

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

$$P = h\rho g$$

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

- 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.