

Kinetic Theory of Gases and Gas Laws

Last-minute revision: the key ideas, standard results and traps of every part. The formula sheet is the last page.

If you only have five minutes

- Units first: T in kelvin, M in kg/mol, P in Pa, V in m^3 ($1 \text{ L} = 10^{-3} \text{ m}^3$).
- $PV = nRT = NkT$. Open air or density given: $P = \frac{\rho RT}{M}$. Gas moves between vessels: count moles.
- $P = \frac{1}{3}\rho v_{\text{rms}}^2$ and KE per molecule = $\frac{3}{2}kT$: depends on T only.
- Every speed $\propto \sqrt{T/M}$; $v_{\text{mp}} : v_{\text{mean}} : v_{\text{rms}} \approx 1 : 1.13 : 1.22$.
- $\frac{1}{2}kT$ per degree of freedom; $f = 3, 5, 6$ (+ vibration); $\gamma = 1 + \frac{2}{f}$.
- $U = \frac{f}{2}nRT$. Mixing in a rigid insulated vessel: weight temperatures by fn .
- van der Waals: add $\frac{an^2}{V^2}$ to P , subtract nb from V .
- $\lambda = \frac{kT}{\sqrt{2}\pi d^2 P}$: higher P or bigger molecules, shorter λ .

1 Postulates of Kinetic Theory

- A gas has $\sim 10^{22}$ molecules per litre, so kinetic theory predicts **averages**, not single molecules.
- Ideal gas: molecules are points (size $\ll$ separation), collisions are elastic, no forces except during collisions (so **no PE**), collision time $\ll$ time between collisions, motion is random, gravity is ignored (uniform density).
- Real gas $\approx$ ideal at **high T** (KE $\gg$ attraction) and **low P** (molecules far apart).
- An ideal gas can never liquefy: nothing pulls its molecules together.

TRAPS

- An ideal gas has potential energy from attractions.** No forces act between collisions, so its internal energy is purely kinetic.
- Real gases are ideal at high pressure.** The opposite: low pressure and high temperature make a real gas behave ideally.

- Dalton: each gas fills all the space it can reach; partial pressures add.
- Pistons: balance forces. Weighted free piston: $P_{\text{gas}} = P_{\text{atm}} + \frac{Mg}{S}$.

STANDARD RESULTS

1 mol at STP occupies 22.4 L.

0.6 mol mixture in 8.3 L at 300 K: $P \approx 1.80 \times 10^5 \text{ Pa}$; $M_{\text{mix}} \approx 37.3 \text{ g/mol}$.

Bulbs 3 L + 1 L at 76 cm Hg, 30 °C; 3 L bulb heated to 100 °C: $P \approx 88.45 \text{ cm Hg}$.

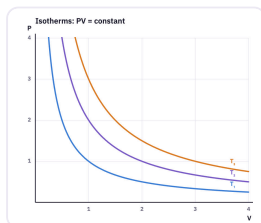
Vertical cylinder, free piston, 1 mol each side, $V_U/V_L = 4$ at 300 K $\rightarrow$ 2 at 750 K.

TRAPS

- Using °C in $PV = nRT$.** Temperatures must be in kelvin: $T = t + 273.15$.
- Using M in g/mol in $P = \rho RT/M$.** In SI units M is in kg/mol (O_2 : 0.032).
- Forgetting the piston's weight.** A weighted free piston gives $P_{\text{gas}} = P_{\text{atm}} + \frac{Mg}{S}$, not P_{atm} .

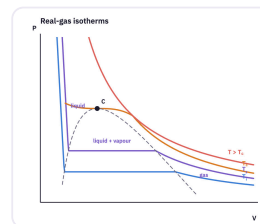
2 Gas Laws

- Boyle (T, n fixed): $PV = \text{constant}$. The P - V isotherm is a rectangular hyperbola; a hotter isotherm lies further out.
- Charles (P fixed): $V \propto T$. Gay-Lussac (V fixed): $P \propto T$. Every V - t line meets -273.15 °C , which defines absolute zero.
- Fixed amount: $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$. Gas leaks or flows between bulbs: conserve $n = \frac{PV}{RT}$.
- Avogadro: equal volumes at the same P and T hold equal numbers of molecules, so one R fits every gas.



3 Real Gases, Change of Phase and van der Waals Equation

- Andrews isotherms (CO_2): at high P a real gas takes **less** volume than an ideal one, because molecules attract.
- Below T_c : the flat part is liquid + vapour together; volume falls at constant pressure. The steep left branch is liquid, almost incompressible.
- Critical point C : the T_c isotherm has a horizontal inflection. Above T_c no pressure can liquefy the gas.
- b : molecules take up space, so use $V - nb$ ($b \approx$ volume of 1 mol of molecules). a : attraction lowers wall pressure by $\frac{an^2}{V^2}$, so add it back.



- At low P or high T both corrections vanish: $PV = nRT$.

STANDARD RESULTS

Good to know: $V_c = 3b$, $P_c = \frac{a}{27b^2}$, $T_c = \frac{8a}{27Rb}$.

TRAPS

- ✗ **Getting the signs backwards.** Pressure is added to $\left(P + \frac{an^2}{V^2}\right)$; volume is subtracted from $(V - nb)$.
- ✗ **Any gas liquefies under enough pressure.** Only below its critical temperature T_c .

4 Pressure of Air and Barometric Relation

- Torricelli: a mercury column about 76 cm tall balances the atmosphere, with a vacuum above it. Points at the same level in the same liquid are at the same pressure.
- Trapped gas in a tube: $P_{\text{gas}} = P_{\text{atm}} \pm$ the **vertical** mercury height ($l \cos \theta$ if tilted from vertical); then Boyle: $P_1 L_1 = P_2 L_2$.
- Faulty barometer (air above the mercury): $P_{\text{air}} = P_{\text{true}} - \text{reading}$; apply Boyle to that air for two readings.
- Isothermal atmosphere: $dP = -\rho g dh$ with $\rho = \frac{PM}{RT}$, so P and ρ both fall as $e^{-Mgh/RT}$.
- Rotating tube: the centripetal term replaces g : $P = P_0 e^{M\omega^2 r^2 / 2RT}$.

STANDARD RESULTS

Open tube, 20 cm Hg traps 43 cm of gas ($P_{\text{atm}} = 76$ cm Hg), turned through 60° : 48 cm.

Centre of gravity of a very tall gas column: $\frac{RT}{Mg}$.

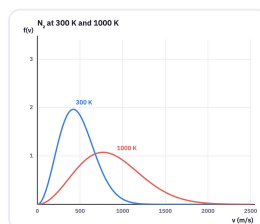
Mass in a tall vessel (base S , height h): $m = (1 - e^{-Mgh/RT}) \frac{P_0 S}{g}$.

TRAPS

- ✗ **Using the mercury thread's length in a tilted tube.** Pressure depends on the vertical height: $l \cos \theta$ from the vertical.
- ✗ **Assuming constant density with height.** For a tall gas column $\rho = \frac{PM}{RT}$ falls with P , which gives the exponential.

5 Distribution of Molecular Speeds

- Maxwell-Boltzmann: $dN = f(v) dv$ molecules have speeds between v and $v + dv$; the area under the curve is N .
- Hotter: the peak moves right and gets lower and wider (same area). Heavier gas at the same T : peak further left.



- $v_{\text{mp}} < v_{\text{mean}} < v_{\text{rms}}$, in the ratio $\sqrt{2} : \sqrt{8/\pi} : \sqrt{3}$. All scale as $\sqrt{T/M}$.
- Average **velocity** is zero (random directions); mean **speed** is not.
- Given P and ρ instead of T : $v_{\text{rms}} = \sqrt{\frac{3P}{\rho}}$.

STANDARD RESULTS

Air at 25°C : $v_{\text{mean}} \approx 466.5$ m/s.

1300 mol N_2 in 8.0 m^3 at 2.1 atm: $T \approx 157.5$ K, $v_{\text{rms}} \approx 374.6$ m/s.

$T \times 4 \Rightarrow$ every speed $\times 2$. Same T : $v_{\text{O}_2} : v_{\text{H}_2} = 1 : 4$.

TRAPS

- ✗ **Using M in g/mol.** $M = 0.029$ kg/mol for air, not 29.
- ✗ **Confusing average velocity with mean speed.** Average velocity is zero; mean speed is not.

6 Pressure, Kinetic Energy and Temperature

- One molecule hitting a wall: $\Delta p = 2m'v_x$, once every $\frac{2l}{v_x}$. Add up all molecules and average over 3 directions: $P = \frac{1}{3}\rho v_{\text{rms}}^2$, for any container shape.
- $P = \frac{2}{3}E$: pressure is $\frac{2}{3}$ of the translational KE per unit volume.
- Compare with $PV = NkT$: $\frac{1}{2}m'v_{\text{rms}}^2 = \frac{3}{2}kT$. Temperature measures the average translational KE.
- Same $T \Rightarrow$ same average KE per molecule, whatever the gas, P or V .
- k is per molecule (J/K); $R = N_A k$ is per mole (J/mol·K).

STANDARD RESULTS

H_2 at STP ($\rho = 0.09$ kg/m³): $v_{\text{rms}} \approx 1837$ m/s.

Translational KE of 1 mol at STP: $\frac{3}{2}RT \approx 3.40 \times 10^3$ J (any gas).

One molecule at 300 K: $\frac{3}{2}kT \approx 6.2 \times 10^{-21}$ J.

TRAPS

- ✗ **Writing k in J/mol·K.** k is per molecule: J/K. J/mol·K is the unit of R .
- ✗ **Hotter gas at higher pressure has more KE per molecule.** Average KE per molecule depends only on T .

7 Degrees of Freedom and Equipartition of Energy

- Degree of freedom: an independent way to store energy. Equipartition: each one holds $\frac{1}{2}kT$ per molecule ($\frac{1}{2}RT$ per mole).
- Monatomic (He, Ar): $f = 3$, translation only.
- Diatomic (O_2 , N_2): $f = 3 + 2 = 5$; no rotation about the bond axis. Vibration adds 2 (KE + PE), so $f = 7$ above ~ 5000 K. H_2 below ~ 50 K: $f = 3$.

- Polyatomic: linear (CO_2) $3 + 2 + x$; non-linear (H_2O , CH_4) $3 + 3 + x$, where x counts vibration.

STANDARD RESULTS

$$\gamma = 1 + \frac{2}{f}: \text{monatomic } \frac{5}{3}, \text{ diatomic } \frac{7}{5}, \text{ rigid non-linear } \frac{4}{3}.$$

TRAPS

✗ **Counting rotation about a diatomic's bond axis.**

Its moment of inertia is almost zero, so it stores no energy: $f = 5$, not 6.

✗ **Using $f = 7$ for a diatomic at room temperature.**

Vibration only switches on at high temperature (around 5000 K).

TRAPS

✗ **Writing m for π in $\lambda = \frac{kT}{\sqrt{2} \pi d^2 P}$.** It's a geometric factor from the cross-section πd^2 .

✗ **Doubling P at constant T leaves λ unchanged.** $n_0 = P/kT$ doubles, so λ halves.

8 Internal Energy of a Gas

- Ideal gas: no PE, so $U = \frac{f}{2} nRT$ depends on T only, not on P or V .
- $C_V = \frac{f}{2} R$, $C_P = C_V + R$, $\gamma = \frac{C_P}{C_V}$.
- Mixture: $f_{\text{eq}} = \frac{\sum f_i n_i}{\sum n_i}$, then $\gamma_{\text{mix}} = 1 + \frac{2}{f_{\text{eq}}}$.
- Rigid, insulated vessel: no heat, no work, so U is conserved: $T_f = \frac{\sum f_i n_i T_i}{\sum f_i n_i}$.

STANDARD RESULTS

1 mol He + 1 mol O_2 : $f_{\text{eq}} = 4$, $\gamma = 1.5$.

1 mol He at 600 K + 1 mol N_2 at 200 K $\rightarrow$ 350 K (not 400 K).

TRAPS

✗ **Taking the simple average of temperatures.**

Weight each gas by $f \cdot n$: a diatomic stores more energy per kelvin than a monatomic gas.

✗ **Weighting by C_P in a rigid vessel.** At constant volume the energy per kelvin is $\frac{f}{2} R = C_V$.

9 Mean Free Path and Diffusion

- Molecules move at ~ 500 m/s, yet a smell crosses a room slowly: collisions turn each path into a zigzag.
- Mean free path λ : average distance between collisions. A molecule sweeps a collision cylinder of radius d ; $\sqrt{2}$ accounts for the other molecules moving.
- $\lambda = \frac{1}{\sqrt{2} \pi d^2 n_0}$, and with $n_0 = \frac{P}{kT}$: $\lambda = \frac{kT}{\sqrt{2} \pi d^2 P}$. Rigid vessel (fixed n_0): λ doesn't change with T .
- Diffusion: net flow from high to low concentration, stops when they are equal. Fick: $J = D \frac{C_1 - C_2}{\Delta x}$; D depends on the substances, T and P .

STANDARD RESULTS

Air at STP: $\lambda \sim 10^{-7}$ m.

$P \times 2$ at fixed $T \Rightarrow \lambda \div 2$. $d \times 2 \Rightarrow \lambda \div 4$.

Kinetic Theory of Gases and Gas Laws

R 8.314 J mol⁻¹K⁻¹

k 1.38 × 10⁻²³ J/K

N_A 6.02 × 10²³ mol⁻¹

1 atm 76 cm Hg = 1.013 × 10⁵ Pa

STP 1 atm, 273 K, 22.4 L/mol

Notation m' molecule mass · $n_0 = N/V$ · f degrees of freedom

1 Postulates of Kinetic Theory

- Ideal gas: point molecules, elastic collisions, no forces between collisions (so no PE), random motion, uniform density.
- Real gases behave ideally at **high T** and **low P**.

2 Gas Laws

$$P_1 V_1 = P_2 V_2$$

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

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

$$PV = nRT$$

$$PV = NkT$$

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

$$P = \frac{\rho RT}{M}$$

$$N_A = 6.023 \times 10^{23} \text{ mol}^{-1}$$

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

$$P_{\text{total}} = P_1 + P_2 + \dots + P_n$$

$$M_{\text{mix}} = \frac{\sum n_i M_i}{\sum n_i}$$

- Always use kelvin: $T = t + 273.15$. All $V-t$ lines meet at -273.15°C .
- M in kg/mol in $P = \rho RT/M$ (air 0.029). STP: 1 atm, 273 K, 22.4 L/mol.
- Weighted free piston: $P_{\text{gas}} = P_{\text{atm}} + Mg/S$.

3 Real Gases, Change of Phase and van der Waals Equation

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

- Add to P , subtract from V . a : attraction, $b \approx$ volume of 1 mol of molecules.
- Above T_c no pressure liquefies the gas; at C the isotherm has a horizontal inflection.

4 Pressure of Air and Barometric Relation

$$P = \rho gh$$

$$P = P_0 e^{-Mgh/RT}$$

- 1 atm = 76 cm Hg = 1.013 × 10⁵ Pa. Tilted tube: use vertical height $l \cos \theta$.
- Faulty barometer: $P_{\text{air}} = P_{\text{true}} -$ reading, then Boyle on the trapped air.
- Centre of gravity of a tall column: RT/Mg . Rotating tube: $P = P_0 e^{M\omega^2 r^2/2RT}$.

5 Distribution of Molecular Speeds

$$f(v) = 4\pi N v^2 \left(\frac{M}{2\pi RT}\right)^{3/2} e^{-Mv^2/2RT}$$

$$v_{\text{rms}} = \sqrt{\frac{3RT}{M}}$$

$$v_{\text{mean}} = \sqrt{\frac{8RT}{\pi M}}$$

$$v_{\text{mp}} = \sqrt{\frac{2RT}{M}}$$

- $v_{\text{mp}} : v_{\text{mean}} : v_{\text{rms}} = \sqrt{2} : \sqrt{8/\pi} : \sqrt{3} \approx 1 : 1.13 : 1.22$.
- Average velocity = 0; mean speed $\neq 0$. Hotter: peak moves right and flattens; heavier: slower.

6 Pressure, Kinetic Energy and Temperature

$$P = \frac{1}{3} \rho v_{\text{rms}}^2$$

$$P = \frac{1}{3} \frac{N}{V} m' v_{\text{rms}}^2$$

$$P = \frac{2}{3} E \quad (E = \text{KE per unit volume})$$

$$E_K = \frac{1}{2} m' v_{\text{rms}}^2 = \frac{3}{2} kT$$

$$E_{\text{total}} = \frac{3}{2} NkT = \frac{3}{2} nRT$$

$$T = \frac{2}{3} \frac{E_T}{k}$$

- Same $T \Rightarrow$ same average KE per molecule, for every gas. k is in J/K.
- H₂ at STP: $v_{\text{rms}} \approx 1837$ m/s; 1 mol H₂ at STP: KE $\approx 3.40 \times 10^3$ J.

7 Degrees of Freedom and Equipartition of Energy

$$\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle = \frac{v_{\text{rms}}^2}{3}$$

$$\frac{1}{2} m' \langle v_x^2 \rangle = \frac{1}{2} kT$$

$$E = \frac{f}{2} kT \text{ per molecule}$$

- f : monatomic 3 · rigid diatomic 5 (7 above ~5000 K; H₂ below ~50 K: 3) · linear 3 + 2 + x · non-linear 3 + 3 + x .
- $\gamma = 1 + \frac{2}{f}$: $\frac{5}{3}$, $\frac{7}{5}$, $\frac{4}{3}$. Never count the bond-axis rotation.

8 Internal Energy of a Gas

$$U = \frac{f}{2} nRT$$

$$\text{monatomic: } U = \frac{3}{2} nRT$$

$$\text{diatomic: } U = \frac{5}{2} nRT$$

$$\text{linear polyatomic: } U = \frac{5+x}{2} nRT$$

$$\text{non-linear: } U = \frac{6+x}{2} nRT$$

$$f_{\text{eq}} = \frac{f_1 n_1 + f_2 n_2 + \dots}{n_1 + n_2 + \dots}$$

$$T_f = \frac{f_1 n_1 T_1 + f_2 n_2 T_2 + \dots}{f_1 n_1 + f_2 n_2 + \dots}$$

- Ideal gas: U depends only on T .
- Insulated rigid mixing: weight by $f n$, not by n . He 600 K + N₂ 200 K (1 mol each) $\rightarrow$ 350 K.

9 Mean Free Path and Diffusion

$$\lambda = \frac{1}{\sqrt{2} \pi d^2 (N/V)}$$

$$\lambda = \frac{kT}{\sqrt{2} \pi d^2 P}$$

$$J = D \frac{C_1 - C_2}{\Delta x}$$

- Air at STP: $\lambda \sim 10^{-7}$ m. $\lambda \propto T/(d^2 P)$: doubling P at fixed T halves λ .
- It's π (not m) in λ . Diffusion stops when concentrations are equal.