

# 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  $\text{m}^3$  ( $1 \text{ L} = 10^{-3} \text{ m}^3$ ).
- $PV = nRT = NkT$ . 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  $\lambda$ .

## 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:  $P \approx 88.45 \text{ cm Hg}$ .

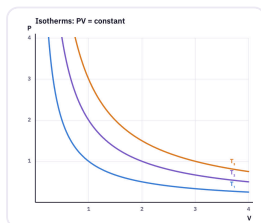
Vertical cylinder, free piston, 1 mol each side,  $V_U/V_L = 4$  at 300 K  $\rightarrow$  2 at 750 K.

### 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 ( $\text{O}_2$ : 0.032).
- Forgetting the piston's weight.** A weighted free piston gives  $P_{\text{gas}} = P_{\text{atm}} + \frac{Mg}{S}$ , not  $P_{\text{atm}}$ .

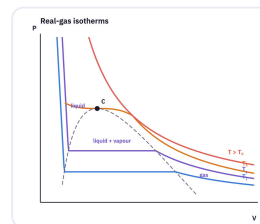
## 2 Gas Laws

- 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  $-273.15^\circ\text{C}$ , 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 ( $\text{CO}_2$ ): 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  $\rho$  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  $60^\circ$ : 48 cm.

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

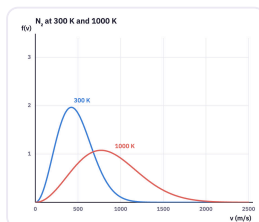
Mass in a tall vessel (base  $S$ , height  $h$ ):  $m = (1 - e^{-Mgh/RT}) \frac{P_0 S}{g}$ .

#### 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  $\rho$  instead of  $T$ :  $v_{\text{rms}} = \sqrt{\frac{3P}{\rho}}$ .

#### STANDARD RESULTS

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

1300 mol  $\text{N}_2$  in  $8.0 \text{ m}^3$  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

$\text{H}_2$  at STP ( $\rho = 0.09$  kg/m<sup>3</sup>):  $v_{\text{rms}} \approx 1837$  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 ( $\text{O}_2$ ,  $\text{N}_2$ ):  $f = 3 + 2 = 5$ ; no rotation about the bond axis. Vibration adds 2 (KE + PE), so  $f = 7$  above  $\sim 5000$  K.  $\text{H}_2$  below  $\sim 50$  K:  $f = 3$ .

- Polyatomic: linear ( $\text{CO}_2$ )  $3 + 2 + x$ ; non-linear ( $\text{H}_2\text{O}$ ,  $\text{CH}_4$ )  $3 + 3 + x$ , 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  $\pi$  in  $\lambda = \frac{kT}{\sqrt{2} \pi d^2 P}$ .** It's a geometric factor from the cross-section  $\pi d^2$ .

✗ **Doubling  $P$  at constant  $T$  leaves  $\lambda$  unchanged.**  $n_0 = P/kT$  doubles, so  $\lambda$  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  $\text{O}_2$ :  $f_{\text{eq}} = 4$ ,  $\gamma = 1.5$ .

1 mol He at 600 K + 1 mol  $\text{N}_2$  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  $\sim 500$  m/s, yet a smell crosses a room slowly: collisions turn each path into a zigzag.
- Mean free path  $\lambda$ : 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  $n_0$ ):  $\lambda$  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<sup>-1</sup>K<sup>-1</sup>

$k$  1.38 × 10<sup>-23</sup> J/K

$N_A$  6.02 × 10<sup>23</sup> mol<sup>-1</sup>

1 atm 76 cm Hg = 1.013 × 10<sup>5</sup> 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  $-273.15^\circ\text{C}$ .
- $M$  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

$$P = h\rho g$$

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

- 1 atm = 76 cm Hg = 1.013 × 10<sup>5</sup> 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.
- H<sub>2</sub> at STP:  $v_{\text{rms}} \approx 1837$  m/s; 1 mol H<sub>2</sub> 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; H<sub>2</sub> 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 + N<sub>2</sub> 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  $\lambda$ .
- It's  $\pi$  (not  $m$ ) in  $\lambda$ . Diffusion stops when concentrations are equal.