

Chapter 9 – Behaviour of Perfect Gas and Kinetic Theory

1. Introduction

Gases are everywhere — the air we breathe, the fuel that powers rockets, even the atmosphere of stars.

Understanding how gases behave is essential to understand **pressure, temperature, and energy at the molecular level**.

In earlier chapters, we studied gases macroscopically using parameters like **P, V, and T**.

Now we dive deeper to connect those macroscopic properties with the **microscopic motion of molecules** — this connection forms the foundation of the **Kinetic Theory of Gases (KTG)**.

The Kinetic Theory explains:

- What happens inside gases at the atomic level,
 - Why pressure arises,
 - How temperature relates to molecular motion,
 - And how energy distributes among molecules.
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2. Ideal Gas and Equation of State

Ideal Gas

An **ideal gas** is a hypothetical gas that strictly obeys:

$$PV=nRT \quad PV = nRTPV = nRTPV = nRT$$

at all temperatures and pressures.

Where:

- P → pressure
- V → volume
- n → number of moles
- R → universal gas constant = 8.314 J/mol·K
- T → temperature (in kelvin)

This is called the **Ideal Gas Law**.

It combines three experimental laws:

1. **Boyle's Law:** $PV=\text{constant}$ $PV = \text{constant}$ at constant T.

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2. **Charles's Law:** $V \propto T$ $\rightarrow V = kT$ at constant P.
 3. **Avogadro's Law:** $V \propto n$ $\rightarrow V = kn$ at constant P, T.
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◆ **Equation in Different Forms**

$$PV = nRT = NkTP \Rightarrow nRT = NkT$$

Where N = number of molecules and $k = R/N_A = 1.38 \times 10^{-23} \text{ J/K}$ $\Rightarrow k = N_A R = 1.38 \times 10^{-23} \text{ J/K}$ is the **Boltzmann constant**.

3. Pressure and Volume Relation

Boyle's law says pressure decreases as volume increases — the famous inverse relation. If you compress air to half its volume, its pressure doubles, as long as temperature remains constant.

Graph: **P–V curve** is a rectangular hyperbola.

4. Temperature and Volume Relation

According to Charles's Law:

$$VT = \text{constant} \quad (\text{at constant } P) \Rightarrow \frac{V}{T} = \text{constant} \quad (\text{at constant } P)$$

This gives absolute zero (-273.15°C) where volume theoretically becomes zero.

Temperature in **Kelvin** starts from this absolute zero.

5. Pressure and Temperature Relation

Gay-Lussac's Law:

$$PT = \text{constant} \quad (\text{at constant } V) \Rightarrow \frac{P}{T} = \text{constant} \quad (\text{at constant } V)$$

As temperature increases, gas pressure increases — molecules hit walls faster and more often.

6. Combined Gas Law

Combining Boyle, Charles, and Gay-Lussac laws:

$$PVT = \text{constant} \Rightarrow \frac{PV}{T} = \text{constant}$$

For given mass of gas:

$$P_1V_1T_1 = P_2V_2T_2 \Rightarrow \frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

7. Avogadro's Law and Molar Volume

At same T and P, equal volumes of gases contain equal number of molecules.

At NTP (1 atm, 273 K):

1 mole = 6.022×10^{23} molecules occupy 22.4 L (0.0224 m^3).

8. Kinetic Theory of Gases

This theory provides molecular explanation for macroscopic behavior of gases.

Postulates:

1. A gas consists of a large number of identical molecules in random motion.
2. Volume of molecules negligible compared to container.
3. Collisions are perfectly elastic.
4. No intermolecular forces except during collisions.
5. Time of collision \ll time between collisions.
6. Average kinetic energy of molecules \propto absolute temperature.

9. Derivation of Pressure of a Gas

Consider a cubic box of side L with N molecules, each of mass m, moving randomly.

A molecule moving in x-direction with velocity v_x hits wall and bounces back, momentum change = $2mv_x$.

Force by one molecule:

$$F = \Delta p / \Delta t = 2mv_x \cdot 2L/v_x = mv_x \cdot 2L/v_x = \frac{2mv_x}{v_x} = 2mv_x$$

For N molecules (considering $1/3$ distribution along x, y, z):

$$P = \frac{1}{3} N m v^2 = \frac{1}{3} N m \overline{v^2}$$

or

$$PV = \frac{1}{3} N m v^2 = \frac{1}{3} N m \overline{v^2} V = \frac{1}{3} N m v^2 V$$

This is the **kinetic theory equation of state**.

It beautifully connects microscopic motion (v) to macroscopic pressure (P).

🔥 10. Root Mean Square Speed

Average of squares of molecular velocities:

$$v_{rms} = \sqrt{v^2} = \sqrt{3kTm} = \sqrt{3RTMv_{rms}} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3RT}{M}}$$

Where M = molar mass.

So, speed $\propto \sqrt{T}$ and $\propto 1/\sqrt{M}$.

→ lighter gases move faster.

Example:

At same T, $v_{rms, H_2} = v_{rms, O_2} = \sqrt{\frac{M_{O_2}}{M_{H_2}}} \cdot v_{rms, H_2} = \sqrt{\frac{32}{2}} = 4$

Hydrogen molecules move 4× faster than oxygen molecules.

11. Kinetic Interpretation of Temperature

From KTG:

$$12mv^2 = 32kT \frac{1}{m} \overline{v^2} = \frac{3}{2} kT$$

→ Average kinetic energy per molecule is directly proportional to temperature.

This explains why gas temperature drops when it expands freely (Joule expansion).

12. Degrees of Freedom and Energy Distribution

A molecule can move in several independent directions — these are its **degrees of freedom (f)**.

Type	Degrees of Freedom (f)
Monoatomic gas	3 (translational)
Diatomeric gas	5 (3 translational + 2 rotational)
Polyatomic gas	6 (3 + 3)

By the **Equipartition of Energy Principle**, each degree of freedom contributes $\frac{1}{2}kT$ energy per molecule.

Total energy per mole:

$$U = f/2RTU = \frac{f}{2} RTU = 2f/2RT$$

13. Specific Heats and γ (Gamma)

From thermodynamics:

$$C_V = (dU/dT)V = f/2R C_V = \left(\frac{dU}{dT} \right)_V = \frac{f}{2} R$$

and

$$C_P = C_V + R C_P = C_V + R$$

So,

$$\gamma = C_P/C_V = f+2/f = \frac{f+2}{f}$$

Gas Type	f	γ
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Monoatomic 3 5/3 ≈ 1.67

Diatomic 5 7/5 = 1.4

Polyatomic 6 4/3 ≈ 1.33

14. Mean Free Path

Average distance a molecule travels between two successive collisions:

$$\lambda = 12\pi d^2 n \lambda = \frac{1}{\sqrt{2}} \pi d^2 n \lambda = 2\pi d^2 n$$

where

d = molecular diameter, n = number density.

Smaller d → larger λ → molecules travel farther before colliding.

15. Real Gases and Deviations

Ideal gases follow $PV = nRT$ under all conditions — but real gases deviate, especially at **high pressure and low temperature**.

Reasons:

- Molecules have finite volume.
- Intermolecular attractions exist.

Van der Waals' Equation:

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

where

a → measure of attraction,

b → effective volume of molecules.

At high T, low P → terms vanish → ideal gas law recovered.

16. Compressibility Factor

$$Z = PV/nRT = \frac{PV}{nRT} Z = nRT/PV$$

For ideal gas $Z = 1$.

For real gases:

$Z < 1$ → dominant attractions (e.g., CO₂)

$Z > 1$ → dominant repulsion (e.g., H₂, He).

17. Mean, Root Mean Square, and Most Probable Speeds

According to Maxwell's distribution:

Speed Type Symbol Expression Relation

Most probable v_p $\sqrt{2kT/m}$ $v_p : v_{avg} : v_{rms} = 1 : 1.128 : 1.225$

Average v_{avg} $\sqrt{8kT/\pi m}$

RMS v_{rms} $\sqrt{3kT/m}$

All increase with temperature; order remains same.

18. Law of Equipartition of Energy

Energy equally divides among all degrees of freedom.

Each degree → $\frac{1}{2}kT$ per molecule or $\frac{1}{2}RT$ per mole.

Thus total energy:

$$U = f/2RTU = \frac{f}{2} RTU = fRT$$

19. Applications of Kinetic Theory

1. Explains gas laws microscopically.

2. Defines temperature as molecular motion.
 3. Derives relation between C_p , C_v , and γ .
 4. Predicts speed of sound in gases.
 5. Helps design engines, turbines, and meteorological models.
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20. Summary

1. Ideal gas law $\rightarrow PV = nRT$.
2. Kinetic theory equation $\rightarrow PV = (1/3) N m v^2$.
3. $12mv^2=32kT\frac{1}{2} m v^2 = \frac{3}{2} kT$
4. Degrees of freedom determine internal energy.
5. $C_p - C_v = R$; $\gamma = C_p/C_v$.
6. Van der Waals equation modifies ideal law.
7. Mean free path depends on pressure and diameter.
8. Maxwell distribution explains molecular speeds.
9. Temperature \propto average kinetic energy.