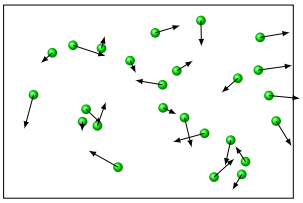
Ideal Gases

Name _____ Date _____

By the end of this topic I can...

- use the mole, the Avogadro constant and molar mass to count molecules
- explain gas pressure in terms of collisions of molecules with the container
- use Boyle's, Charles's, Gay-Lussac's and Avogadro's laws
- use $pV = nRT$ and $pV = NkT$, and state the assumptions of an ideal gas
- derive and use $p = \frac{Nm\langle v^2\rangle}{3V}$ and $\langle E_k\rangle = \frac{3}{2}kT$

Gas molecules



Random motion of gas molecules in a container.

Motion of gas particles

A gas is made of a very large number of ___molecules___. They move ___randomly___ at high speeds, and the randomness comes from ___collisions___ between the fast-moving molecules.

For one molecule the velocity changes constantly as it collides, so at any instant the molecules have a ___range___ of speeds.

Strong evidence for this is ___Brownian motion___:[1] smoke or dust particles seen under a microscope move with jerky, random motion because of collisions with the randomly moving gas molecules.

Molecules move ___faster___ at higher temperature (we prove this later in the chapter).

[1] Named after the botanist Robert Brown, but described much earlier. The Roman poet Lucretius wrote of dust dancing in a sunbeam as a sign of unseen atoms in motion.

Number of molecules

A tangible sample of gas holds a huge number of molecules. The **mole** is the accepted unit for the **amount of substance**, used to measure the size of a collection of particles.

- unit: $[n] =$ ___mol___

One ___mole___ is the amount of substance in ___12 g of carbon-12___.
One mole of any substance contains ___6.02×10^{23}___ particles.

This number is the **Avogadro constant**:[2] $N_A = 6.02 \times 10^{23}\ \text{mol}^{-1}$.

[2] In 2018 the mole was redefined to contain exactly $6.02214076 \times 10^{23}$ particles. The idea is the same: 'amount of substance' counts particles rather than measuring mass.

Converting between number of molecules N and amount of substance n:

$$N = nN_A$$

The **molar mass** M is a useful shortcut.

Molar mass is the mass of a sample divided by the amount of substance in it: $M = \frac{m}{n}$

- amount of substance from the mass of a sample:

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

- mass of a single molecule:

$$m_0 = \frac{M}{N_A}$$

Example 21.1 Find the number of molecules in 160 g of argon-40 gas.

$$n = \frac{m}{M} = \frac{160\ \text{g}}{40\ \text{g mol}^{-1}} = 4.0\ \text{mol}$$
$$N = nN_A = 4.0 \times 6.02 \times 10^{23} \approx 2.41 \times 10^{24}$$

Question 21.1 Find the mass of a sample of uranium-235 that contains 6.0×10^{20} atoms.

$$n = \frac{N}{N_A} = \frac{6.0 \times 10^{20}}{6.02 \times 10^{23}} \approx 1.0 \times 10^{-3}\ \text{mol}$$
$$m = nM = 1.0 \times 10^{-3} \times 235 \approx 0.23\ \text{g}$$

Pressure (qualitative view)

When gas molecules hit the walls of the container and rebound, their momentum changes. By Newton's second law the wall must exert a force on them. By Newton's third law the molecules exert an equal and opposite force on the container. Many molecules together give a steady pressure.

Example 21.2 If a gas is heated with its volume fixed, how does the pressure change?

At higher temperature the molecules move faster.
They collide *harder*, so each collision gives a greater force.
They also collide more *frequently* with the container.
So the pressure **increases**.

Question 21.2 If you pump gas into a bicycle tyre, state and explain how the pressure changes.

Pressure increases: more molecules in the same volume, so more collisions with the tyre wall per second.

Question 21.3 A fixed amount of gas expands at constant temperature. State and explain how the pressure changes.

Pressure decreases: the speed is unchanged (same T), but the molecules have further to travel between collisions with the walls, so collisions are less frequent.

Empirical gas laws

Torricelli's barometer (1643) inspired Robert Boyle to study how the 'spring' of air responds to pressure.[3]

[3] The experiments were carried out by Boyle's assistant, Robert Hooke. Yes, that Hooke, of Hooke's law.

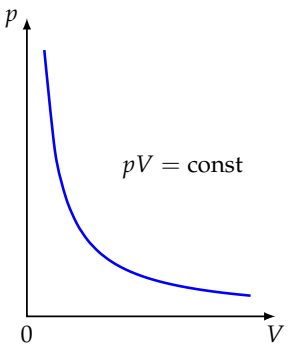
Boyle's law

Discovered by Robert Boyle in 1662. If the temperature T is constant:

$$pV = \text{const} \quad \text{or} \quad p \propto \frac{1}{V}$$

The pressure of a gas is inversely proportional to its volume at fixed temperature, so $p_1V_1 = p_2V_2$.

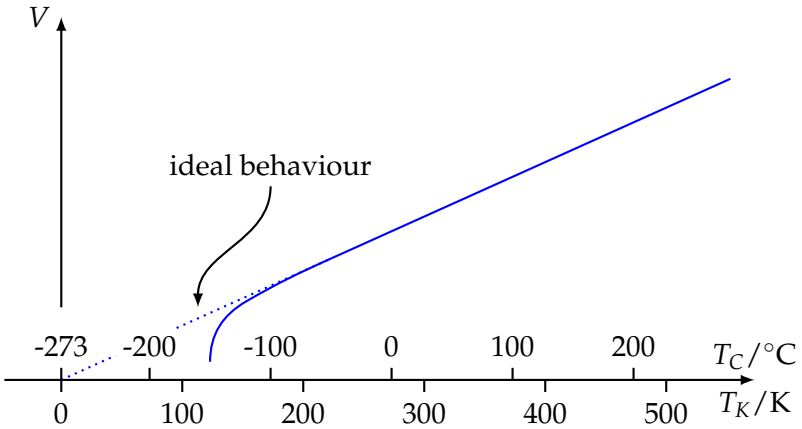
A process at constant temperature is called an isothermal process.



p–V graph for an isothermal process.

Charles's law

Discovered by Jacques Charles in 1787. It has huge consequences:



Charles's law: our first glimpse of absolute zero.

For a fixed pressure p:

$$\frac{V}{T} = \text{const} \quad \text{or} \quad V \propto T$$

The volume of a gas is directly proportional to its temperature.

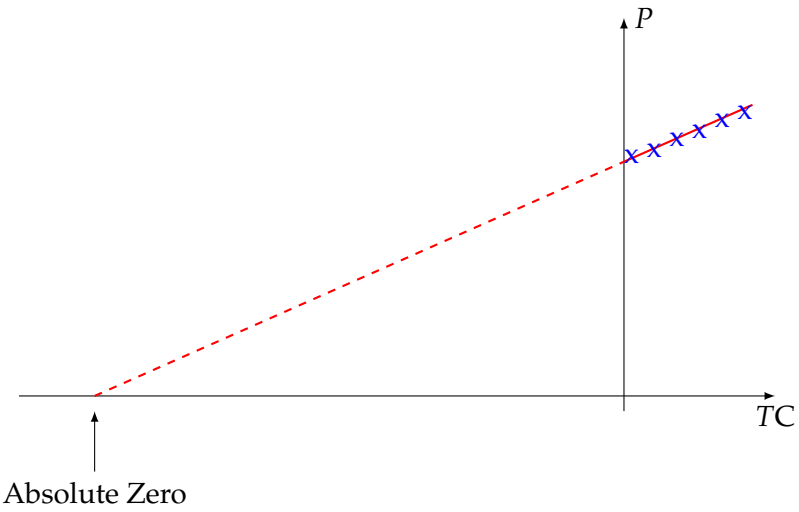
- the proportionality only works with the Kelvin scale.

A process at constant pressure is called an isobaric process.

- Charles's law implies the volume of a gas tends to zero at a certain temperature. This is how the idea of absolute zero first arose. In reality, as $T \to 0$ a real gas condenses to liquid or solid, so there is a deviation from ideal behaviour (dotted line).

Gay-Lussac's law

Discovered by Joseph Louis Gay-Lussac between 1800 and 1802.



Pressure against temperature for a gas.

If the volume V is constant:

$$\frac{p}{T} = \text{const} \quad \text{or} \quad p \propto T$$

The pressure is directly proportional to the temperature.

A process at constant volume is called an isochoric (or isometric) process.

The p–T graph also predicts absolute zero, and again real gases deviate from ideal behaviour as $T \to 0$.

Avogadro's law

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

For a given ideal gas at constant temperature and pressure, volume and amount are directly proportional:

$$\frac{V}{n} = \text{const}$$

The ideal gas

An ideal gas

Combining the laws gives one equation that models the behaviour of real gases. An ideal gas is one where:

- the molecules are numerous, identical and point-like, so far apart that intermolecular forces are negligible
- the molecules move randomly and obey Newton's laws
- collisions with the container walls are elastic
- collisions between molecules are elastic

The ideal gas equation

First stated by Émile Clapeyron in 1834, from Boyle's, Charles's, Avogadro's and Gay-Lussac's laws. For a fixed amount of gas:

$$\frac{pV}{T} = \text{const}$$

A gas obeying

$$pV = nRT \quad \text{or} \quad pV = NkT$$

at any pressure p, volume V and thermodynamic temperature T is an ideal gas.

- molar gas constant: $R =$ $8.31\ \text{J mol}^{-1}\ \text{K}^{-1}$
- Boltzmann constant: $k =$ $1.38 \times 10^{-23}\ \text{J K}^{-1}$

R and k are *universal* constants, the same for any ideal gas. Since $N = nN_A$:

$$R = kN_A \quad \text{so} \quad k = \frac{R}{N_A}$$

The equations need *thermodynamic temperature* (kelvin, K). For a *change* in temperature, Celsius steps are the same size, so Celsius can sometimes be used. To convert:

$$T_K\,(\text{K}) \underset{+273}{\overset{-273}{\rightleftharpoons}} T_C\,(^\circ\text{C})$$

Real gases

Real gases behave like ideal gases at sufficiently ___high___ temperature and ___low___ pressure.

- at very low temperatures a real gas ___condenses___ into a liquid or solid
- at very high pressures ___intermolecular forces___ become important

Under normal conditions ($T \approx 300$ K, $p \approx 1.0 \times 10^5$ Pa) there is no significant difference, so the ideal gas model is accurate enough for most applications.

Example 21.3 A sealed cylinder of volume 0.050 m^3 contains 75 g of air (molar mass 29 g mol^{-1}). (a) Find the air pressure at 30°C. (b) The gas expands at constant pressure. Find its temperature when the volume doubles.

$n = \dfrac{m}{M} = \dfrac{75}{29} \approx 2.59$ mol

(a) $p = \dfrac{nRT}{V} = \dfrac{2.59 \times 8.31 \times (30 + 273)}{0.050} \approx 1.30 \times 10^5$ Pa

(b) $V \propto T$ (constant p): $\dfrac{T_2}{T_1} = \dfrac{V_2}{V_1} = 2 \quad \Rightarrow \quad T_2 = 2 \times 303 = 606$ K $= 333^\circ$C

Example 21.4 A cylinder holds 5000 cm^3 of air at 27°C and 6.0×10^5 Pa. It fills balloons, each containing 1000 cm^3 of air at 27°C and 1.0×10^5 Pa. (a) Find the initial amount of gas in the cylinder. (b) How many balloons can be filled?

(a) $n_0 = \dfrac{p_0 V}{RT} = \dfrac{6.0 \times 10^5 \times 5000 \times 10^{-6}}{8.31 \times 300} \approx 1.203 \text{ mol}$

(b) Gas leaves the cylinder only while its pressure exceeds the balloon pressure. When the two are equal, some gas remains: $n_{\text{remain}} = \dfrac{1.0 \times 10^5 \times 5000 \times 10^{-6}}{8.31 \times 300} \approx 0.201 \text{ mol}$

Each balloon: $n_b = \dfrac{1.0 \times 10^5 \times 1000 \times 10^{-6}}{8.31 \times 300} \approx 0.040 \text{ mol}$

$N = \dfrac{n_0 - n_{\text{remain}}}{n_b} = \dfrac{1.203 - 0.201}{0.040} \approx 25 \text{ balloons}$

Example 21.5 A storage cylinder of volume 5.0×10^{-4} m^3 holds gas at 300 K and 4.0×10^6 Pa. (a) Find the number of molecules. (b) Molecules leak out at 1.6×10^{16} s^{-1}. How long, in days, until the pressure falls by 5.0%?

(a) $N_0 = \dfrac{p_0 V}{kT} = \dfrac{4.0 \times 10^6 \times 5.0 \times 10^{-4}}{1.38 \times 10^{-23} \times 300} \approx 4.83 \times 10^{23}$

(b) V and T fixed, so $N \propto p \quad \Rightarrow \quad \dfrac{\Delta N}{N_0} = \dfrac{\Delta p}{p_0} = 5.0\%$

$\Delta N = 0.05 \times 4.83 \times 10^{23} \approx 2.42 \times 10^{22}$

$t = \dfrac{2.42 \times 10^{22}}{1.6 \times 10^{16}} \approx 1.51 \times 10^6 \text{ s} \approx 17.5 \text{ days}$

Question 21.4 Container A of volume 2.5×10^{-2} m^3 holds gas at 17°C and 1.3×10^5 Pa. Container B, the same size, holds gas at the same temperature and 1.9×10^5 Pa. They are initially isolated. (a) Find the total amount of gas. (b) They are now joined by a tube of negligible volume. With the temperature unchanged, find the final pressure.

(a) $T = 290$ K. $n_A = \dfrac{1.3 \times 10^5 \times 2.5 \times 10^{-2}}{8.31 \times 290} \approx 1.35$ mol, $n_B = \dfrac{1.9 \times 10^5 \times 2.5 \times 10^{-2}}{8.31 \times 290} \approx 1.97$ mol

total $n \approx 3.3$ mol

(b) $V = 5.0 \times 10^{-2}$ m^3: $p = \dfrac{nRT}{V} = \dfrac{3.32 \times 8.31 \times 290}{5.0 \times 10^{-2}} \approx 1.6 \times 10^5$ Pa

Question 21.5 The air in a car tyre has a constant volume of 3.0×10^{-2} m^3. Its pressure is 2.8×10^5 Pa at 25°C. A pump forces 0.015 mol of air into the tyre on each stroke. The final pressure is 3.6×10^5 Pa at 28°C. How many strokes are needed?

Before: $n_1 = \dfrac{p_1 V}{RT_1} = \dfrac{2.8 \times 10^5 \times 3.0 \times 10^{-2}}{8.31 \times 298} \approx 3.39$ mol

After: $n_2 = \dfrac{p_2 V}{RT_2} = \dfrac{3.6 \times 10^5 \times 3.0 \times 10^{-2}}{8.31 \times 301} \approx 4.32$ mol

strokes $= \dfrac{n_2 - n_1}{0.015} = \dfrac{0.926}{0.015} \approx 62$

Kinetic theory of ideal gases

The kinetic model

The **kinetic model** of gases is a theory of the microscopic motion of molecules that explains the macroscopic properties of a gas.

Assumptions of the ideal gas model:
- molecules are in constant random motion
- the separation between molecules is much greater than their size, so their volume is negligible compared with the volume of the gas
- intermolecular forces are negligible
- collisions are perfectly elastic: no kinetic energy is lost
- molecules travel in straight lines between collisions

Example 21.6 20 g of helium-4 at 37°C has a pressure of 1.2×10^5 Pa. Each atom has diameter 280 pm. (a) Find the volume occupied by the gas and the volume of the atoms. (b) Compare them and suggest whether the gas is ideal.

$N = \frac{m}{M}N_A = \frac{20}{4.0} \times 6.02 \times 10^{23} \approx 3.01 \times 10^{24}$

$V_{\text{gas}} = \frac{NkT}{p} = \frac{3.01 \times 10^{24} \times 1.38 \times 10^{-23} \times 310}{1.2 \times 10^5} \approx 0.107 \text{ m}^3$

$V_{\text{atom}} = \frac{4}{3}\pi r^3 = \frac{4}{3}\pi(140 \times 10^{-12})^3 \approx 1.15 \times 10^{-29} \text{ m}^3$

$V_{\text{atoms}} = NV_{\text{atom}} \approx 3.46 \times 10^{-5} \text{ m}^3$

$V_{\text{gas}} \gg V_{\text{atoms}}$, so the gas approximates well to an ideal gas.

Pressure (quantitative view)

Pressure comes from molecules colliding with the container. First consider one molecule moving in one dimension, then generalise to N molecules in three dimensions.

One molecule moves only in the x-direction. The change in momentum at the wall:[4]

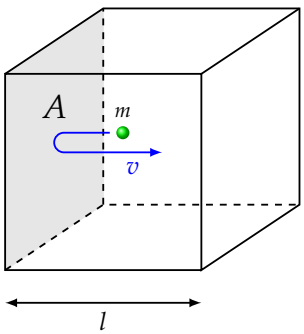
$$\Delta P_x = mv_x - (-mv_x) = 2mv_x$$

Time between collisions with the same wall: $\Delta t = \frac{2l}{v_x}$

Average force: $F_x = \frac{\Delta P_x}{\Delta t} = \frac{2mv_x}{2l/v_x} = \frac{mv_x^2}{l}$

Average pressure: $p_x = \frac{F_x}{A} = \frac{mv_x^2}{lA} = \frac{mv_x^2}{V}$

Now generalise to N molecules in 3-D:



One molecule moving in one dimension in a box of length l.

[4] In this chapter P is the momentum of a particle and p the pressure of a gas, to avoid confusion.

• N molecules give N times the contribution, but with a *distribution* of speeds we take the average of v^2

• in 3-D, $v^2 = v_x^2 + v_y^2 + v_z^2$. No direction is preferred, so

$\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle =$ $\frac{\langle v^2 \rangle}{3}$

• the pressure is shared equally among the three directions

Therefore the pressure of an ideal gas is

$$p = \frac{Nm\langle v^2 \rangle}{3V}$$

• $\langle v^2 \rangle$ is the mean square speed. The **root mean square** speed is $v_{\text{rms}} = \sqrt{\langle v^2 \rangle}$.

• molecules have a range of speeds, so we treat them statistically: we can only talk about mean values.

Nm is the total mass of gas, so $\frac{Nm}{V} = \rho$, the density. Then

$$p = \frac{1}{3}\rho\langle v^2 \rangle$$

So pressure depends only on the density and the mean square speed.
Consequences:

- $N \uparrow$: more molecules, more collisions, p increases
- $m \uparrow$: greater force per collision, p increases
- $v \uparrow$: harder and more frequent impacts, p increases
- $V \uparrow$: less frequent collisions with the container, p decreases

Kinetic energy of a gas

We now have two equations for an ideal gas:

$$pV = nRT \text{ or } pV = NkT \quad \text{(ideal gas law)}$$

$$p = \frac{Nm\langle v^2 \rangle}{3V} \quad \text{(pressure law)}$$

Comparing them: $pV = \frac{1}{3}Nm\langle v^2 \rangle = NkT \quad \Rightarrow \quad m\langle v^2 \rangle = 3kT.$

This gives the *mean kinetic energy* of one molecule:

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

The mean K.E. is proportional to the thermodynamic temperature, so

$$v_{\text{rms}}^2 \propto T$$

This is only the *translational* K.E. (motion through space). The total K.E. can also include rotational and vibrational K.E.[5]

$\frac{3}{2}kT$ is the *mean* K.E. per molecule. Molecules exchange energy in collisions, so an individual K.E. is not constant, but the mean depends on T only. In a mixture of gases the mean K.E. is shared equally, so heavier molecules move more slowly.

[5] *Equipartition*: each independent degree of freedom carries $\frac{1}{2}kT$ on average. Three translational ones give $\frac{3}{2}kT$; many-atom molecules also rotate and vibrate.

Example 21.7 Air is mainly oxygen (O_2, $M = 32$ g mol^{-1}) and nitrogen (N_2, $M = 28$ g mol^{-1}). (a) Calculate the mean translational K.E. at 300 K. (b) Estimate the typical speed of each.

(a) $\langle E_k \rangle = \frac{3}{2}kT = \frac{3}{2} \times 1.38 \times 10^{-23} \times 300 \approx 6.21 \times 10^{-21}$ J

(b) $\frac{1}{2}\frac{M}{N_A}\langle v^2 \rangle = \frac{3}{2}kT \quad \Rightarrow \quad \langle v^2 \rangle = \frac{3kN_AT}{M} = \frac{3RT}{M}$

O_2: $v \approx \sqrt{\frac{3 \times 8.31 \times 300}{0.032}} \approx 483$ m s^{-1}

N_2: $v \approx \sqrt{\frac{3 \times 8.31 \times 300}{0.028}} \approx 517$ m s^{-1}

Example 21.8 Helium-4 gas is at 54°C. (a) Find the mean square speed of the atoms. (b) The temperature rises to 540°C. Find the r.m.s. speed.

$m = 4$ u $= 4 \times 1.66 \times 10^{-27} \approx 6.64 \times 10^{-27}$ kg

(a) $\langle v^2 \rangle = \frac{3kT}{m} = \frac{3 \times 1.38 \times 10^{-23} \times 327}{6.64 \times 10^{-27}} \approx 2.04 \times 10^6$ m^2 s^{-2}

(b) $\langle v^2 \rangle \propto T \quad \Rightarrow \quad v'_{\text{rms}} = \sqrt{\frac{T'}{T}}\, v_{\text{rms}} = \sqrt{\frac{813}{327}} \times \sqrt{2.04 \times 10^6} \approx 2.25 \times 10^3$ m s^{-1}

Question 21.6 A fixed mass of gas expands to twice its volume at constant temperature. (a) How does its pressure change? (b) How does the mean kinetic energy change?

(a) pV is constant (Boyle), so the pressure **halves**.
(b) The mean K.E. depends only on T, so it is **unchanged**.

Question 21.7 To escape the Earth's gravitational field a molecule must have a speed of 1.1×10^4 m s^{-1} at the top of the atmosphere. (a) Estimate the temperature at which helium-4 atoms have this speed. (b) Helium atoms in fact escape at much lower temperatures. Explain how.

(a) $\frac{1}{2}m\langle v^2\rangle = \frac{3}{2}kT \quad \Rightarrow \quad T = \frac{mv^2}{3k} = \frac{6.64 \times 10^{-27} \times (1.1 \times 10^4)^2}{3 \times 1.38 \times 10^{-23}} \approx 1.9 \times 10^4$ K
(b) Atoms have a *range* of speeds. Even when the mean is much lower, a small fraction of atoms in the high-speed tail exceed the escape speed.