Unit 7 · Gas Laws

STUDY NOTES

Key terms

Pressure P: force of a gas on each unit area of the walls; Pa $= \mathrm{N/m^2}$.

Temperature T: how fast the molecules move on average; always in K.

Absolute zero: −273 °C (more exactly −273.15 °C) = 0 K; where a gas's volume line points to zero.

STP: 0 °C (273 K), 1 atm (760 mmHg).

Molar volume: 1 mole of any gas at STP ≈ 22.4 L.

Ideal gas: obeys the gas laws exactly, always; doesn't exist; a model.

Real gas: every gas; obeys closely only at low P, high T.

Diffusion: gas spreading from more to fewer particles by its own random motion.

Effusion: gas leaking molecule by molecule through a tiny hole.

Formulas

- 1 atm = 760 mmHg = 76 cmHg = 101,325 Pa ≈ 101.3 kPa
- 1 L = 1,000 $\mathrm{cm^3}$ = 1 $\mathrm{dm^3}$; 1 $\mathrm{m^3}$ = 1,000 L
- $T = t + 273$

$P_1V_1 = P_2V_2$	P, V before (1), after (2); any unit, the same both sides **Use:** Boyle: fixed mass, fixed T
$\frac{V_1}{T_1} = \frac{V_2}{T_2}$	T **in kelvin** **Use:** Charles: fixed mass, fixed P
$\frac{P_1}{T_1} = \frac{P_2}{T_2}$	closed, rigid container **Use:** pressure law: fixed V
$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$	T in kelvin **Use:** combined: all change; to STP use 273 K, 760 mmHg
$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}}$	r rate, d density, M molar mass **Use:** Graham: same T, P
$\frac{t_1}{t_2} = \sqrt{\frac{M_1}{M_2}}$	t time for the same volume **Use:** slower gas takes longer

7.1 Boyle's law (1662)

The volume of a fixed mass of a gas is inversely proportional to its pressure, provided its temperature stays the same. $V \propto 1/P$, $PV = k$.

- $P \times 2 \rightarrow V \div 2$; $P \times 3 \rightarrow V \div 3$
- P–V graph: falling curve, never reaches zero volume
- P–$1/V$ graph: straight line through the origin
- why: half the space, same speed → hits each wall twice as often → twice the pressure
- Mariotte (France) found it on his own, 1676

Around us

- **breathing**: chest bigger → lung pressure below outside → air in
- **syringe**: plunger back → pressure falls → liquid pushed in
- **ears** pop on a climb: outside P falls; middle-ear air escapes down the tube
- **diver**: bubble grows rising; keep breathing out (10 m under sea ≈ 2 atm: 2 $\mathrm{cm^3}$ → 4 $\mathrm{cm^3}$)
- **weather balloon**: partly filled; much wider by about 30 km; bursts
- **chips packet**: Kathmandu 86 kPa → Namche 66 kPa: 100 → 130 $\mathrm{cm^3}$ (with 25 °C → 5 °C: 122 $\mathrm{cm^3}$)

Charles's law (around 1787; Gay-Lussac, 1802)

The volume of a fixed mass of a gas is directly proportional to its absolute temperature, provided its pressure stays the same. $V \propto T$.

- each 1 °C: ± 1/273 of the volume at 0 °C; every gas the same
- 273 $\mathrm{cm^3}$ at 0 °C → 373 $\mathrm{cm^3}$ at 100 °C; 173 $\mathrm{cm^3}$ at −100 °C
- extended back: zero volume at −273 °C (real gases turn liquid first)
- V–T (K) graph: straight line through the origin
- double the **kelvin** temperature → double V: 2 L at 0 °C → 4 L at 273 °C
- 10 °C → 20 °C: only ≈ 3.5% more

Around us

- hot air balloon (open envelope: air pushed out; warm air lighter than the same volume of cool air)
- dented table tennis ball in hot water
- football harder in the sun

7.2 Combined gas equation

Derive in two steps

1. fixed T_1, $P_1 \rightarrow P_2$ (Boyle): $V = P_1V_1/P_2$ … (i)
2. fixed P_2, $T_1 \rightarrow T_2$ (Charles): $V = V_2T_1/T_2$ … (ii)
3. (i) = (ii), $\times P_2/T_1$: $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

- fixed mass: PV/T constant; n moles: $PV = nRT$, R = 8.314 J/(mol K)
- **fixed** V: $P \propto T$: steel can 27 °C → 327 °C: 100 → 200 kPa ("do not burn"); tyres checked cold

7.3 STP

- why: a volume alone doesn't say how much gas; compare at one agreed condition
- equal volumes at STP: same number of molecules
- newer IUPAC standard (since 1982): 1 bar = 100 kPa, 22.7 L; in the exam: 760 mmHg, 22.4 L

7.4 Kinetic theory of gases

Bernoulli, 1738; Maxwell and Boltzmann, 1860s–70s.

Assumptions

1. very many tiny molecules, alike for one gas
2. own volume negligible; mostly empty space
3. always moving, straight lines, at random
4. collisions **perfectly elastic**: no KE lost
5. no attraction or repulsion except in collisions
6. a collision lasts negligibly short
7. **pressure** = molecules hitting the walls
8. average KE $\propto$ absolute temperature

Gives the laws

- Boyle: same speed, half V $\rightarrow$ hits twice as often
- Charles: $T \uparrow \rightarrow$ faster, more and harder hits; to keep P, $V \uparrow$
- pressure law: faster, nowhere to go $\rightarrow$ $P \uparrow$
- diffusion: random motion spreads them

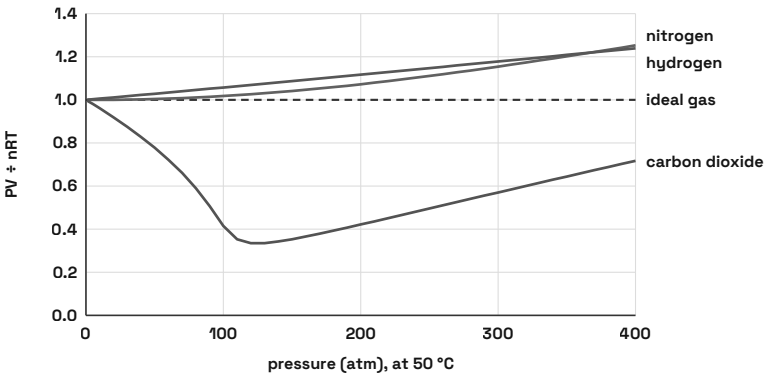
- N_2 at 27 °C: $\approx$ 500 m/s, but hits another after $\approx$ 70 nm, about 7 billion times a second $\rightarrow$ smell takes minutes

7.5 Real and ideal gases

Ideal	Real
obeys laws always	only at low P, high T
molecules: no volume	small volume of their own
no attraction	weak attraction
never a liquid	liquid when cooled and squeezed
a model	every gas

Why real gases stray (high P, low T)

- own volume counts $\rightarrow$ squeezed **less** than Boyle $\rightarrow$ PV more
- attraction: tugged back, hits wall gently $\rightarrow$ squeezed **more** $\rightarrow$ PV less



At 50 °C. Ideal gas: $PV \div nRT = 1$ always. H_2 rises from the start; $N_2 \approx 1$ up to about 100 atm, then rises; CO_2 (strong attraction) drops, lowest near 120 atm, then rises.

- around 1 atm, room temperature: H_2, He, N_2, O_2 right to better than 1%
- CO_2, NH_3, SO_2 stray more; easiest to liquefy
- LPG: real gas, liquid under a few atm in the cylinder
- van der Waals (1873): corrected for volume and attraction; **critical temperature**: above it no squeezing liquefies (CO_2 31 °C; N_2 −147 °C)

7.6 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.

- same T $\rightarrow$ same average KE, $\frac{1}{2}mv^2$: 16 times heavier $\rightarrow$ 4 times slower
- density $\propto M$ at the same T, P
- H_2 vs O_2: $\sqrt{32/2} = 4$ times faster; same volume 60 s $\rightarrow$ 15 s
- unknown gas at ¼ helium's rate: $M = 64$ (could be SO_2)

Ammonia tube (plugs 100 cm apart)

- NH_3 (17) + HCl (36.5) $\rightarrow$ NH_4Cl, white ring
- $d_{NH_3}/d_{HCl} = \sqrt{36.5/17} = 1.465$; add to 100 $\rightarrow$ 59.4 cm from NH_3, 40.6 cm from HCl
- nearer the heavier gas; real tube not exact: air jostles

Uses

- find molar masses
- separate isotopes: UF_6, 349 vs 352 $\rightarrow$ 1.0043 times; thousands of walls (centrifuges now)
- helium balloon flat sooner: $\sqrt{29/4} \approx 2.7$ times faster than air
- smells, gas leaks: LPG has ethyl mercaptan added; heavier than air, collects near the floor

COMMON MISTAKES

✗ °C in the gas laws
✓ change to kelvin first; 20 °C $\rightarrow$ 40 °C is only about 7% more.

✗ answer in K given as °C
✓ 546 K = 273 °C, not 546 °C.

✗ different pressure units in one sum
✓ both the same unit; any unit will do.

✗ r ratio = M ratio
✓ the **square root**: H_2 vs O_2 4 times, not 16.

✗ rate and time the same way
✓ heavier gas is slower, so takes **longer**.

✗ heating makes molecules bigger
✓ they move faster.

✗ ring in the middle of the tube
✓ nearer the heavier gas (HCl).