Unit 7

Gas Laws

This unit online, with its interactives:
science-playground.com/s/9a7

Buy a packet of chips in Kathmandu and carry it up to Namche Bazaar, at 3,440 m. By the time you get there, the packet is tight and round, like a little pillow, even though nobody has opened it. Nothing has been added to it. The same air is inside, and the packet hasn't been heated. So why has it grown?

Up at Namche, the air outside presses on the packet much less than the air in Kathmandu does. The air inside pushes the packet's walls outward until its own pressure matches the weaker push from outside, and to do that it has to spread into a bigger space. Gases behave like this everywhere, in a football, a pressure cooker, a diver's bubbles and your own lungs, and they follow a few simple rules: the **gas laws**. This unit is about those rules, and about why moving molecules make gases obey them.



Figure 7.1 *Namche Bazaar, about 3,440 m up in Solukhumbu. The air pressure here is about two-thirds of the air pressure at sea level.*
Photo: stevehicks, CC BY 2.0

Describing a gas

A solid has its own shape and a liquid its own volume, but a gas has neither: it fills whatever container it is in. To describe a fixed amount of gas, we measure three things.

Volume (V) is the space the gas fills, which is the volume of its container. It is measured in cubic centimeters (cm^3), liters (L) or cubic meters (m^3): 1 L = 1,000 cm^3 = 1 dm^3, and 1 m^3 = 1,000 L.

Pressure (P) is the force with which the gas pushes on each unit area of its container's walls. Its SI unit is the pascal (Pa), 1 N/m^2. Chemists also use the **atmosphere (atm)**, the average pressure of the air at sea level, and the **millimeter of mercury (mmHg)**, the height of a column of mercury that the pressure can hold up in a barometer:

$$1\ \text{atm} = 760\ \text{mmHg} = 76\ \text{cmHg} = 101{,}325\ \text{Pa} \approx 101.3\ \text{kPa}$$

Temperature (T) tells how fast the gas's molecules are moving on average. In every gas law it must be in **kelvin (K)**: $T = t + 273$, where t is the temperature in °C.

The three quantities are linked. Change one, and at least one of the others changes too. The trick, first found more than 350 years ago, is to hold one of them fixed and watch how the other two change.

7.1 Boyle's law and Charles's law

Boyle's law

Put your finger over the nozzle of a syringe full of air and push the plunger. The air squeezes into a smaller space, and the harder you push, the smaller it gets. Let go, and the plunger springs back. Robert Boyle measured exactly how the volume of a trapped gas depends on the pressure on it, and in 1662 published what we now call **Boyle's law**:

Boyle's law: the volume of a fixed mass of a gas is inversely proportional to its pressure, provided its temperature stays the same.

"Inversely proportional" means that if the pressure becomes two times bigger, the volume becomes two times smaller; three times the pressure, a third of the volume. In symbols,

$$V \propto \frac{1}{P} \quad \text{or} \quad V = \frac{k}{P} \quad \text{so} \quad PV = k$$

where k is a constant for that amount of gas at that temperature. So for any two states of the same gas at the same temperature,

$$P_1 V_1 = P_2 V_2$$

Here P_1, V_1 are the pressure and volume before the change, and P_2, V_2 after it. Any unit will do, as long as both pressures are in the same unit and both volumes in the

same unit.

Plot pressure against volume and you get a curve: as the pressure goes up, the volume goes down, quickly at first and then more and more slowly. It never reaches zero volume, however hard you squeeze. Plot pressure against **1 ÷ volume** instead and the same readings fall on a straight line through the origin. A straight line through the origin is the sign of direct proportion: P is directly proportional to $1/V$, which is just another way of saying Boyle's law.

Why Boyle's law happens

The pressure of a gas comes from its molecules hitting the walls of the container (you will see why in 7.4). Squeeze the same molecules into half the space, at the same temperature, and they move just as fast as before, but each one now crosses the box in half the time, so it reaches a wall twice as often. Twice as many hits on each square centimeter every second means twice the pressure.

WORKED EXAMPLE

Squeezing a gas

A gas occupies 200 cm³ at a pressure of 100 kPa. What will its volume be if the pressure is raised to 250 kPa at the same temperature?

Answer

$P_1 = 100$ kPa, $V_1 = 200$ cm³, $P_2 = 250$ kPa, $V_2 = ?$

By Boyle's law, $P_1V_1 = P_2V_2$, so

$$V_2 = \frac{P_1V_1}{P_2} = \frac{100 \times 200}{250} = 80 \text{ cm}^3$$

The volume becomes 80 cm³. Check: the pressure went up 2.5 times, and 200 ÷ 2.5 = 80. A bigger pressure, a smaller volume, as it should be.

Boyle's law around us

Breathing. To breathe in, your diaphragm moves down and your ribs move out, so your chest and lungs get bigger. The air in your lungs now has more room, so its pressure falls a little below the air outside, and air flows in. To breathe out, the chest gets smaller, the pressure inside rises above the air outside, and air is pushed out.

A syringe and a bicycle pump. Pulling a syringe's plunger back makes more space, the pressure inside falls, and the liquid is pushed in by the air outside. Pushing a pump's handle down squeezes the air into a smaller volume until its pressure is higher than the tyre's, and then it pushes past the valve into the tyre.

WORKED EXAMPLE

The chips packet

A packet of chips holds 100 cm³ of air when it is sealed in Kathmandu, where the air pressure is about 86 kPa. What would the volume of the air be at Namche, where the pressure is about 66 kPa, if its temperature didn't change and the packet could stretch freely?

Answer

$P_1 = 86$ kPa, $V_1 = 100$ cm³, $P_2 = 66$ kPa

$$V_2 = \frac{P_1 V_1}{P_2} = \frac{86 \times 100}{66} = 130 \text{ cm}^3$$

About 130 cm³, almost a third bigger. A real packet can't stretch that much, so it goes tight and the air inside stays at a little more than the pressure outside. A packet sealed at sea level, at about 101 kPa, puffs up even more.

Check 1

A gas is squeezed at a steady temperature until its pressure is four times what it was. What happens to its volume?

a it becomes four times bigger
b it stays the same
c it becomes a quarter of what it was
d it becomes half of what it was

Ears on a flight or a bus ride. On a flight from Kathmandu to Lukla, or a long climb by bus, the air pressure outside falls. The air trapped in your middle ear pushes outward on the eardrum until it escapes down the tube to your throat, and your ears "pop". Swallowing or yawning opens that tube and helps.

A diver's bubbles. A bubble breathed out by a diver deep in the sea grows as it rises, because the pressure of the water above it gets less and less. A diver coming up must keep breathing out: air held in the lungs would expand and could tear them.

Weather balloons. A balloon carrying weather instruments is let go only partly filled. As it rises, the air pressure around it falls and the gas inside spreads out, so by about 30 km up the balloon is several times wider. It finally bursts, and the instruments come down by parachute.

Charles's law

Put a dented table tennis ball into hot water and the dent pops out: the air inside expands when it is warmed. Leave a football in the sun and it gets harder; in the cold of a winter morning it feels softer. Gases expand when heated and contract when cooled,

much more than solids and liquids do. The French scientist Jacques Charles studied this around 1787, and Joseph Louis Gay-Lussac measured it carefully and published it in 1802.

They found that every gas expands by the same fraction for each degree it is warmed, as long as its pressure is kept the same: about $\frac{1}{273}$ of its volume at 0 °C for every 1 °C rise. So a gas that fills 273 cm³ at 0 °C fills 274 cm³ at 1 °C, 373 cm³ at 100 °C, and would shrink to 173 cm³ at −100 °C.



Figure 7.2 *A NASA meteorologist getting a weather balloon ready for launch. Big as it looks, it is filled to only a small part of what it can hold: as it rises into thinner air, the gas inside spreads out until the balloon is several times wider.*

Photo: NASA Armstrong Flight Research Center / NASA/Carla Thomas, Public domain

WORKED EXAMPLE

A bubble from the deep

A diver 10 m under the sea breathes out a bubble of 2 cm³. The pressure there is about 2 atm (1 atm from the air, about 1 atm more from 10 m of water). What is the bubble's volume when it reaches the surface, where the pressure is 1 atm? (Take the temperature to be the same.)

Answer

$$V_2 = \frac{P_1 V_1}{P_2} = \frac{2 \times 2}{1} = 4 \text{ cm}^3$$

The bubble doubles to about 4 cm³. Here the pressures were in atm, and that is fine: Boyle's law only needs both pressures in the same unit.

Run that rule backward and something remarkable happens. At −273 °C, the gas would have lost 273 parts in 273 of its volume: its volume would be **zero**. No gas actually gets there, because every real gas turns liquid first, but the line on the graph points to −273 °C (more exactly −273.15 °C) as the coldest any temperature could ever be: **absolute zero**. The kelvin scale starts from it, so that 0 K = −273 °C. On the kelvin scale, the rule becomes very simple:

Charles's law: the volume of a fixed mass of a gas is directly proportional to its absolute temperature, provided its pressure stays the same.

$$V \propto T \quad \text{or} \quad \frac{V}{T} = k \quad \text{so} \quad \frac{V_1}{T_1} = \frac{V_2}{T_2}$$

A STORY FROM SCIENCE

Robert Boyle and the J-shaped tube

Robert Boyle (1627–1691) was born in Ireland and did his experiments in Oxford and London with his assistant Robert Hooke. He took a long glass tube bent like the letter J, with the short arm sealed, and poured mercury into the long arm. The mercury trapped some air in the short arm. As he poured in more mercury, the extra weight of mercury squeezed the trapped air into less and less space. Boyle measured the length of the trapped air and the difference in the mercury levels, and found that when the pressure doubled, the air's volume halved. He published his results in 1662. In France, Edme Mariotte found the same rule on his own in 1676, so in France and some other countries it is called Mariotte's law.

Here T_1 and T_2 **must be in kelvin**. Double the kelvin temperature, and the volume doubles.

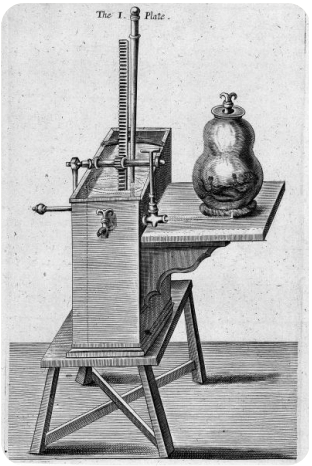


Figure 7.3 *Boyle's second air pump, from his book of 1669. It pumped the air out of the glass vessel on the right, so that he could watch what happened to things inside it.*
Photo: Wellcome Collection, CC BY 4.0

Charles's law around us

Hot air balloons. Heating the air inside the balloon's envelope makes it expand. Since the envelope is open at the bottom, some of the air is pushed out, so the warm air left inside is lighter than the same volume of cool air outside, and the balloon rises.

Tyres and footballs. A tyre pumped hard in the cool of the morning becomes harder still after a long drive in the afternoon sun, as the warmed air inside tries to expand. Its rubber stops it expanding much, so its pressure rises instead (you will see this in 7.2). That's why tyre pressures are best checked when the tyres are cold.

Puffed rice and popcorn. The water inside a grain of rice or maize turns to steam when it is heated, and hot steam takes up a huge volume; the grain bursts open. (Here the gas is being made as well as heated, so it's more than Charles's law alone.)

CAREFUL

Always change °C into kelvin first

Charles's law is about the **absolute** temperature. Heating a gas from 10 °C to 20 °C doesn't double its volume: in kelvin it goes from 283 K to 293 K, a rise of only about 3.5%. Doubling the volume of a gas at 10 °C means heating it to $2 \times 283 = 566$ K, which is 293 °C. Using °C in the formula is the most common mistake in gas law problems.

WORKED EXAMPLE

Warming a gas

A gas occupies 500 cm³ at 27 °C. What will its volume be at 87 °C, if the pressure stays the same?

Answer

$V_1 = 500$ cm³, $T_1 = 27 + 273 = 300$ K, $T_2 = 87 + 273 = 360$ K

$$V_2 = \frac{V_1 T_2}{T_1} = \frac{500 \times 360}{300} = 600 \text{ cm}^3$$

The volume becomes 600 cm³. (Using °C by mistake would have given $500 \times 87 \div 27 = 1{,}611$ cm³, far too much.)

WORKED EXAMPLE

How cold to halve it?

To what temperature must a gas at 27 °C be cooled, at constant pressure, so that its volume becomes half of what it was?

Answer

$T_1 = 300$ K, and $V_2 = \frac{1}{2} V_1$. By Charles's law,

$$T_2 = \frac{V_2}{V_1} \times T_1 = \frac{1}{2} \times 300 = 150 \text{ K}$$

$t_2 = 150 - 273 = -123\ ^\circ\text{C}$. **It must be cooled to −123 °C.**

Check 2

A balloon holds 2 L of air at 0 °C. At the same pressure, at what temperature would it hold 4 L?

a 0 °C
b 2 °C
c 273 °C
d 546 °C



Figure 7.4 *On 1 December 1783, Jacques Charles and Nicolas-Louis Robert rose over Paris in a balloon filled with hydrogen, the first time people flew in a gas balloon. Charles studied how gases expand when heated a few years later.*

Photo: unknown; Esnauts et Rapilly editors, Paris, Public domain

7.2 Combined gas equation

In real life, pressure and temperature often change together. A gas going up a mountain meets lower pressure **and** colder air. We can combine Boyle's law and Charles's law into one equation.

Take a fixed mass of gas from a first state (P_1, V_1, T_1) to a second state (P_2, V_2, T_2) in two steps, one law at a time.

In the first step, keep the temperature at T_1 and change the pressure from P_1 to P_2. Call the new volume V. By Boyle's law,

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

In the second step, keep the pressure at P_2 and change the temperature from T_1 to T_2. The volume goes from V to V_2. By Charles's law,

$$\frac{V}{T_1} = \frac{V_2}{T_2} \quad \text{so} \quad V = \frac{V_2 T_1}{T_2} \tag{ii}$$

Both (i) and (ii) give the same V, so

$$\frac{P_1 V_1}{P_2} = \frac{V_2 T_1}{T_2}$$

Rearranging (multiply both sides by P_2 and divide both by T_1) gives the **combined gas equation**:

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

In other words, for a fixed mass of any gas, $\frac{PV}{T}$ stays the same, however its pressure, volume and temperature change. Boyle's and Charles's laws are both inside it: keep T fixed and it becomes $P_1 V_1 = P_2 V_2$; keep P fixed and it becomes $\frac{V_1}{T_1} = \frac{V_2}{T_2}$. Keep V fixed, and it gives a third law, $\frac{P_1}{T_1} = \frac{P_2}{T_2}$: in a closed, rigid container, **the pressure is proportional to the absolute temperature**. This is sometimes called the pressure law, or Gay-Lussac's law.

WORKED EXAMPLE

Using the combined gas equation

A gas occupies 400 cm³ at 27 °C and a pressure of 750 mmHg. Find its volume at 77 °C and 600 mmHg.

Answer

	First state	Second state
Pressure	$P_1 = 750$ mmHg	$P_2 = 600$ mmHg
Volume	$V_1 = 400$ cm³	$V_2 = ?$
Temperature	$T_1 = 27 + 273 = 300$ K	$T_2 = 77 + 273 = 350$ K

$$V_2 = \frac{P_1 V_1 T_2}{T_1 P_2} = \frac{750 \times 400 \times 350}{300 \times 600} = \frac{105{,}000{,}000}{180{,}000} = 583.3 \text{ cm}^3$$

The volume becomes about 583 cm³. Check: the pressure fell (more volume) and the temperature rose (more volume again), so the volume should grow, and it did.

WORKED EXAMPLE

The chips packet again

The packet holding 100 cm³ of air was sealed in Kathmandu at 86 kPa and 25 °C. At Namche the pressure is 66 kPa and the air is at 5 °C. Find the air's volume there, if the packet could stretch freely.

Answer

$T_1 = 25 + 273 = 298$ K, $T_2 = 5 + 273 = 278$ K

$$V_2 = \frac{P_1 V_1 T_2}{T_1 P_2} = \frac{86 \times 100 \times 278}{298 \times 66} = 121.6 \text{ cm}^3$$

About 122 cm³. The lower pressure makes the air spread out, but the cold makes it shrink a little, so the packet grows by about a fifth instead of the third we found with Boyle's law alone.

WORKED EXAMPLE

Don't throw it in the fire

A sealed steel can holds air at 100 kPa and 27 °C. It is thrown into a fire and heated to 327 °C. What does the pressure inside become?

Answer

The steel can hardly stretches, so $V_1 = V_2$ and the combined gas equation becomes $\frac{P_1}{T_1} = \frac{P_2}{T_2}$.

$T_1 = 300$ K, $T_2 = 327 + 273 = 600$ K

$$P_2 = \frac{P_1 T_2}{T_1} = \frac{100 \times 600}{300} = 200 \text{ kPa}$$

The pressure doubles to 200 kPa. That's why spray cans carry the warning "Do not burn or pierce, even when empty": they still hold gas, and in a fire its pressure can burst the can.

DID YOU KNOW?

The ideal gas equation

The constant in $\frac{PV}{T}$ depends on how much gas there is: twice the gas, twice the constant. Chemists count gas in **moles** (you will meet the mole in Grade 10 Optional Science), and for n moles of any gas the constant is nR, where $R = 8.314$ J/(mol K) is the **gas constant**, the same for every gas. So $PV = nRT$, the ideal gas equation, holds for all gases at once.

7.3 STP

The volume of a gas means nothing on its own: 100 cm³ of hydrogen at a high pressure holds more hydrogen than 100 cm³ at a low pressure, and 100 cm³ at 0 °C more than at 100 °C. To compare amounts of gas fairly, chemists quote volumes at one agreed temperature and pressure, called **standard temperature and pressure (STP)**:

Standard temperature: 0 °C, which is 273 K.

Standard pressure: 1 atm, which is 760 mmHg, 76 cmHg or 101,325 Pa.

To change a volume to STP, use the combined gas equation with 273 K and 760 mmHg (or 101.3 kPa, or 1 atm) as the second state. At STP, one mole of any gas occupies about **22.4 L**, its **molar volume**. A liter of hydrogen and a liter of carbon dioxide at STP contain the same number of molecules, even though the carbon dioxide is 22 times heavier.

CAREFUL

Two STPs

Our textbooks, and most exam questions in Nepal, use the older STP: 0 °C and 1 atm (760 mmHg), with a molar volume of 22.4 L. Since 1982, IUPAC, the international body of chemists, has defined standard pressure as 1 bar, which is 100 kPa, a little less than 1 atm; at 0 °C and 1 bar a mole of gas occupies 22.7 L. Both are right for their own definition. In your exam, use 760 mmHg and 22.4 L unless the question says otherwise.

WORKED EXAMPLE

Changing a volume to STP

380 cm³ of a gas is collected at 27 °C and 780 mmHg. What is its volume at STP?

Answer

$P_1 = 780$ mmHg, $V_1 = 380$ cm³, $T_1 = 300$ K; at STP, $P_2 = 760$ mmHg, $T_2 = 273$ K

$$V_2 = \frac{P_1 V_1 T_2}{T_1 P_2} = \frac{780 \times 380 \times 273}{300 \times 760} = 354.9 \text{ cm}^3$$

About 355 cm³ at STP. It is a little smaller because STP is colder than 27 °C; the slightly higher pressure in the lab makes STP's volume a little bigger, but the cold matters more.

WORKED EXAMPLE

A breath of Kathmandu air

You breathe in 1 L of air in Kathmandu, at 20 °C and 86 kPa. What would that air's volume be at STP?

Answer

$$V_2 = \frac{P_1 V_1 T_2}{T_1 P_2} = \frac{86 \times 1 \times 273}{293 \times 101.3} = 0.79 \text{ L}$$

About 0.79 L. In other words, a liter of Kathmandu air holds about a fifth less air than a liter at STP. Compared at the same temperature, a breath in Kathmandu carries about 15% less oxygen than the same breath at sea level, and a breath at the top of Everest, where the pressure is about 34 kPa, only a third.

Check 3

Which of these is standard temperature and pressure, as used in this book?

a 25 °C and 760 mmHg
b 273 K and 760 mmHg
c 0 K and 1 atm
d 273 °C and 76 cmHg

7.4 Kinetic theory of gases

Boyle's and Charles's laws describe what gases do, but not why. The **kinetic theory of gases** explains them by picturing a gas as a crowd of tiny particles in constant motion ("kinetic" comes from the Greek word for moving). Daniel Bernoulli first suggested it in 1738, and James Clerk Maxwell and Ludwig Boltzmann worked it out in the 1860s and 1870s. Its **assumptions** (postulates) are:

1. A gas is made of a very large number of tiny particles, its molecules (or atoms, in a gas like helium). All the molecules of one gas are alike.
2. The molecules are so small, and so far apart, that their own volume is negligible compared with the volume of the container. A gas is mostly empty space.
3. The molecules move all the time, in straight lines, in every direction at random, until they hit another molecule or a wall.
4. Their collisions with each other and with the walls are **perfectly elastic**: no kinetic energy is lost, so the molecules never slow down and stop.
5. There are no forces of attraction or repulsion between the molecules, except at the moment they collide.
6. A collision lasts a negligibly short time compared with the time between collisions.
7. The **pressure** of a gas is caused by its molecules hitting the walls of the container.
8. The **average kinetic energy** of the molecules is directly proportional to the absolute temperature of the gas.

From these assumptions, the gas laws follow.

Boyle's law. At a fixed temperature, the molecules keep the same average speed. Halve the volume, and the same molecules, at the same speed, hit each part of the walls twice as often. The pressure doubles.

Charles's law. Heat the gas and its molecules move faster (assumption 8), hitting the walls more often and harder. If the pressure is to stay the same, the gas must spread into a bigger space, so that the hits on each square centimeter are fewer again. The higher the temperature, the bigger the volume.

The pressure law. In a closed, rigid container, faster molecules have nowhere to spread to, so the walls take more and harder hits, and the pressure rises.

Diffusion. Molecules moving at random in straight lines spread through any space open to them, which is why the smell of food cooking soon reaches the next room (see 7.6).

DID YOU KNOW?

Faster than sound

At 27 °C, a nitrogen molecule in the air moves at about 500 m/s on average, faster than sound travels through air (343 m/s). It doesn't cross a room in a second, though: it hits another molecule after only about 70 nanometers (about two hundred of its own widths), about seven billion times a second, and is sent off in a new direction every time. So a smell spreads through a room in minutes, not milliseconds.

Check 4

According to the kinetic theory of gases, what happens to the molecules of a gas when its temperature is raised?

a they get bigger

b they attract one another more strongly

c their average kinetic energy increases, so they move faster

d they stop colliding with the walls

7.5 Real and ideal gases

An **ideal gas** is a gas that obeys the gas laws, $\frac{PV}{T} = \text{constant}$, exactly, at every temperature and every pressure. It would be a gas whose molecules behave exactly as the kinetic theory assumes: with no volume of their own and no attraction for each other.

No such gas exists. Every gas we know is a **real gas**, and real gases follow the gas laws closely only at **low pressure** and **high temperature**. At high pressure or low temperature they stray from them, for two reasons, both of them assumptions of the kinetic theory that aren't quite true.

The molecules do have a volume. At ordinary pressures, the molecules fill only about a thousandth of the space, and their own size doesn't matter. Squeeze a gas to hundreds of atmospheres and the molecules are packed so close that they fill a real part of it. The gas can't be squeezed as much as Boyle's law says, so PV comes out **more** than for an ideal gas.

The molecules do attract each other. The attraction is weak, but when molecules are close together and moving slowly (at high pressure and low temperature), it pulls them toward one another. A molecule about to hit the wall is tugged back by its neighbors, so it hits more gently, and the gas can be squeezed **more** than Boyle's law says; PV comes out **less**.

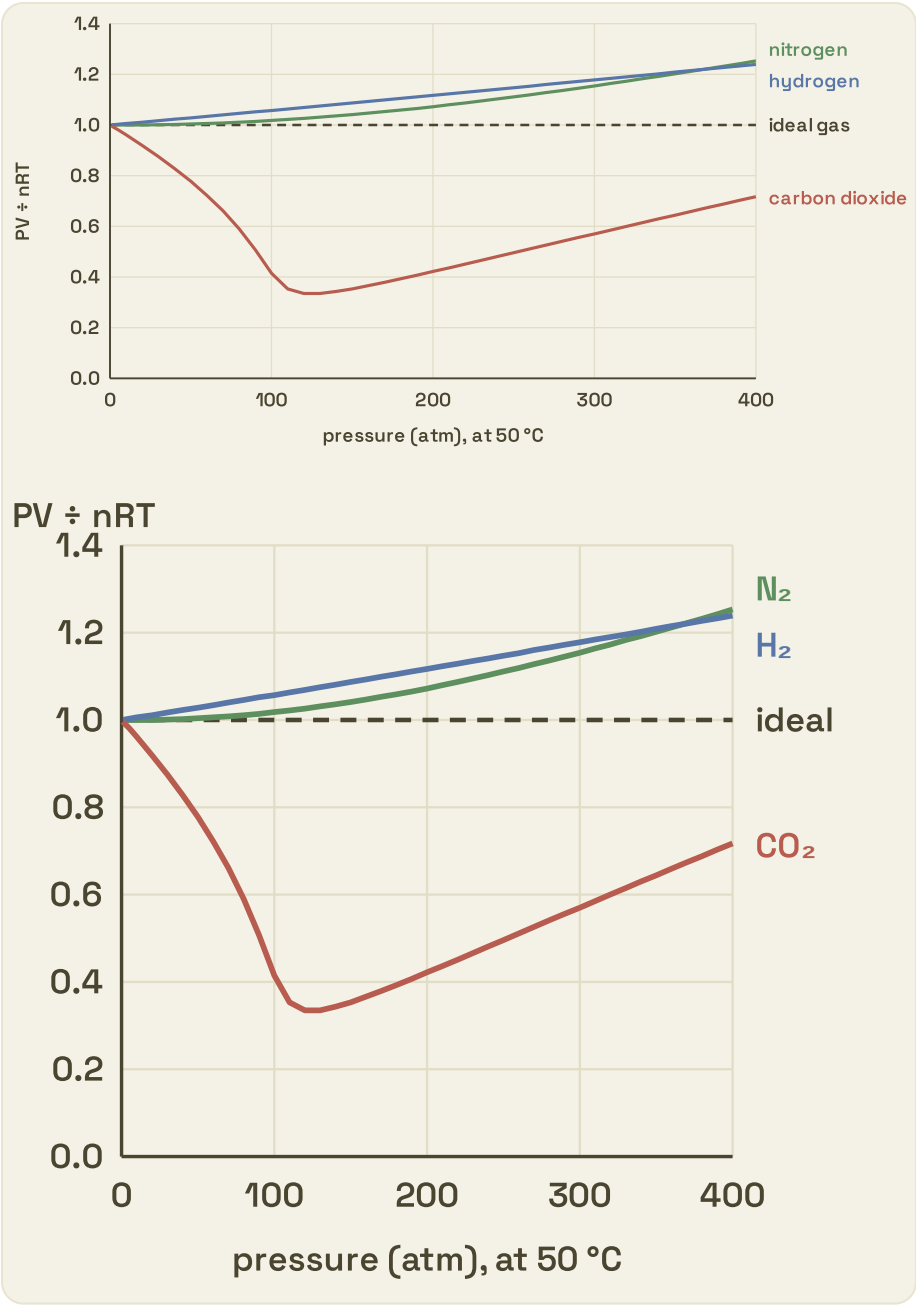


Figure 7.5 *How far three real gases stray from an ideal gas at 50 °C. For an ideal gas, PV ÷ nRT is always 1. Hydrogen rises slowly above 1 from the start, and nitrogen stays at 1 up to about 100 atm before it rises too, as*

their molecules' own volume starts to count (in nitrogen, the weak attraction at first cancels it). Carbon dioxide, whose molecules attract each other more strongly, drops far below 1, lowest near 120 atm, and rises again only when it is squeezed so hard that the volume of its molecules counts most. (Values from measured equations of state.)

In everyday conditions, around 1 atm and room temperature, gases such as hydrogen, helium, nitrogen and oxygen behave almost exactly like an ideal gas: the gas laws are right to better than 1%. Gases whose molecules attract each other more strongly, such as carbon dioxide, ammonia and sulphur dioxide, stray more, and they are also the gases that are easiest to turn into liquids.

Ideal gas	Real gas
Obeys the gas laws exactly at all temperatures and pressures.	Obeys them closely only at low pressure and high temperature.
Its molecules have no volume.	Its molecules have a small volume of their own.
No attraction between its molecules.	Weak attraction between its molecules.
Could never be turned into a liquid.	Turns into a liquid when cooled enough and squeezed.
Doesn't exist; a model.	Every gas there is: hydrogen, oxygen, carbon dioxide…

DID YOU KNOW?

Gas you can pour into a cylinder

The cooking gas in Nepal's kitchens (LPG, mostly propane and butane) is a real gas that becomes liquid when it is squeezed: inside the cylinder it is mostly a liquid, under a pressure of a few atmospheres. That's how a 14.2 kg cylinder can hold enough gas for weeks of cooking. Open the regulator and the liquid boils back into gas. An ideal gas could never be stored like this: with no attraction between its molecules, it would never become a liquid however hard it was squeezed.

A STORY FROM SCIENCE

Van der Waals and the real gases

In 1873 the Dutch physicist Johannes Diderik van der Waals changed the ideal gas equation to allow for the two things the kinetic theory leaves out: the volume of the molecules and the attraction between them. His equation explained why gases turn into liquids and why each gas has a **critical temperature** above which no amount of squeezing will liquefy it (31 °C for carbon dioxide; −147 °C for nitrogen). He was awarded the Nobel Prize in Physics in 1910. The weak attractions between molecules are still called van der Waals forces.

7.6 Graham's law of diffusion

Open a bottle of perfume in one corner of a room and soon it can be smelled in the other. Its molecules spread through the air by themselves, without being blown. This spreading of the particles of a gas from where there are more of them to where there are fewer, by their own random motion, is called **diffusion**. Gases also **effuse**: they leak out, molecule by molecule, through a tiny hole, as helium slowly escapes through the rubber of a party balloon.

Do all gases spread equally fast? In the 1830s and 1840s the Scottish chemist Thomas Graham timed many gases diffusing and effusing, and found that light gases spread much faster than heavy ones:

Graham's law of diffusion: at the same temperature and pressure, the rate of diffusion of a gas is inversely proportional to the square root of its density.

$$r \propto \frac{1}{\sqrt{d}} \quad \text{so, for two gases,} \quad \frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}}$$

At the same temperature and pressure, the density of a gas is proportional to its molar mass M (the same volume holds the same number of molecules), so the law can also be written

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

The rate is how much gas diffuses in a given time. If the same volume of each gas is timed, the time taken is longer for the slower gas, so the times go the other way: $\frac{t_1}{t_2} = \sqrt{\frac{M_1}{M_2}}$.

Why the square root? At the same temperature, the molecules of every gas have the same average kinetic energy, $\frac{1}{2}mv^2$. A molecule 16 times heavier must then move

$\sqrt{16} = 4$ times more slowly, and the gas spreads 4 times more slowly.

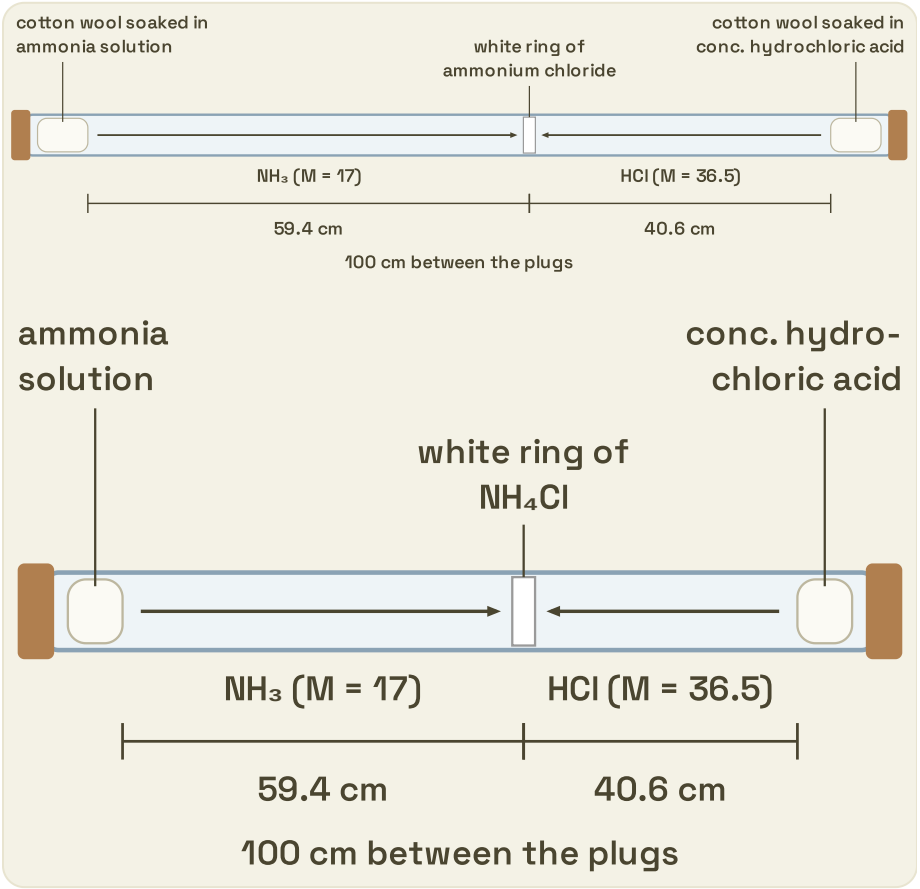


Figure 7.6 *Ammonia gas comes off the cotton wool at one end of a long tube, hydrogen chloride gas at the other. Where they meet, they react to make a white ring of solid ammonium chloride: $NH_3 + HCl \rightarrow NH_4Cl$. Graham's law puts the ring 59.4 cm from the ammonia end, because the lighter ammonia spreads faster.*

Applications of Graham's law

Smells spread, and some faster than others. The smell of food cooking, a perfume or a gas leak reaches us by diffusion through the air. The cooking gas in an LPG cylinder has no smell of its own, so a strong-smelling compound (ethyl mercaptan) is added to it in tiny amounts, to warn of a leak. LPG is heavier than air (propane is about one and a half times as dense, butane about twice), so it spreads slowly and collects near the floor: open the doors and windows, and never switch on a light or a fan near a leak.

WORKED EXAMPLE

Where does the ring form?

In the tube in Figure 7.6, the plugs are 100 cm apart. The molar mass of ammonia (NH_3) is 17 g/mol and that of hydrogen chloride (HCl) 36.5 g/mol. Where will the white ring form?

Answer

Both gases start at the same moment and travel until they meet, so the distances they cover are in the same ratio as their rates:

$$\frac{d_{\mathrm{NH_3}}}{d_{\mathrm{HCl}}} = \frac{r_{\mathrm{NH_3}}}{r_{\mathrm{HCl}}} = \sqrt{\frac{36.5}{17}} = \sqrt{2.147} = 1.465$$

The two distances add up to 100 cm: $d_{\mathrm{NH_3}} + d_{\mathrm{HCl}} = 100$. So $1.465\, d_{\mathrm{HCl}} + d_{\mathrm{HCl}} = 100$, giving $d_{\mathrm{HCl}} = 100 \div 2.465 = 40.6$ cm, and $d_{\mathrm{NH_3}} = 59.4$ cm.

The ring forms about 59.4 cm from the ammonia end, closer to the hydrogen chloride. In a real tube the ring does form nearer the hydrogen chloride end, though not always at exactly this spot: the gases are spreading through the air in the tube, jostled by its molecules, and Graham's law holds closely only for a gas escaping through a tiny hole into empty space.

WORKED EXAMPLE

Hydrogen and oxygen

Compare the rates of diffusion of hydrogen (H_2, M = 2) and oxygen (O_2, M = 32). If 100 cm³ of oxygen takes 60 s to diffuse through a porous pot, how long will 100 cm³ of hydrogen take?

Answer

$$\frac{r_{\mathrm{H_2}}}{r_{\mathrm{O_2}}} = \sqrt{\frac{M_{\mathrm{O_2}}}{M_{\mathrm{H_2}}}} = \sqrt{\frac{32}{2}} = \sqrt{16} = 4$$

Hydrogen diffuses 4 times faster than oxygen, so the same volume takes a quarter of the time: $60 \div 4 = \mathbf{15\ s}$.

Helium balloons go flat sooner. A party balloon filled with helium (M = 4) goes soft within about a day, while one blown up with air (M about 29) lasts much longer. The small, fast helium atoms escape through the rubber about $\sqrt{29/4} \approx 2.7$ times faster than air does, and more easily still because they are so small.

WORKED EXAMPLE

Finding a molar mass

An unknown gas diffuses at a quarter of the rate of helium (M = 4) under the same conditions. Find its molar mass. Which gas could it be?

Answer

$$\frac{r_X}{r_{\text{He}}} = \sqrt{\frac{M_{\text{He}}}{M_X}} \quad \text{so} \quad \frac{1}{4} = \sqrt{\frac{4}{M_X}}$$

Square both sides: $\frac{1}{16} = \frac{4}{M_X}$, so $M_X = 64$ g/mol. **The molar mass is 64 g/mol**; the gas could be sulphur dioxide, SO_2 ($32 + 2 \times 16 = 64$).

Check 5

Which of these gases diffuses fastest at the same temperature and pressure?

a oxygen, O_2 (M = 32)

b carbon dioxide, CO_2 (M = 44)

c methane, CH_4 (M = 16)

d chlorine, Cl_2 (M = 71)

Finding molar masses. Timing how fast an unknown gas diffuses or effuses, beside a gas whose molar mass is known, gives the unknown gas's molar mass, as in the example above.

Separating isotopes. Natural uranium is mostly uranium-238, with only 0.7% of the uranium-235 that nuclear power stations need. Turned into the gas uranium hexafluoride (UF_6), the two isotopes differ in molar mass only a little, 349 against 352 g/mol, so the lighter one diffuses through a porous wall only $\sqrt{352/349} = 1.0043$ times faster. Pumping the gas through thousands of such walls, one after another, slowly built up the uranium-235. This was the main way uranium was enriched from the 1940s; the last such plants closed in the 2010s, and fast-spinning centrifuges are used instead.



Figure 7.7 *The K-25 site in Oak Ridge, United States, in 1945. Its plant, built to separate uranium isotopes by gaseous diffusion, was the largest building in the world when it was finished in 1944: four stories high, U-shaped and about 800 m (half a mile) long.*

Photo: Ed Westcott / DoE Oak Ridge, Public domain

IN SHORT

- A gas is described by its pressure P, volume V and temperature T, always in kelvin: $T = t + 273$.
- **Boyle's law:** at constant temperature, $V \propto \frac{1}{P}$, so $P_1V_1 = P_2V_2$.
- **Charles's law:** at constant pressure, $V \propto T$, so $\frac{V_1}{T_1} = \frac{V_2}{T_2}$. A gas's volume points to zero at −273 °C, absolute zero.
- **Combined gas equation:** $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$ for a fixed mass of gas; with V fixed, $P \propto T$.
- **STP:** 0 °C (273 K) and 1 atm (760 mmHg); one mole of any gas occupies 22.4 L at STP.
- **Kinetic theory:** a gas is tiny molecules, with negligible volume and no attraction, moving at random with perfectly elastic collisions; their hits on the walls make the pressure, and their average kinetic energy is proportional to T.
- An **ideal gas** obeys the gas laws exactly; **real gases** do so only at low pressure and high temperature, because their molecules have volume and attract each other.
- **Graham's law:** $\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}}$; lighter gases diffuse faster.

Exercise

1. Choose the correct option

a. A graph of the pressure of a fixed mass of gas against 1 ÷ its volume, at constant temperature, is:

- **a** a curve that falls
- **b** a straight line through the origin
- **c** a straight line parallel to the 1 ÷ volume axis
- **d** a straight line that cuts the pressure axis above zero

b. At constant pressure, a gas is heated from 100 K to 200 K. Its volume:

- **a** stays the same
- **b** halves
- **c** doubles
- **d** becomes four times bigger

c. Which equation is the combined gas equation?

- **a** $P_1V_1T_1 = P_2V_2T_2$
- **b** $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$
- **c** $\frac{P_1T_1}{V_1} = \frac{P_2T_2}{V_2}$
- **d** $\frac{V_1}{P_1T_1} = \frac{V_2}{P_2T_2}$

d. Absolute zero is:

- **a** 0 °C
- **b** −100 °C
- **c** −273 °C
- **d** 273 K

e. Which is an assumption of the kinetic theory of gases?

- **a** gas molecules attract each other strongly
- **b** gas molecules lose energy every time they hit a wall
- **c** the volume of the gas molecules is negligible compared with the volume of the container
- **d** gas molecules stay still until they are heated

f. A real gas behaves most like an ideal gas at:

- **a** high pressure and low temperature
- **b** high pressure and high temperature
- **c** low pressure and high temperature
- **d** low pressure and low temperature

g. Under the same conditions, the rate of diffusion of hydrogen (M = 2) compared with that of oxygen (M = 32) is:

- **a** 16 times faster
- **b** 4 times faster
- **c** 4 times slower
- **d** the same

h. Standard pressure, as used in this book, is:

- **a** 1 mmHg
- **b** 76 mmHg
- **c** 760 mmHg
- **d** 7,600 mmHg

2. Give reasons

a. A balloon blown up indoors shrinks when it is taken out on a cold winter night.

b. Temperatures in the gas laws must be written in kelvin, not in degrees Celsius.

c. A weather balloon is filled only partly before it is launched.

d. Ammonia spreads through a room faster than hydrogen chloride gas.

e. Air in a car's tyres is checked when the tyres are cold.

3. Differentiate between

i. Boyle's law and Charles's law

ii. Real gas and ideal gas

iii. Diffusion and effusion

4. Answer the following questions

a. State Boyle's law. Explain it using the kinetic theory of gases.

b. State Charles's law. How does it lead to the idea of absolute zero?

c. Derive the combined gas equation from Boyle's law and Charles's law.

d. What is STP? Why is it needed?

e. Write any four assumptions of the kinetic theory of gases.

f. Why do real gases stray from the gas laws at high pressure and low temperature?

g. State Graham's law of diffusion, and write two of its uses.

5. Numerical problems

a. A gas occupies 600 cm^3 at 760 mmHg. What will its volume be at 380 mmHg, at the same temperature?

b. A balloon holds 2.0 L of air at sea level, where the pressure is 101 kPa. It is carried to the top of Mount Everest, where the pressure is 33.7 kPa. Find its volume there, taking the temperature to be the same.

c. 250 cm^3 of a gas at 7 °C is heated to 147 °C at constant pressure. Find its new volume.

d. At what temperature will 100 cm^3 of a gas at 0 °C occupy 150 cm^3, the pressure staying the same?

e. 2.0 L of a gas is at 27 °C and 1 atm. Find its volume at 127 °C and 2 atm.

f. A glass bottle is sealed with air inside at 27 °C and 1 atm. To what pressure does the air rise if the bottle is heated to 127 °C? (Take the bottle's volume to stay the same.)

g. 500 cm^3 of a gas is collected at 27 °C and 700 mmHg. Find its volume at STP.

h. Compare the rates of diffusion of methane (CH_4, M = 16) and sulphur dioxide (SO_2, M = 64).

i. 50 cm^3 of oxygen (M = 32) diffuses through a small hole in 40 s. How long will 50 cm^3 of carbon dioxide (M = 44) take under the same conditions?

j. A gas diffuses through a porous plug at half the rate of methane (M = 16). Find its molar mass.

k. A weather balloon holds 5.0 m^3 of hydrogen at the ground, where the pressure is 100 kPa and the temperature 27 °C. It rises to 30 km, where the pressure is 1.2 kPa and the temperature −46 °C. What would the hydrogen's volume be there, if the balloon's rubber didn't hold it back? Is it surprising that such balloons burst?

l. **Think:** A student says, "If I heat a gas from 20 °C to 40 °C at constant pressure, its volume doubles." Explain the mistake and find the real change in volume.

Found a mistake? Please tell us.