^{-1}}$). Measured carefully at low pressure, it comes out the **same for every gas**:

$$\gamma_P = \frac{1}{273.15}\ \mathrm{K^{-1}}$$

So at constant pressure, the volume of a given mass of any gas grows or shrinks by $\frac{1}{273.15}$ of its volume at 0 °C for each degree it is heated or cooled. That is **Charles's law**.

Pressure coefficient

The **pressure coefficient** γ_V of a gas is the increase in pressure of a given mass of gas, **per unit of its pressure at 0 °C**, for each degree rise in temperature, at **constant volume**:

$$\gamma_V = \frac{P_\theta - P_0}{P_0\,\theta}$$

where P_0 is the pressure at 0 °C and P_θ the pressure at θ °C. Its unit is $\mathrm{K^{-1}}$ (or $\mathrm{°C^{-1}}$), and again it is the **same for every gas**, and equal to γ_P:

$$\gamma_V = \frac{1}{273.15}\ \mathrm{K^{-1}}$$

At constant volume, the pressure of a given mass of any gas rises or falls by $\frac{1}{273.15}$ of its pressure at 0 °C for each degree it is heated or cooled. That is the **pressure law** (Gay-Lussac's law).

CAREFUL

Measured from 0 °C, not from where you start

Both coefficients are defined per unit of the volume or pressure **at 0 °C**. Heat a gas at constant pressure from 100 °C to 101 °C and its volume grows by $\frac{1}{273.15}$ of its volume at 0 °C, which is less than $\frac{1}{273.15}$ of its volume at 100 °C. (Real gases have coefficients very slightly different from $\frac{1}{273.15}$, and from each other; the difference vanishes as the pressure is lowered. For an ideal gas they are exactly $\frac{1}{273.15}$.)

Check 1

A gas has a volume of 546 cm³ at 0 °C. It is heated at constant pressure to 50 °C. Its new volume is about:

a 550 cm³ b 646 cm³
c 596 cm³ d 1092 cm³

13.3 Absolute zero temperature

Take a gas at constant volume and plot its pressure against its temperature in °C: the points lie on a straight line. Do the same for its volume at constant pressure: another straight line. Carry each line on, below the coldest temperature at which you can measure, and it meets the temperature axis at the same point: **−273.15 °C**. Every gas, and every amount of gas, gives the same point (Figure 13.2).

From the definition of γ_V, with $\gamma_V = \frac{1}{273.15}$:

$$P_\theta = P_0(1 + \gamma_V\theta) = P_0\left(1 + \frac{\theta}{273.15}\right) = \frac{P_0}{273.15}\,(273.15 + \theta)$$

and in the same way $V_\theta = \dfrac{V_0}{273.15}(273.15 + \theta)$. Both the pressure and the volume are proportional to the quantity $(273.15 + \theta)$. That quantity is the **absolute temperature**, $T = \theta + 273.15$, measured in kelvin, and its zero, where the pressure (or the volume) of an ideal gas would fall to zero, is **absolute zero**:

$$T = 0\ \mathrm{K} \quad\Rightarrow\quad \theta + 273.15 = 0 \quad\Rightarrow\quad \theta = -273.15\ \mathrm{°C}$$

Absolute zero is the temperature at which the pressure of a given mass of gas would become zero at constant volume, or its volume zero at constant pressure. Below it, the pressure or volume would have to be negative, which is impossible: so no temperature can be lower, and on the Kelvin scale no temperature is negative.

Why it matters. The absolute temperature of a gas is proportional to the average kinetic energy of its molecules (Section 13.13). As a gas is cooled towards absolute zero, its molecules slow down, and at absolute zero the energy of their random motion would be the **least possible**. It is a true zero, not an agreed one like the zero of the Celsius scale. Real gases never reach it as gases: long before it they become liquids and solids, with their molecules packed close together.

Check 15

10. At what temperature will nitrogen molecules have the same rms speed as oxygen molecules at 127 °C?

a 77 °C b 127 °C
c 273 °C d 350 °C

Check 16

11. At 273 K and 1.01×10^5 Pa there are 2.70×10^{25} molecules in each cubic meter of a gas. How many are there in each cubic meter at 223 K and 1.33×10^{-4} Pa?

a 4.30×10^{12} b 4.35×10^{16}
c 4.35×10^{20} d 4.35×10^{22}

Check 17

12. A cylinder holds 150 cm³ of an ideal gas at 27 °C and 650 mm of Hg. What is its volume at 0 °C at the same pressure?

a 130 cm³ b 136.5 cm³
c 140 cm³ d 150 cm³

Check 18

13. Which of these is a universal constant? (C_p and C_v are the molar heat capacities of a gas at constant pressure and constant volume.)

a C_p/C_v b $C_p + C_v$
c $C_p - C_v$ d C_v/C_p

Check 19

14. A gas at 1.0×10^5 Pa and 27 °C has a density of 0.09 kg/m³. What is its density at 4.0×10^5 Pa and 127 °C, in kg/m³?

a 0.94 b 0.27
c 0.36 d 0.15

Check 20

15. A box contains N molecules of a gas. If the number of molecules is increased to 2N at the same temperature, the pressure of the gas will:

a become half b become 4 times
c remain unchanged d become twice

17. a. Why is carbon dioxide less likely than hydrogen to escape from the Earth's atmosphere?
b. There is practically no atmosphere on the Moon. Why?
c. The correct pressure in a tyre at 20 °C is 2 kgf/cm². After a long drive, the tyres are at 50 °C. What should the pressure reading be now? (Take 1 kgf = 9.8 N, and the tyre's volume as unchanged.)

18. a. Two containers, A and B, hold an ideal gas at the same temperature and pressure. A has twice the volume of B. Compare the numbers of molecules in A and B, and justify your answer with the ideal gas equation.
b. A cylindrical tank has a tight-fitting piston, so its volume can be changed. It holds 0.110 m³ of air at 3.4 atm. The piston is slowly pulled out until the volume is 0.390 m³. If the temperature stays the same, what is the final pressure?

19. a. Would you expect all the molecules of a gas in a given volume to have the same speed? Explain.
b. A sealed container is filled with an ideal gas, and the gas is heated. Using the kinetic molecular model, explain what happens to the average kinetic energy of the molecules, the spread of their speeds, and the pressure of the gas.
c. Find the number of molecules in 1 cm³ of an ideal gas at 27 °C and a pressure of 65 cm of mercury. (Density of mercury 13.6 g/cm³, $g = 9.8$ m/s², $k_B = 1.38 \times 10^{-23}$ J/K.)

Exercise

Choose the correct option

Check 6

1. The rms speed of the molecules of a gas is proportional to:

a T b T^2
c $\sqrt{T}$ d $\sqrt{M}$

Check 7

2. The pressure exerted by a gas on the walls of its container is proportional to:

a c_{rms} b $(c_{\text{rms}})^{-1}$
c $(c_{\text{rms}})^{1/2}$ d $(c_{\text{rms}})^2$

Check 8

3. The ratio of the rms speed of oxygen molecules to that of hydrogen molecules at NTP is:

a 1 : 16 b 4 : 1
c 1 : 4 d 16 : 1

Check 9

4. The kinetic energy per unit volume of a gas is:

a P b $\frac{3}{2}P$
c $\frac{2}{3}P$ d $\frac{4}{3}P$

Check 10

5. The kinetic energy of a molecule of an ideal gas at 0 °C is E. If the temperature is raised to 273 °C, its kinetic energy becomes:

a E b $\sqrt{2}\,E$
c 2E d $E/\sqrt{2}$

Check 11

6. The ratio of the average kinetic energy of an oxygen molecule to that of a hydrogen molecule at NTP is:

a 1 : 16 b 4 : 1
c 1 : 4 d 1 : 1

Check 12

7. Which of these is the same for the molecules of all gases at a given temperature?

a rms speed b density
c potential energy d average kinetic energy

Check 13

8. At what temperature will the rms speed of a gas's molecules be twice its value at 0 °C?

a 546 °C b 1096 °C
c 819 °C d 546 K

Check 14

9. Boltzmann's constant is 1.36×10^{-23} J/K. What is the average kinetic energy of a molecule of hydrogen gas at 527 °C?

a 1.088×10^{-20} J b 1.632×10^{-20} J
c 1.075×10^{-20} J d 0.725×10^{-20} J

Answer these questions

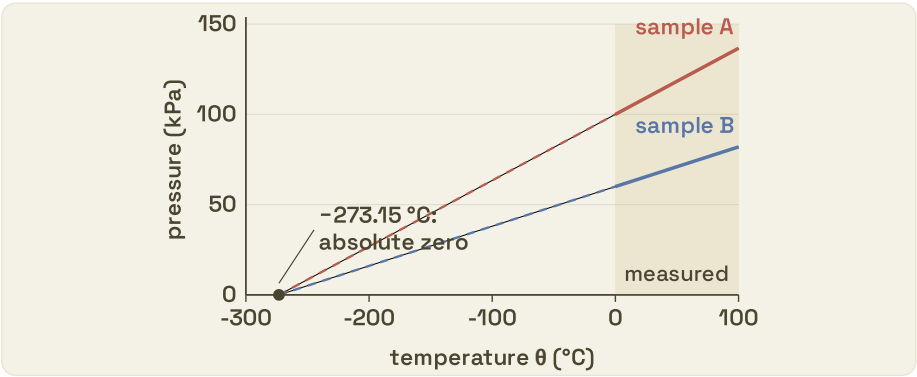


Figure 13.2 *The pressure of two samples of gas kept at constant volume, against temperature. Measured (solid), each is a straight line; carried on (dashed), both reach zero pressure at −273.15 °C. A graph of volume at constant pressure looks the same. Real gases turn to liquid before they get there.*

CAREFUL

Not "completely at rest"

Some books say the molecules are "completely at rest" at absolute zero. That is the classical picture. Quantum physics shows that particles keep a tiny, unavoidable motion even at absolute zero, the zero-point energy. Say instead that at absolute zero the kinetic energy of random motion is the **least possible** (zero, in the classical picture). More in Unit 9, Absolute scale and absolute zero.

DID YOU KNOW?

How close can we get?

Absolute zero can never be reached exactly, but laboratories come astonishingly near: clouds of atoms have been cooled to less than a billionth of a kelvin above it (the record, set in 2021, is 38 trillionths of a kelvin, 3.8×10^{-11} K). Space itself is warmer: the faint glow left over from the Big Bang keeps it at about 2.7 K.

13.4 Ideal gas

An **ideal gas** is a gas whose molecules have **no forces between them** (except when they collide) and **no volume of their own**. It obeys Boyle's law and Charles's law exactly, at every pressure and temperature.

No real gas is ideal: real molecules do take up some room, and they do attract each other a little. But at **low pressure** (the molecules far apart, so their size and their attraction hardly matter) and **high temperature** (the molecules so fast that the weak attraction has little effect), a real gas behaves very nearly like an ideal one. Air, hydrogen, helium, nitrogen and oxygen at room temperature and normal pressure follow the ideal gas equation to better than 1%.

Ideal gas equation

Boyle's law says that for a fixed mass of gas at constant temperature, $PV =$ constant; Charles's law says that at constant pressure, $V/T =$ constant. To join them, take one mole of an ideal gas in a cylinder closed by a light, frictionless, airtight piston, from a state (P_1, V_1, T_1) to a state (P_2, V_2, T_2) in two steps, one law at a time (Figure 13.3).

1. **Step 1, constant temperature T_1.** Push the piston in until the pressure becomes P_2; call the volume then V. By Boyle's law,

$$P_1V_1 = P_2V \quad \Rightarrow \quad V = \frac{P_1V_1}{P_2} \tag{i}$$

2. **Step 2, constant pressure P_2.** Heat the gas from T_1 to T_2; its volume grows from V to V_2. By Charles's law,

$$\frac{V}{T_1} = \frac{V_2}{T_2} \quad \Rightarrow \quad V = \frac{V_2T_1}{T_2} \tag{ii}$$

3. Both give the same V, so

$$\frac{P_1V_1}{P_2} = \frac{V_2T_1}{T_2} \quad \Rightarrow \quad \frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \tag{13.1}$$

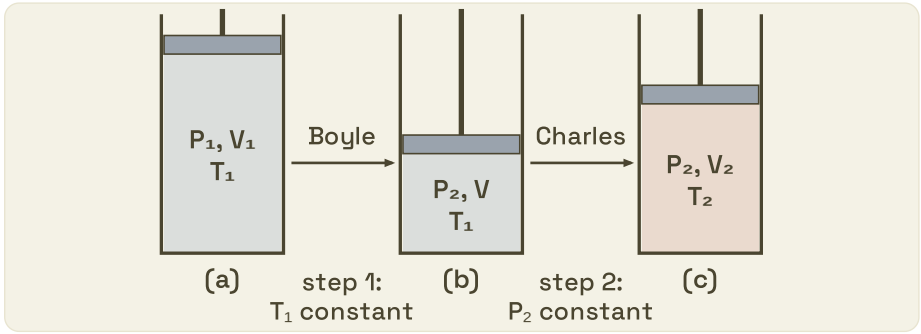


Figure 13.3 *From state (a) to state (c) in two steps. Step 1: squeeze the gas at the constant temperature T_1 until its pressure is P_2 (Boyle's law). Step 2: heat it at the constant pressure P_2 until its temperature is T_2 (Charles's law).*

This is the **combined gas equation**. Since the two states were any two states,

$$\frac{PV}{T} = \text{constant}$$

for a given amount of gas. For **one mole**, this constant is found to be the **same for every gas**. It is called the **molar gas constant** (or universal gas constant), R:

$$\boxed{PV = RT} \quad \text{(one mole)} \tag{13.2}$$

For n moles, the volume at the same pressure and temperature is n times as much, so

$$\boxed{PV = nRT} \tag{13.3}$$

This is the **ideal gas equation**, or **equation of state** of an ideal gas: it gives any one of P, V, T and n once the other three are known. Here P is in pascals (N/m²), V in m³, T in kelvin and n in moles.

In terms of mass. If the gas has mass m and its molar mass (the mass of one mole) is M, then $n = m/M$, and

$$PV = \frac{m}{M}RT = mrT, \qquad r = \frac{R}{M} \tag{13.4}$$

r is the **gas constant per unit mass** of that gas (the **ordinary** or **specific** gas constant). Unlike R, it is different for each gas. For 1 g of gas, $PV = rT$.

> CAREFUL
> **Two different M's**
>
> In this unit, M is always the **molar mass** (kg/mol, or g/mol), and m a mass of gas (or, from Section 13.9, the mass of one molecule). Some books use M also for the total mass of the gas in a container: watch which one a formula means.

Numerical value of R

One mole of any gas at NTP (0 °C and 1 atm) occupies 22.4 L. So

- $P = 760$ mm of Hg $= 1.013 \times 10^5$ Pa
- $V = 22.4$ L $= 22.4 \times 10^{-3}$ m³
- $T = 273$ K, $n = 1$ mol

$$R = \frac{PV}{nT} = \frac{1.013 \times 10^5 \times 22.4 \times 10^{-3}}{1 \times 273} = 8.31 \text{ J/(mol K)}$$

The accepted value is $R = 8.314$ J/(mol K).

Unit of R. $\dfrac{\text{unit of } P \times \text{unit of } V}{\text{unit of } n \times \text{unit of } T} = \dfrac{\text{N/m}^2 \times \text{m}^3}{\text{mol} \times \text{K}} = \dfrac{\text{N m}}{\text{mol K}} = \text{J/(mol K)}$, or J mol^{-1} K^{-1}.

Dimensions of R. $[R] = \dfrac{[\text{energy}]}{[\text{amount}][\text{temperature}]} = [\text{ML}^2\text{T}^{-2}\text{K}^{-1}\text{mol}^{-1}]$.

Physical meaning of R

PV has the unit of energy, J. What energy? Heat one mole of gas at constant pressure P by 1 K. From $PV = RT$, its volume grows by ΔV, where

The kinetic energy per unit volume of a gas is $\frac{3}{2}$ times its pressure. Pressure (N/m², which is J/m³) is itself an energy per unit volume: the air around you, at about 85 kPa in the Kathmandu Valley, holds about $1.5 \times 85\,000 \approx 130\,000$ J of molecular kinetic energy in every cubic meter.

> Check 5
> A gas exerts a pressure of 2.0×10^5 Pa. The kinetic energy of its molecules in each cubic meter is:
> a 1.3×10^5 J b 2.0×10^5 J
> c 3.0×10^5 J d 6.0×10^5 J

13.13 Kinetic interpretation of temperature

The average translational kinetic energy of a gas molecule is

$$\frac{1}{2}mc_{\text{rms}}^2 = \frac{3}{2}k_BT \quad \Rightarrow \quad \frac{1}{2}mc_{\text{rms}}^2 \propto T$$

This is what temperature **means**, in the kinetic theory: the absolute temperature of a gas is a measure of the **average kinetic energy of the random motion of its molecules**. A hot gas is one whose molecules are, on average, flying about fast; heating a gas makes them faster. Two gases at the same temperature have molecules of the same average kinetic energy, whatever the gases are. (Only the **random** motion counts: a gas in a moving bus is not hotter because the bus moves.)

At absolute zero, $T = 0$, so

$$\frac{1}{2}mc_{\text{rms}}^2 = \frac{3}{2}k_B \times 0 = 0 \quad \Rightarrow \quad c_{\text{rms}} = 0$$

since $m \neq 0$: in this classical picture, the random motion of the molecules would stop. (Quantum physics adds the small zero-point motion that remains even then, Section 13.3.) And since $m > 0$ and $c_{\text{rms}}^2 \geq 0$, the kinetic energy can't be negative, so neither can T: **no Kelvin temperature is negative**.

> IN SHORT
> **Key ideas of Unit 13**
>
> - Volume coefficient $\gamma_P = \dfrac{V_\theta - V_0}{V_0\theta}$ (constant pressure) and pressure coefficient $\gamma_V = \dfrac{P_\theta - P_0}{P_0\theta}$ (constant volume): both $\frac{1}{273.15}$ K^{-1} for every gas.
> - Carried on, the P–θ and V–θ lines of every gas reach zero at **–273.15 °C, absolute zero**: $T = \theta + 273.15$. No temperature is lower.
> - An **ideal gas** has no forces between its molecules and no molecular volume; real gases come close at low pressure and high temperature.
> - $\dfrac{P_1V_1}{T_1} = \dfrac{P_2V_2}{T_2}$; $PV = nRT$, $R = 8.31$ J/(mol K); $PV = mrT$ with $r = R/M$.
> - One mole is $N_A = 6.02 \times 10^{23}$ particles; $n = m/M$. Avogadro's law: equal volumes of gases at the same T and P hold equal numbers of molecules; 22.4 L per mole at NTP.
> - Kinetic theory: $P = \frac{1}{3}\rho c_{\text{rms}}^2$, from the change of momentum $2mu$ at each bounce, once every $2l/u$.
> - $c_{\text{rms}} = \sqrt{\dfrac{3P}{\rho}} = \sqrt{\dfrac{3RT}{M}}$: $\propto \sqrt{T}$, $\propto 1/\sqrt{M}$.
> - $(\text{KE})_{\text{molar}} = \frac{3}{2}RT$; per molecule $\frac{1}{2}mc_{\text{rms}}^2 = \frac{3}{2}k_BT$, $k_B = R/N_A = 1.38 \times 10^{-23}$ J/K. Kinetic energy per unit volume $= \frac{3}{2}P$.
> - The absolute temperature measures the average kinetic energy of the molecules' random motion.

(Since 2019 its value is fixed exactly, $1.380\,649 \times 10^{-23}$ J/K, and it defines the kelvin.) The average kinetic energy of a gas molecule is directly proportional to the absolute temperature. With k_B, the ideal gas equation for N molecules is also $PV = Nk_BT$.

WORKED EXAMPLE

Energies and speeds at 27 °C

At 27 °C, find a. the average translational kinetic energy of a molecule of an ideal gas, b. the total random translational kinetic energy of the molecules in 1 mole of it, c. the rms speed of oxygen molecules. ($R = 8.31$ J/(mol K), $N_A = 6.02 \times 10^{23}$ mol^{-1}, molar mass of oxygen 32 g/mol.)

Answer

$T = 27 + 273 = 300$ K.

a. $\frac{1}{2}mc_{\text{rms}}^2 = \frac{3}{2}k_BT = \frac{3}{2} \times \frac{8.31}{6.02 \times 10^{23}} \times 300 = \mathbf{6.21 \times 10^{-21}\ J}$

b. $(\text{KE})_{\text{molar}} = \frac{3}{2}RT = \frac{3}{2} \times 8.31 \times 300 = \mathbf{3740\ J}$ (about the energy needed to lift a 38 kg sack through 10 m).

c. $c_{\text{rms}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.31 \times 300}{32 \times 10^{-3}}} = \mathbf{483\ m/s}$

WORKED EXAMPLE

Hot enough to escape?

At what temperature would the rms speed of oxygen molecules equal the Earth's escape speed, 11.2 km/s? (Mass of an oxygen molecule 5.34×10^{-26} kg, $k_B = 1.38 \times 10^{-23}$ J/K.)

Answer

Set $c_{\text{rms}} = v = 11\,200$ m/s in $\frac{1}{2}mc_{\text{rms}}^2 = \frac{3}{2}k_BT$:

$$T = \frac{mv^2}{3k_B} = \frac{5.34 \times 10^{-26} \times (11\,200)^2}{3 \times 1.38 \times 10^{-23}} = \mathbf{1.6 \times 10^5\ K}$$

About 160 000 K, far hotter than any part of our atmosphere. Yet a planet can lose a gas at much lower temperatures: a few molecules in the fast tail of the spread of speeds always exceed the escape speed. Over billions of years, a gas whose rms speed is more than about a sixth of the escape speed leaks away. That is why the Earth has kept its oxygen and nitrogen but lost nearly all its hydrogen and helium.

WORKED EXAMPLE

Molecules in a cubic centimeter

Find the number of molecules in 1 cm^3 of an ideal gas at 27 °C and a pressure of 65 cm of mercury. (Density of mercury 13.6 g/cm^3, $g = 9.8$ m/s^2, $k_B = 1.38 \times 10^{-23}$ J/K.)

Answer

$P = h\rho g = 0.65 \times 13\,600 \times 9.8 = 8.66 \times 10^4$ Pa, $T = 300$ K.

From $P = \frac{1}{3}mn_Vc_{\text{rms}}^2 = \frac{2}{3}n_V\left(\frac{1}{2}mc_{\text{rms}}^2\right) = \frac{2}{3}n_V \times \frac{3}{2}k_BT = n_Vk_BT$:

$$n_V = \frac{P}{k_BT} = \frac{8.66 \times 10^4}{1.38 \times 10^{-23} \times 300} = 2.09 \times 10^{25}\ \text{molecules per m}^3$$

A cubic centimeter is 10^{-6} m^3, so it holds $2.09 \times 10^{25} \times 10^{-6} = 2.09 \times 10^{19}$ **molecules**: twenty million million million.

Sample questions

13.12 Relation between pressure and kinetic energy of a gas

The pressure of a gas of density ρ is $P = \frac{1}{3}\rho c_{\text{rms}}^2$. A gas of mass m and volume V has total kinetic energy $\text{KE} = \frac{1}{2}mc_{\text{rms}}^2$, so its kinetic energy per unit volume is

$$E' = \frac{\text{KE}}{V} = \frac{1}{2}\frac{m}{V}c_{\text{rms}}^2 = \frac{1}{2}\rho c_{\text{rms}}^2$$

Compare with the pressure: $\frac{1}{2}\rho c_{\text{rms}}^2 = \frac{3}{2} \times \frac{1}{3}\rho c_{\text{rms}}^2$, so

$$\boxed{E' = \frac{3}{2}P} \quad \text{or} \quad P = \frac{2}{3}E' \tag{13.11}$$

$$P\,\Delta V = R\,\Delta T = R \times 1\ \text{K}$$

and $P\,\Delta V$ is the **work the gas does** pushing its surroundings back as it expands (force PA times distance $\Delta V/A$). So R is the **work done by one mole of an ideal gas when it is heated through 1 K at constant pressure**: 8.31 J. More broadly, R is the constant that turns a temperature into an energy, per mole.

Gas constant per unit mass, r

$$r = \frac{R}{M}$$

- **Hydrogen**, $M = 2$ g/mol: $r = \frac{8.31}{2} = 4.16$ J/(g K)
- **Oxygen**, $M = 32$ g/mol: $r = \frac{8.31}{32} = 0.26$ J/(g K)

A gram of hydrogen contains sixteen times as many molecules as a gram of oxygen, so its r is sixteen times larger.

Check 2

Which of these is the same for one mole of every ideal gas?

a its mass
b its gas constant per unit mass, r
c PV/T
d the speed of its molecules at 0 °C

13.5 One mole

A **mole** is an amount of substance: the amount that contains exactly $6.022\,140\,76 \times 10^{23}$ particles (atoms, molecules, ions: whichever the substance is made of). That number is **Avogadro's number**, N_A. Its symbol is **mol**, and it is one of the seven base units of the SI.

Until 2019 the mole was defined as the amount of substance with as many particles as there are atoms in 12 g of carbon-12; the new definition fixes the number itself, and 12 g of carbon-12 still holds almost exactly one mole. A mole is an amount counted by the number of particles, as a dozen is twelve of anything: a mole of hydrogen molecules and a mole of oxygen molecules contain the same number of molecules, though not the same mass.

The mass of one mole of a substance is its **molar mass**, M. In grams, it is the same number as the relative molecular (or atomic) mass:

- Hydrogen, H_2: relative molecular mass 2, so 1 mol of H_2 = 2 g = the mass of 6.02×10^{23} H_2 molecules.
- Oxygen, O_2: 1 mol = 32 g = the mass of 6.02×10^{23} O_2 molecules.
- Water, H_2O: 1 mol = 18 g = the mass of 6.02×10^{23} water molecules.

If a container holds a mass m of a substance of molar mass M, the number of moles in it is

$$n = \frac{m}{M}$$

and the number of molecules is $N = nN_A$.

Check 3

How many molecules are there in 9 g of water? ($N_A = 6.02 \times 10^{23}$ mol^{-1})

a 6.02×10^{23}
b 3.01×10^{23}
c 5.42×10^{24}
d 1.20×10^{24}

13.6 Avogadro's law

Avogadro's law: equal volumes of all gases, at the same temperature and pressure, contain **equal numbers of molecules**.

It follows from $PV = nRT$: if P, V and T are the same, $n = PV/RT$ is the same for every gas. So one mole of any gas at NTP (0 °C, 1 atm) occupies the same volume, the **molar volume**, 22.4 L, and contains 6.02×10^{23} molecules. At NTP, 2 g of hydrogen and 32 g of oxygen each fill 22.4 L, and each holds 6.02×10^{23} molecules.

CAREFUL

Two standard pressures

Our textbooks, and exam questions in Nepal, use NTP or STP as 0 °C and 1 atm (760 mm of Hg, 1.013×10^5 Pa), with a molar volume of 22.4 L. Since 1982 IUPAC, the chemists' international body, has taken standard pressure as 1 bar (1.00×10^5 Pa), at which a mole of gas at 0 °C fills 22.7 L. Use 1 atm and 22.4 L unless a question says otherwise.

Avogadro's number

Avogadro's number, $N_A = 6.02 \times 10^{23}$ mol^{-1}, is the number of particles in one mole of **any** substance, solid, liquid or gas, at any temperature and pressure (it is the gas's **volume** that depends on the conditions, not the number in a mole). One mole of H_2 contains 6.02×10^{23} H_2 molecules; one mole of O_2 contains 6.02×10^{23} O_2 molecules.

With it, we can find:

1. the number of molecules in a given volume of gas;
2. the number of atoms in a given mass of an element;
3. the number of molecules in a given mass of a substance;
4. the mass of one atom of an element (its molar mass $\div N_A$);
5. the mass of one molecule of a substance.

For example, the mass of one oxygen molecule is

$$m = \frac{M}{N_A} = \frac{32 \times 10^{-3}}{6.02 \times 10^{23}} = 5.32 \times 10^{-26}\ \text{kg}$$

WORKED EXAMPLE

Two bulbs joined by a tube

Two bulbs of equal volume are joined by a narrow tube and filled with a gas at STP. One bulb is then kept in melting ice and the other in boiling water. Find the new pressure of the gas.

Answer

Let each bulb have volume V. The pressure is the same in both bulbs (they are joined), but the gas moves from the hot bulb to the cold one until it is. The **total amount of gas** doesn't change. From $PV = nRT$, the number of moles in a bulb is $n = PV/RT$.

Before: both bulbs at 273 K and 760 mm of Hg, so

$$n_{\text{total}} = 2 \times \frac{760\,V}{R \times 273}$$

After: pressure P' in both, one bulb at 273 K and the other at 373 K, so

$$n_{\text{total}} = \frac{P'V}{R \times 273} + \frac{P'V}{R \times 373}$$

The amount is conserved, so (cancel V/R):

$$\frac{2 \times 760}{273} = P'\left(\frac{1}{273} + \frac{1}{373}\right) \quad \Rightarrow \quad P' = \frac{2 \times 760}{1 + \frac{273}{373}} = \frac{1520}{1.732} = \textbf{877.6 mm of Hg}$$

(Pressures may stay in mm of Hg here: they appear on both sides.) The pressure rises, but not by as much as if both bulbs were heated, since some gas has moved into the cold bulb.

2. **For different gases at the same temperature**, $c_{\text{rms}} \propto \frac{1}{\sqrt{M}}$: lighter molecules move faster.

$$\frac{(c_{\text{rms}})_1}{(c_{\text{rms}})_2} = \sqrt{\frac{M_2}{M_1}}$$

At room temperature, 300 K, nitrogen molecules move at an rms speed of about 517 m/s, faster than sound in air; hydrogen molecules at about 1930 m/s.

CAREFUL

Not every molecule at c_rms

The rms speed is one figure for a crowd. In any gas, some molecules are nearly at rest and a few move several times faster than c_{rms}, and each molecule's speed changes at every collision. The spread, worked out by James Clerk Maxwell in 1860, has a peak a little below c_{rms} and a long tail of fast molecules, and it widens and shifts to higher speeds as the gas is heated.

WORKED EXAMPLE

Hydrogen at NTP

Find the rms speed of hydrogen molecules at NTP. At what temperature will their rms speed be twice that at 0 °C? (Molar mass of hydrogen 2 g/mol, $R = 8.31$ J/(mol K).)

Answer

$T_0 = 273$ K, $M = 2 \times 10^{-3}$ kg/mol.

$$(c_{\text{rms}})_0 = \sqrt{\frac{3RT_0}{M}} = \sqrt{\frac{3 \times 8.31 \times 273}{2 \times 10^{-3}}} = \sqrt{3.40 \times 10^6} = \textbf{1845 m/s}$$

(The same comes from $\sqrt{3P/\rho}$, with $P = 1.013 \times 10^5$ Pa and $\rho = 2 \times 10^{-3}$ kg $\div$ 22.4×10^{-3} m^3.)

For twice the speed: $\frac{c_{\text{rms}}}{(c_{\text{rms}})_0} = \sqrt{\frac{T}{T_0}} = 2$, so $\frac{T}{T_0} = 4$ and

$$T = 4 \times 273 = \textbf{1092 K}, \text{ or } 1092 - 273 = \textbf{819 °C}$$

Doubling the speed needs **four times** the absolute temperature.

Sample questions

13.11 Kinetic energy of a gas

For one mole. From Section 13.10, for one mole of gas (molar mass M):

$$PV = \frac{1}{3}Mc_{\text{rms}}^2 \quad \text{and} \quad PV = RT \quad \Rightarrow \quad \frac{1}{3}Mc_{\text{rms}}^2 = RT$$

Multiply both sides by $\frac{3}{2}$:

$$\frac{1}{2}Mc_{\text{rms}}^2 = \frac{3}{2}RT$$

The left side is the total kinetic energy of the random (translational) motion of all the molecules in one mole. So

$$\boxed{(\text{KE})_{\text{molar}} = \frac{3}{2}RT} \tag{13.9}$$

The kinetic energy of the molecules of a mole of gas depends **only on its temperature**, not on what gas it is. For n moles: $\text{KE} = \frac{3}{2}nRT$.

For one molecule. One mole has N_A molecules, so $M = N_A m$, where m is the mass of one molecule. The average kinetic energy of one molecule is

$$\frac{1}{2}mc_{\text{rms}}^2 = \frac{(\text{KE})_{\text{molar}}}{N_A} = \frac{3}{2}\frac{R}{N_A}T$$

$$\boxed{\frac{1}{2}mc_{\text{rms}}^2 = \frac{3}{2}k_BT} \tag{13.10}$$

where $k_B = R/N_A$ is **Boltzmann's constant**, the gas constant per molecule:

$$k_B = \frac{R}{N_A} = \frac{8.31}{6.02 \times 10^{23}} = 1.38 \times 10^{-23}\ \text{J/K}$$

Check 4

If the rms speed of the molecules of a gas is doubled, at constant density, its pressure becomes:

a twice as much
b four times as much
c half as much
d the same

WORKED EXAMPLE

Density from the rms speed

At a pressure of 700 mm of Hg, the rms speed of the molecules of a gas is 400 m/s. What is its density? (Density of mercury 13 600 kg/m^3, $g = 10$ m/s^2.)

Answer

$P = h\rho_{\text{Hg}}g = 0.700 \times 13\,600 \times 10 = 9.52 \times 10^4$ Pa, $c_{\text{rms}} = 400$ m/s.

$$P = \frac{1}{3}\rho c_{\text{rms}}^2 \quad \Rightarrow \quad \rho = \frac{3P}{c_{\text{rms}}^2} = \frac{3 \times 9.52 \times 10^4}{400^2} = \mathbf{1.785\ kg/m^3}$$

(With $g = 9.8$ m/s^2, the pressure is 9.33×10^4 Pa and the density 1.75 kg/m^3.)

WORKED EXAMPLE

The gas in an old TV tube

In a cathode ray tube there are 6.80×10^{15} hydrogen molecules in each cm^3, and their rms speed is 1.90×10^3 m/s. Find the pressure of the hydrogen in mm of mercury. ($N_A = 6.02 \times 10^{23}$ mol^{-1}; relative molecular mass of hydrogen 2.02.)

Answer

Molecules per m^3: $n_V = 6.80 \times 10^{15} \times 10^6 = 6.80 \times 10^{21}$ m^{-3} (1 m^3 = 10^6 cm^3).

Mass of one molecule: $m = \dfrac{M}{N_A} = \dfrac{2.02 \times 10^{-3}}{6.02 \times 10^{23}} = 3.36 \times 10^{-27}$ kg.

$$P = \frac{1}{3} m n_V c_{\text{rms}}^2 = \frac{1}{3} \times 3.36 \times 10^{-27} \times 6.80 \times 10^{21} \times (1.90 \times 10^3)^2 = 27.5 \text{ Pa}$$

760 mm of Hg is 1.013×10^5 Pa, so

$$P = 27.5 \times \frac{760}{1.013 \times 10^5} = \mathbf{0.206\ mm\ of\ Hg}$$

A very good vacuum by everyday standards: about a four-thousandth of the air's pressure.

13.10 Root mean square speed

The molecules of a gas don't all move at one speed. The **root mean square (rms) speed** is the square root of the mean of the squares of the speeds of all the molecules. If the N molecules have speeds $c_1, c_2, \ldots, c_N$,

$$c_{\text{rms}} = \sqrt{\frac{c_1^2 + c_2^2 + \cdots + c_N^2}{N}} \tag{13.6}$$

It is the speed that matters for pressure and kinetic energy, since both depend on c^2. (It is a little more than the ordinary average speed: for five molecules with speeds 1, 2, 3, 4 and 5 m/s, the average is 3 m/s and the rms speed $\sqrt{55/5} = 3.32$ m/s.)

From the pressure. From $P = \frac{1}{3}\rho c_{\text{rms}}^2$:

$$c_{\text{rms}} = \sqrt{\frac{3P}{\rho}} \tag{13.7}$$

From the temperature. Take one mole of gas, of molar mass M and volume V: its density is $\rho = M/V$, so

$$P = \frac{1}{3}\frac{M}{V}c_{\text{rms}}^2 \quad \Rightarrow \quad PV = \frac{1}{3}Mc_{\text{rms}}^2$$

For one mole, $PV = RT$, so

$$RT = \frac{1}{3}Mc_{\text{rms}}^2 \quad \Rightarrow \quad \boxed{c_{\text{rms}} = \sqrt{\frac{3RT}{M}}} \tag{13.8}$$

with M in **kg/mol**. Two conclusions:

1. **For one gas**, $c_{\text{rms}} \propto \sqrt{T}$: the rms speed is proportional to the square root of the absolute temperature. At two temperatures,

$$\frac{(c_{\text{rms}})_1}{(c_{\text{rms}})_2} = \sqrt{\frac{T_1}{T_2}}$$



Figure 13.4 *Gas cylinders outside a house. Most of the LPG inside is liquid; the gas above it is far from an ideal gas (Sample question 5).*
Photo: Evil Monkey, CC BY 2.5

WORKED EXAMPLE

Gas used from a cylinder

A cylinder holds 10 kg of a gas at a pressure of 8 atm at 27 °C. After some of the gas is used in a cold room at −3 °C, the gas left in the cylinder at that temperature has a pressure of 6.4 atm. Find the mass of gas used.

Answer

$m_1 = 10$ kg, $P_1 = 8$ atm, $T_1 = 27 + 273 = 300$ K; $P_2 = 6.4$ atm, $T_2 = -3 + 273 = 270$ K; the volume V (the cylinder's) is the same.

From $PV = mrT$: $P_1V = m_1rT_1$ and $P_2V = m_2rT_2$. Divide the first by the second:

$$\frac{P_1}{P_2} = \frac{m_1T_1}{m_2T_2} \quad \Rightarrow \quad m_2 = m_1 \times \frac{P_2}{P_1} \times \frac{T_1}{T_2} = 10 \times \frac{6.4}{8} \times \frac{300}{270} = 8.89 \text{ kg}$$

Mass used: $10 - 8.89 = \mathbf{1.11\ kg}$.

Sample questions

13.7 Molecules, molecular properties of matter and intermolecular force

All matter is made of a vast number of tiny particles, **molecules** (or atoms, or ions). How the molecules move and how they act on one another decide the **physical properties** of a substance.

The properties of matter are of two kinds:

- **Physical properties**: mechanical, thermal, electrical, magnetic, optical, acoustic. They describe how matter responds to forces and energy, and are measured as density, temperature, viscosity, surface tension, conductivity and so on. Changing them only **rearranges or moves the molecules** (melting, boiling, stretching): the molecules stay the same.
- **Chemical properties**: stability, reactivity, toxicity, flammability. They describe how a substance reacts. A chemical change rearranges the atoms **inside** the molecules, making new substances.

Breaking the bonds inside molecules usually takes much more energy than pulling molecules apart from each other, so physical changes generally need less energy than chemical ones: boiling a mole of water takes about 41 kJ, splitting a mole of water into hydrogen and oxygen about 286 kJ.

The forces between molecules, **intermolecular forces**, decide most physical behavior. They are electrical: an attraction when molecules are a little apart, and a strong repulsion when they are pushed into each other. In a **solid**, the attraction holds each molecule in place, vibrating; in a **liquid**, the molecules are still close and attract each other, but slide past one another; in a **gas**, the molecules are so far apart, on average about ten times their own width at NTP, that the forces hardly act except during collisions. That is why gases are the simplest state of matter to explain, and why one equation fits them all.

13.8 Kinetic molecular model of gases

The **kinetic molecular model** pictures a gas as a very large number of molecules in constant, random motion. Except at absolute zero, they fly in all directions with all sorts of speeds, colliding with each other and with the walls of the container. Each

time a molecule bounces off a wall, its momentum changes, so (by Newton's second law) the wall pushes on it, and it pushes back on the wall (Newton's third law). The total push of all the molecules on each unit area of wall is the **pressure** of the gas.

A molecule is so small compared with the distances between molecules that its volume is taken as zero: each molecule is free to move through the whole container. With this model, the gas laws (Boyle's, Charles's, Avogadro's) can be **derived**, and the macroscopic properties (pressure, volume, temperature) connected with the microscopic ones (the mass, velocity and kinetic energy of the molecules).

Postulates

The model rests on these assumptions:

1. A gas consists of a very large number of identical molecules, tiny, perfectly elastic spheres.
2. The **volume of the molecules** themselves is negligible compared with the volume of the container.
3. There are **no forces between the molecules**, except during collisions. Between collisions, each molecule moves in a straight line at a steady speed (gravity's effect is negligible).
4. The molecules move **randomly**, in all directions equally, with a range of speeds.
5. Collisions with each other and with the walls are **perfectly elastic**: the total kinetic energy doesn't change.
6. A collision lasts a negligible time compared with the time between collisions.
7. Newton's laws of motion apply to every molecule.
8. The gas is uniform: its density, and the number of molecules per unit volume, are the same throughout.

13.9 Pressure exerted by a gas

The **pressure** of a gas is the force its molecules exert, through their collisions, on each unit area of the wall of its container. Here we work it out from the motion of the molecules, carefully, one step at a time.

Take a **cube** of side l holding N molecules of a gas, each of mass m (Figure 13.5). Set axes X, Y and Z along its edges. Look at the shaded wall on the right, perpendicular to the X-axis, of area l^2.

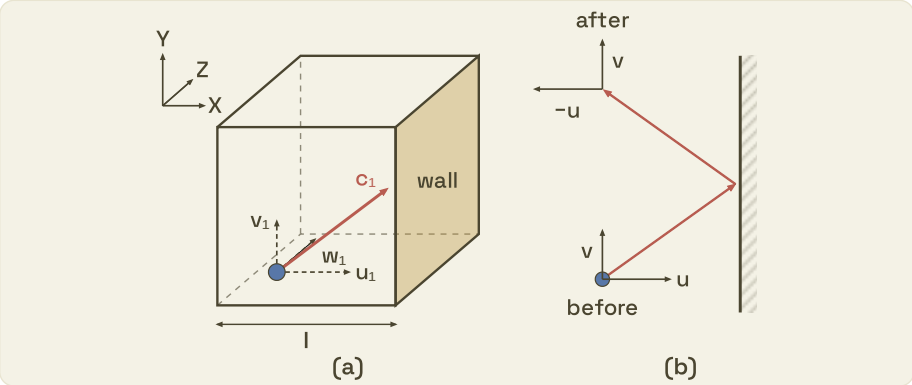


Figure 13.5

a. A molecule of mass m in a cube of side l, moving with velocity c_1, whose components along the axes are u_1, v_1 and w_1.

b. Close-up of its bounce off the shaded wall, seen edge-on, looking along the Z axis: the component u_1, towards the wall, is reversed to $-u_1$; the components along the wall don't change.

Step 1: one molecule, one bounce. Molecule 1 moves with velocity c_1, whose components along X, Y and Z are u_1, v_1 and w_1, so that

$$c_1^2 = u_1^2 + v_1^2 + w_1^2$$

It hits the shaded wall. The collision is elastic and the wall is smooth, so only the component **perpendicular to the wall** changes: u_1 becomes $-u_1$, while v_1 and w_1 stay as they were. Its momentum along X changes from mu_1 to $-mu_1$:

$$\text{change in momentum of the molecule} = -mu_1 - mu_1 = -2mu_1$$

By Newton's third law, the wall receives the opposite: $+2mu_1$, outward.

Step 2: how often it hits. After the bounce, the molecule crosses to the opposite wall and back, a distance $2l$ along X, at the speed u_1 along X, before it hits the shaded wall again. (Its motion along Y and Z, and bounces off the other walls, don't change u_1.) So the time between its hits on the shaded wall is

$$t = \frac{2l}{u_1}$$

Step 3: the average force of one molecule. The wall receives $2mu_1$ of momentum every $2l/u_1$ seconds. The average force is the rate of change of momentum (Newton's second law):

$$F_1 = \frac{2mu_1}{2l/u_1} = \frac{mu_1^2}{l}$$

The force comes in short kicks, but there are so many molecules, each giving billions of kicks a second, that together they press on the wall steadily.

Step 4: all the molecules. The molecules move independently (no forces between them), so their forces add. The total force on the shaded wall is

$$F_x = \frac{mu_1^2}{l} + \frac{mu_2^2}{l} + \cdots + \frac{mu_N^2}{l} = \frac{m}{l}\left(u_1^2 + u_2^2 + \cdots + u_N^2\right)$$

and the pressure on it, force per unit area, with area l^2 and volume $V = l^3$:

$$P_x = \frac{F_x}{l^2} = \frac{m}{l^3}\left(u_1^2 + u_2^2 + \cdots + u_N^2\right) = \frac{m}{V}\left(u_1^2 + u_2^2 + \cdots + u_N^2\right)$$

Step 5: every direction is the same. In the same way, the pressures on the walls perpendicular to Y and Z are

$$P_y = \frac{m}{V}\left(v_1^2 + v_2^2 + \cdots + v_N^2\right), \qquad P_z = \frac{m}{V}\left(w_1^2 + w_2^2 + \cdots + w_N^2\right)$$

The molecules move at random, with no direction preferred, and there are a vast number of them, so the pressure is the same on every wall: $P_x = P_y = P_z = P$. So P is their average:

$$P = \frac{P_x + P_y + P_z}{3} = \frac{m}{3V}\left[\left(u_1^2 + v_1^2 + w_1^2\right) + \left(u_2^2 + v_2^2 + w_2^2\right) + \cdots + \left(u_N^2 + v_N^2 + w_N^2\right)\right]$$

Each bracket is one molecule's c^2, so

$$P = \frac{m}{3V}\left(c_1^2 + c_2^2 + \cdots + c_N^2\right)$$

Step 6: the root mean square speed. Define the **root mean square (rms) speed** c_{rms} of the molecules (Section 13.10) by

$$c_{\text{rms}}^2 = \frac{c_1^2 + c_2^2 + \cdots + c_N^2}{N}$$

the mean of the squares of their speeds. Then $c_1^2 + c_2^2 + \cdots + c_N^2 = Nc_{\text{rms}}^2$, and

$$P = \frac{mN}{3V}\,c_{\text{rms}}^2$$

Step 7: in terms of density. mN is the total mass of the gas, and mN/V its density ρ. So

$$\boxed{P = \frac{1}{3}\rho\, c_{\text{rms}}^2} \tag{13.5}$$

This is the pressure exerted by a gas, from the kinetic theory. Written with the number of molecules per unit volume, $n_V = N/V$, it is also $P = \frac{1}{3}\,m\,n_V\,c_{\text{rms}}^2$.

> CAREFUL
> **Where the 1/3 comes from**
>
> The $\frac{1}{3}$ is not a guess. A molecule's speed is shared among three directions, and only the part towards a wall pushes on that wall. On average, each direction gets a third of c^2: $\overline{u^2} = \overline{v^2} = \overline{w^2} = \frac{1}{3}\overline{c^2}$. (A simpler proof, which sends a sixth of the molecules towards each face, gets the same $\frac{1}{3}$ by luck: it ignores the spread of directions and speeds.)

What equation (13.5) says:

- **Pressure is proportional to density**, at a given c_{rms}: squeeze a gas into half the volume and the same molecules, at the same speeds, hit each square meter of wall twice as often. That is Boyle's law, explained.
- **Pressure is proportional to c_{rms}^2**: faster molecules hit both **more often** and **harder**, each factor growing with the speed.