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CUET · PHYSICS · CLASS XI · CODE 322

Kinetic Theory

CUET unit: Kinetic Theory

By **UniDrill** · NCERT-grounded study material

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📌 Snapshot

- Establishes the molecular picture of matter: gases as collections of rapidly moving atoms/molecules with negligible inter-atomic forces (NCERT §12.1–12.2).
- Derives the ideal gas equation $PV = \mu RT = k_B NT$ from Boyle's, Charles' and Avogadro's laws, plus Dalton's law of partial pressures (§12.3).
- Derives gas pressure $P = (1/3)\, n\, m\, \overline{v^2}$ from molecular collisions with the container wall, leading to the kinetic interpretation of temperature: $\frac{1}{2} m \overline{v^2} = (3/2)\, k_B T$ (§12.4).
- States the law of equipartition of energy ($\frac{1}{2} k_B T$ per quadratic term) and uses degrees of freedom to predict C_v, C_p and γ for monatomic, diatomic and polyatomic gases (§12.5–12.6).
- Defines the mean free path $\lambda = 1/(\sqrt{2}\, n \pi d^2)$ — explains why gases diffuse slowly despite high molecular speeds (§12.7). CUET typically tests numerical applications (v_{rms}, $C_v/C_p/\gamma$, λ) and statement-based questions on assumptions of kinetic theory.

📖 Detailed Notes

2.1 Core concepts

Kinetic theory explains the macroscopic properties of gases — pressure, temperature, specific heat, viscosity, diffusion — by treating a gas as a collection of huge numbers of tiny atoms or molecules in rapid, random motion. The inter-atomic forces between gas molecules are negligible compared to those in solids and liquids; they are short-ranged and ignorable except during the brief instants of collision (NCERT §12.1, p. 244). The theory was developed in the nineteenth century by Maxwell, Boltzmann and others, but its roots run back to John Dalton's atomic hypothesis at the start of the 1800s.

Richard Feynman called the atomic hypothesis the single most important sentence in physics: "all things are made of atoms — little particles that move around in perpetual motion, attracting each other when they are a little distance apart, but repelling upon being squeezed into one another" (NCERT §12.2, p. 244). Dalton's atomic theory explained the laws of definite and multiple proportions in chemistry; Gay-Lussac's law of combining gas volumes (in small whole-number ratios when gases react) and Avogadro's law (equal volumes of any gas at the same temperature and pressure contain the same number of molecules) made the molecular picture quantitative (NCERT §12.2, p. 245).

The scale of atoms is set by the Bohr radius: an atom is roughly 1 Å = 10^{-10} m across. In solids and liquids the inter-atomic spacing is about 2 Å — atoms are essentially touching. In gases at ordinary conditions the inter-atomic distance is tens of ångströms and the **mean free path** between collisions is thousands of ångströms (NCERT §12.2, p. 245). This is why a gas can be compressed easily, a liquid much less, and a solid hardly at all.

The ideal gas equation (NCERT §12.3, p. 246–247). At low pressures and temperatures well above their liquefaction point, real gases approximately satisfy a single combined law. For a fixed amount of gas, PV/T = constant. Including the number of molecules, the constant becomes Nk_B where k_B is Boltzmann's constant, the same for every gas — exactly what Avogadro's hypothesis predicts. Equivalently, working with moles, $PV = \mu RT$, where $\mu = N/N_A$ is the number of moles, $N_A = 6.02 \times 10^{23}$ is the Avogadro number, and $R = N_A k_B = 8.314$ J mol^{-1} K^{-1} is the universal gas constant. Three other useful forms follow: $PV = k_B NT$, $P = k_B nT$ (n = number density), and $P = \rho RT/M_0$ (ρ = mass density, M_0 = molar mass). A gas that satisfies $PV = \mu RT$ exactly at all P and T is an **ideal gas**; real gases deviate but approach ideal behaviour at low P and high T (NCERT Fig. 12.1, p. 246). Boyle's law (PV = const at fixed T), Charles' law ($V \propto T$ at fixed P) and **Dalton's law of partial pressures** ($P_{total} = P_1 + P_2 + \cdots$ for a non-reacting mixture of ideal gases) all fall out as special cases (NCERT §12.3, p. 247).

The molar volume of any gas at STP (0 °C, 1 atm) is 22.4 L, and the mass of 22.4 L equals the gas's molecular weight in grams — i.e., one mole. This single number underwrites almost every numerical problem in stoichiometry.

Kinetic-theory derivation of pressure (NCERT §12.4.1, p. 248–249). Consider a gas in a cube of side l. A molecule of mass m moving with x-velocity v_x bounces elastically off the wall normal to the x-axis; its x-momentum changes by $2mv_x$. The number of molecules striking unit area of that wall per unit time is ½ n v_x (factor of ½ because only molecules with $v_x > 0$ move toward the wall). The total momentum delivered per unit area per unit time is the **pressure**:

$P = n m \bar{v}_x^2$ (where $\bar{v}_x^2$ is averaged over molecules).

By isotropy $\bar{v}_x^2 = \bar{v}_y^2 = \bar{v}_z^2 = (1/3)\,\bar{v^2}$, so

$\mathbf{P = (1/3)\, n\, m\, \bar{v^2}}$ (NCERT Eq. 12.14, p. 249).

This is the central result of kinetic theory. Two things are remarkable about it. First, it relates a macroscopic quantity (pressure) to a microscopic one (mean-square molecular speed). Second, multiplying through by V gives $PV = (2/3)\, N \times (\frac{1}{2} m \bar{v^2}) = (2/3)\, E$, where E is the total translational kinetic energy of all the molecules.

Kinetic interpretation of temperature (NCERT §12.4.2, p. 250). Comparing $PV = (2/3)\, E$ with $PV = N k_B T$ gives

$\langle \frac{1}{2} m v^2 \rangle = (3/2)\, k_B T$ (NCERT Eq. 12.19, p. 250).

The average translational kinetic energy of a molecule depends only on the absolute temperature T — not on the nature of the gas, the pressure or the volume. This is the deep content of "temperature": it measures the random kinetic energy of microscopic motion.

From the same relation the **root-mean-square (rms) speed** of a molecule is

$v_{rms} = \sqrt{\langle v^2 \rangle} = \sqrt{3 k_B T/m} = \sqrt{3 RT/M_0} = \sqrt{3 P/\rho}$ (NCERT p. 250 & Summary p. 256).

For nitrogen (M_0 = 28 g/mol) at 300 K, $v_{rms} \approx 516$ m s^{-1}, comparable to the speed of sound in air — which is no coincidence, since sound waves are pressure disturbances carried by molecular motion. At the same T, lighter molecules have larger v_{rms}; that is why hydrogen and helium escape Earth's upper atmosphere but heavier gases like nitrogen and oxygen are retained.

A direct consequence is the kinetic-theory derivation of Dalton's law (NCERT Eq. 12.21, p. 250). For a mixture of non-reacting gases at the same T, each species contributes a partial pressure $n_i k_B T$ independent of the others, and the total pressure is the sum.

Degrees of freedom and equipartition (NCERT §12.5, p. 252–253). A point particle free in three-dimensional space needs three numbers (v_x, v_y, v_z) to specify its instantaneous state; we say it has 3 translational **degrees of freedom (DOF)**. A particle constrained to a plane has 2 DOF; on a line, 1. Each translational DOF contributes a quadratic term $\frac{1}{2} m v_i^2$ to the kinetic energy.

A diatomic molecule (O_2, N_2) is like a dumb-bell; in addition to translating it can rotate about two axes perpendicular to its interatomic line, giving 2 rotational DOF. Rotation about the interatomic line itself is ignored — the moment of inertia is negligibly small. So a rigid diatomic has 3 trans + 2 rot = 5 DOF. If the bond can also vibrate, the vibration contributes both a kinetic term $\frac{1}{2} m(dy/dt)^2$ and a potential term $\frac{1}{2} ky^2$, i.e., **two** quadratic terms per vibrational mode.

The **law of equipartition of energy** (Maxwell) says that in thermal equilibrium at absolute temperature T, every quadratic term in the molecular energy expression carries an average energy of $\frac{1}{2} k_B T$. So each translational and rotational DOF contributes $\frac{1}{2} k_B T$; each vibrational mode contributes $2 \times \frac{1}{2} k_B T = k_B T$ (NCERT §12.5, p. 253).

Specific heats (NCERT §12.6, p. 253–254).

- **Monatomic gas** (He, Ar, Ne): 3 trans DOF. Internal energy per mole U = (3/2) RT. So **$C_v = (3/2)$ R**, **$C_p = (5/2)$ R**, **$\gamma = C_p/C_v = 5/3 \approx 1.67$** (Table 12.1).
- **Rigid diatomic gas** (O_2, N_2 at moderate T): 3 trans + 2 rot = 5 DOF. U = (5/2) RT, so **$C_v = (5/2)$ R**, **$C_p = (7/2)$ R**, **$\gamma = 7/5 = 1.40$**.
- **Non-rigid diatomic** (one vibrational mode also excited): U = (7/2) RT, so **$C_v = (7/2)$ R**, **$C_p = (9/2)$ R**, **$\gamma = 9/7 \approx 1.29$** (Eq. 12.35).

- **Polyatomic** (3 trans + 3 rot + f vibrational modes): **$C_v = (3 + f) R$**, **$C_p = (4 + f) R$**, **$\gamma = (4 + f)/(3 + f)$** (Eq. 12.36).

For any ideal gas the Mayer relation **$C_p - C_v = R$** holds. The experimental measurements in Table 12.2 agree well with these predictions for monatomic and rigid-diatomic gases at moderate temperatures.

Solids (NCERT §12.6.4, p. 254). Each atom in a solid vibrates about a fixed equilibrium position in 3 dimensions; each dimension has 2 quadratic terms (KE + PE of harmonic motion), so each atom has 6 quadratic terms, contributing $3 k_B T$ to the energy. For one mole this gives U = 3 RT and the molar specific heat C = 3R ≈ 24.9 J $mol^{-1} K^{-1}$ — the empirical **Dulong–Petit law** (Eq. 12.37). Carbon as diamond is a notable exception at room temperature because its vibration frequencies are so high that quantum freezing-out reduces the effective DOF.

Mean free path (NCERT §12.7, p. 255). Treating molecules as hard spheres of diameter d, two molecules collide whenever their centres come within distance d. In time Δt a molecule of mean speed $\langle v \rangle$ sweeps out a cylinder of volume $\pi d^2 \langle v \rangle \Delta t$. If we naively imagine all other molecules at rest, the average distance between collisions is $l = 1/(n \pi d^2)$. Accounting for the fact that **all** molecules are moving (so the relevant speed is the relative speed $\sqrt{2} \langle v \rangle$), the correct mean free path is

$\lambda = 1/(\sqrt{2} n \pi d^2)$ (NCERT Eq. 12.40, p. 255).

For air at STP $n \approx 2.7 \times 10^{25}$ m^{-3}, $d \approx 2 \times 10^{-10}$ m gives $\tau \approx 6 \times 10^{-10}$ s and $\lambda \approx 2.9 \times 10^{-7}$ m ≈ 1500 d. That is why a gas, despite molecular speeds of hundreds of metres per second, diffuses across a room only in minutes — each molecule executes a random walk of step size ~λ. Because $n \propto P/T$ (ideal gas), the mean free path scales as **$\lambda \propto T/P$** (NCERT Example 12.9, p. 255) — it grows when the gas is rarefied (low P) or heated (high T), and shrinks under compression.

2.2 Definitions to memorise

Term	Definition	Page
Atomic hypothesis	All matter is made of atoms in perpetual motion, attracting at small distances and repelling when squeezed	244
Avogadro's hypothesis	Equal volumes of all gases at the same T and P contain the same number of molecules	245
Avogadro number (N_A)	6.02×10^{23} — number of molecules in one mole	246
Mole	Amount of substance containing N_A elementary entities; mass equals molecular weight in grams	246
Boltzmann constant (k_B)	Universal constant 1.38×10^{-23} J K^{-1}; $k_B = R/N_A$	246
	$R = N_A k_B = 8.314$ J $mol^{-1} K^{-1}$	246

Term	Definition	Page
Universal gas constant (R)		
Ideal (perfect) gas	A gas that satisfies $PV = \mu RT$ exactly at all pressures and temperatures	247
Boyle's law	At fixed μ, T: PV = constant	247
Charles' law	At fixed μ, P: $V \propto T$ (absolute)	247
Dalton's law of partial pressures	Total pressure of a non-reactive mixture = sum of partial pressures of constituent gases	247
Number density (n)	Number of molecules per unit volume	246
Pressure of ideal gas (kinetic)	$P = (1/3)\, n\, m\, \overline{v^2}$	249
Mean square speed	$\overline{v^2} = \langle v^2 \rangle$ averaged over all molecules	249
RMS speed	$v_{rms} = \sqrt{\overline{v^2}} = \sqrt{3 k_B T/m} = \sqrt{3 RT/M_0} = \sqrt{3P/\rho}$	250
Average KE per molecule	$\frac{1}{2} m \overline{v^2} = (3/2) k_B T$ (depends only on T)	250
Degree of freedom	An independent quadratic term in the molecular energy expression	252
Translational DOF	3 for a free molecule (motion along x, y, z)	252
Rotational DOF	2 for a rigid diatomic (rotation about two perpendicular axes)	252
Vibrational mode	Pair of quadratic terms (KE + PE) for an oscillating bond	252
Law of equipartition of energy	In equilibrium, each quadratic energy term carries an average $\frac{1}{2} k_B T$	253
Mayer's relation	$C_p - C_v = R$ for any ideal gas	253
Specific heat ratio (γ)	$\gamma = C_p/C_v$	253
Dulong–Petit law	Molar specific heat of a solid ≈ 3R	254
Mean free path (λ)	Average distance a molecule travels between two successive collisions; $\lambda = 1/(\sqrt{2}\, n\, \pi\, d^2)$	255
Molar volume at STP	22.4 litres for any ideal gas	246

2.3 Diagrams / processes to remember

- **Fig. 12.1 (p. 246):** $PV/\mu T$ vs P plot — real gases approach the constant ideal-gas value at low P and high T; deviations grow at high P or near liquefaction.
- **Fig. 12.2 (p. 247):** Experimental P–V isotherms (steam) compared with Boyle's-law curves — verifies PV = const at high T.
- **Fig. 12.3 (p. 247):** V–T plot (CO_2) showing $V \propto T$ at fixed pressure (Charles' law).

- **Fig. 12.4 (p. 249):** Elastic collision of a gas molecule with a cube wall — the geometry that yields $P = (1/3)\, n\, m\, \overline{v^2}$.
- **Fig. 12.5 (p. 251):** Gas molecules diffusing through a porous wall — basis of isotope enrichment (^{235}U vs ^{238}U via UF_6 diffusion).
- **Fig. 12.6 (p. 252):** The two independent rotational axes of a diatomic molecule, perpendicular to the inter-atomic axis.
- **Fig. 12.7 (p. 255):** Volume $\pi\, d^2 \langle v \rangle\, \Delta t$ swept by a molecule of diameter d — geometric basis for the mean-free-path estimate.
- **Tables 12.1–12.2 (p. 254):** Predicted vs measured C_v, C_p, C_p – C_v and γ for monatomic, diatomic and triatomic gases — direct memorisation table.
- **Table 12.3 (p. 254):** Specific heat capacity of solids ≈ 3R (Dulong–Petit), with carbon (diamond) as the quantum-frozen exception.

2.4 Common confusions / NTA trap points

- Pressure formula uses **number density n** (molecules per unit volume), not total N or moles; $P = (1/3)\, n\, m\, \overline{v^2}$ and P = k_B nT (§12.3–12.4).
- $\overline{v^2}$ uses absolute temperature T (kelvin), and m is the **mass of a single molecule**; $v_{rms} = \sqrt{3RT/M_0}$ uses molar mass M_0, while $\sqrt{3 k_B T/m}$ uses single-molecule mass. NTA often swaps these and offers a wrong-by-N_A distractor.
- Average translational KE per molecule is (3/2) k_B T, but for a rigid diatomic molecule the **total** average energy is (5/2) k_B T. Confusing "translational KE" with "total internal energy" is a classic trap.
- A vibrational mode contributes **two** quadratic terms (KE + PE) ⇒ k_B T per vibration, not ½ k_B T (Point to Ponder 3, p. 257).
- For a rigid diatomic $\gamma = 7/5 = 1.40$; if vibration is included $\gamma = 9/7 \approx 1.29$. Do not mix the two unless the question explicitly mentions vibration.
- $\langle v^2 \rangle \neq \langle v \rangle^2$ in general — the average of a squared quantity is not the square of the average (Point to Ponder 5, p. 257); mean speed and rms speed are different.
- Mean free path uses **$\sqrt{2}$** in the denominator: $\lambda = 1/(\sqrt{2}\, n\, \pi\, d^2)$. The naive (target-at-rest) estimate $1/(n\pi d^2)$ is the wrong distractor.
- Because PV = k_B NT ⇒ n ∝ P/T, the mean free path $\lambda \propto T/P$ — increases with T at fixed P, decreases with P at fixed T.
- For helium (monatomic) C_v = (3/2) R ≈ 12.5 J mol^{-1} K^{-1}; for **any** ideal gas C_p – C_v = R, independent of atomicity.
- Boyle's law is isothermal (T constant); Charles' law is isobaric (P constant). Mixing the two yields wrong answers.
- Dalton's law applies only to **non-reacting** gases.
- Carbon at room temperature does not obey Dulong–Petit because of quantum freezing of high-frequency modes.

2.5 Key formulas table

Symbol	Formula	Meaning	NCERT page
Ideal gas	$PV = \mu RT$	Mole form of ideal gas law	246
Ideal gas	$PV = N k_B T$	Molecule form	246
Ideal gas	$P = n k_B T$	Number-density form	246
Mass-density form	$P = \rho RT/M_0$	Using density and molar mass	246
Boyle's law	PV = const (T fixed)	Isothermal	247
Charles' law	$V \propto T$ (P fixed)	Isobaric	247
Dalton's law	$P_{total} = \Sigma P_i$	Non-reactive mixture	247
KT pressure	$P = (1/3) n m \overline{v^2}$	Kinetic-theory pressure	249, Eq. 12.14
Avg. translational KE	$\frac{1}{2} m \overline{v^2} = (3/2) k_B T$	Per molecule	250, Eq. 12.19
RMS speed	$v_{rms} = \sqrt{3 k_B T/m}$	Per single molecule	250
RMS speed (molar)	$v_{rms} = \sqrt{3 RT/M_0}$	Per mole form	250
Equipartition	$\langle \varepsilon_{quad} \rangle = \frac{1}{2} k_B T$	Per quadratic term	253
Monatomic C_v, C_p, γ	(3/2)R, (5/2)R, 5/3	He, Ar, Ne	253
Rigid diatomic	(5/2)R, (7/2)R, 7/5	O_2, N_2	253
Diatomic + vibration	(7/2)R, (9/2)R, 9/7	Non-rigid diatomic	253
Polyatomic (general)	$C_v = (3+f)R$, $\gamma = (4+f)/(3+f)$	f = vibrational modes	253, Eq. 12.36
Mayer's relation	$C_p - C_v = R$	Any ideal gas	253
Dulong–Petit	C = 3R	Solids	254, Eq. 12.37
Mean free path	$\lambda = 1/(\sqrt{2} n \pi d^2)$	Hard-sphere molecules	255, Eq. 12.40
Mean free path (P,T)	$\lambda \propto T/P$	Scaling with macroscopic vars	255
Collision time	$\tau = \lambda/\langle v \rangle$	Time between collisions	255
Avg. mol. KE (total)	U = (3 + r + 2v)RT/2 per mole	r = rot, v = vib modes	253

🎯 Practice MCQs

📊 PYQ Alignment

CUET (UG) Physics consistently includes 6–8 questions per year drawn from this chapter, with calculation-heavy items on v_rms, average kinetic energy/temperature relationships and C_v/C_p/γ from degrees of freedom (especially distinguishing monatomic vs rigid-diatomic), plus statement-based questions on the assumptions and limits of the kinetic-theory derivation and on mean free path scaling ($\lambda \propto T/P$).

CUET 2023–25 — Actual PYQs from this chapter

No PYQs from this chapter appeared in CUET 2023, 2024 or 2025.