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***Mathematical Principles of
Thermodynamics Applied to Ideal Gases
and Heat Engines and Their Cycles***

Thermo-Fluid Mechanics (ACMA5011)

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1 Part A: Calculations

1.1 Question 1

A container of volume $8.0 \times 10^{-3} \text{ m}^3$ contains oxygen gas at a pressure of $1.5 \times 10^6 \text{ Nm}^{-2}$ and a temperature of 127 degrees Celsius. Calculate:

- (i) The number of moles of the gas

$$v = 8.0 \times 10^{-3} \text{ m}^3$$

$$P = 1.5 \times 10^6 \text{ Nm}^{-2}$$

$$T = 127^\circ\text{C} = 400\text{K}$$

$$PV = nRT$$

$$\frac{PV}{RT} = n$$

$$n = \frac{1.5 \times 10^6 \times 8 \times 10^{-3}}{8.31 \times 400}$$

$$n = 3.61 \text{ mol}$$

- (ii) The number of molecules of the gas

$$N_A = 6.023 \times 10^{23}$$

$$\text{No. of molecules} = n \times N_A$$

$$\text{No. of molecules} = 3.61 \times 6.023 \times 10^{23}$$

$$\text{No. of molecules} = 2.17 \times 10^{24} \text{ Molecules}$$

- (iii) The mass of one molecule of the gas.

$$M_m = 32 \times 10^{-3} \text{ kg}$$

$$R = 8.31 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

$$N_A = 6.023 \times 10^{23}$$

$$\text{Mass of 1 Molecule} = \frac{\text{Molar mass}(M_m)}{\text{Avoagadros Constant } (N_A)} \text{ kg}$$

$$\text{Mass of 1 Molecule} = \frac{32 \times 10^{-3}}{6.023 \times 10^{23}}$$

$$\text{Mass of 1 Molecule} = 5.31 \times 10^{-26} \text{ kg}$$

1.2 Question 2

A glass bulb 'A' of volume $2.0 \times 10^{-3} \text{ m}^3$ is connected to a second bulb B of volume $1.0 \times 10^{-3} \text{ m}^3$ and the whole system is full of air at STP. If bulb 'A' is heated to 500 K whilst 'B' remains constant at 273 K, find the new pressure of the system (STP: Standard temperature and pressure $1 \times 10^5 \text{ Pa}$ and 273 K).

Before

$$V_A = 2.0 \times 10^{-3} \text{ m}^3$$

$$V_B = 1.0 \times 10^{-3} \text{ m}^3$$

$$P_A = 1 \times 10^5 \text{ Pa}$$

$$P_B = 1 \times 10^5 \text{ Pa}$$

$$T_A = 273 \text{ K}$$

$$T_B = 273 \text{ K}$$

After

$$V_A = 2.0 \times 10^{-3} \text{ m}^3$$

$$V_B = 1.0 \times 10^{-3} \text{ m}^3$$

$$P_A = 1 \times 10^5 \text{ Pa}$$

$$P_{B\text{new}} = 1 \times 10^5 \text{ Pa}$$

$$T_A = 500 \text{ K}$$

$$T_B = 273 \text{ K}$$

$$P_A = P_B = P$$

As mass of gas is fixed in the system

$$\frac{P_A V_A}{T_A} + \frac{P_B V_B}{T_B} = \frac{P V_A}{T_{A\text{new}}} + \frac{P V_B}{T_B}$$

$$\left(\frac{1 \times 10^5 \times 2.0 \times 10^{-3}}{273} \right) + \left(\frac{1 \times 10^5 \times 1.0 \times 10^{-3}}{273} \right) = P \left(\frac{2 \times 10^{-3}}{500} + \frac{1 \times 10^{-3}}{273} \right)$$

$$1.1 = P \left(\frac{2 \times 10^{-3}}{500} + \frac{1 \times 10^{-3}}{273} \right)$$

$$\frac{1.1}{\left(\frac{2 \times 10^{-3}}{500} + \frac{1 \times 10^{-3}}{273} \right)} = P$$

$$P = 1.3 \times 10^5 \text{ Pa}$$

1.3 Question 3

A cubical box of dimensions 1.0m by 1.0m by 1.0 m contains, 9.0×10^{24} molecules of a gas. The mass of each molecule is 5.0×10^{-26} kg and each molecule has an average velocity of 500m/s.

Assume if 1/3 of the molecules collide on each face.

Find:

- (i) The time between collisions on two parallel faces of the cube.

$$\text{Distance} = \text{Speed} \times \text{Time}$$

$$2(1) = 500 \times t$$

$$\frac{2}{500} = t$$

$$t = 4 \times 10^{-3} \text{ s}$$

- (ii) The change in momentum on a face of a single gas molecule.

$$\text{Momentum} = \text{Mass} \times \text{Velocity}$$

$$\text{Momentum} = 5 \times 10^{-26} \times 500$$

$$\text{Final Momentum (opposite direction)} = -5 \times 10^{-26} \times 500$$

$$\Delta \text{Momentum} = \text{Initial Momentum} - \text{Final Momentum}$$

$$\Delta \text{Momentum} = 5 \times 10^{-26} \times 500 - (-5 \times 10^{-26} \times 500)$$

$$\Delta \text{Momentum} = 5 \times 10^{-23} \text{ kgms}^{-1}$$

- (iii) The total force experienced on this face of the box.

$$\text{Force} = \text{Rate of Change of Momentum}$$

$$\text{Force} = \frac{\Delta \text{Momentum}}{\text{Time Between Collisions}}$$

$$\text{Force} = \frac{5 \times 10^{-23}}{4 \times 10^{-3}} \text{ kgms}^{-1}$$

$$\text{Force} = 1.25 \times 10^{-20} \text{ N}$$

Force on the wall due to 1 particle

$$\text{Force} = 1.25 \times 10^{-20} \times 10^3$$

$$\text{Force} = 1.25 \times 10^{-20} \text{ N}$$

$$\text{Total Force by all particles on the wall} = \frac{9 \times 10^{24} \times 1.25 \times 10^{-20}}{3}$$

$$\text{Total Force by all particles on the wall} = 3 \times 10^{24} \times 1.25 \times 10^{-20}$$

$$\text{Total Force by all particles on the wall} = 37,500 \text{ N}$$

(iv) The pressure on this face of the box.

$$Pressure = \frac{Force}{Area}$$

$$Pressure = \frac{37500}{1 \times 1}$$

$$Pressure = 37,500 Pa$$

1.4 Question 4

A fixed mass of a polyatomic gas, initially at 17 degrees Celsius and a pressure of 2.0×10^6 Pa is compressed isothermally to a third of its original volume, it is then allowed to expand adiabatically to its original volume. Calculate the final pressure of the system.

Take $\gamma=1.3$

$$T = 27^\circ C = 290 K$$

$$P = 2 \times 10^6 Pa$$

Ideal Gas Equation

$$PV = nRT$$

$$V_1 = V m^3$$

$$V_2 = \frac{V}{3} m^3$$

$$P_1 = 2 \times 10^6 Pa$$

$$P_2 = ?$$

$$T_1 = 290 K$$

$$T_2 = 290 K$$

$$\frac{PV}{T} = Constant$$

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

T_1 and T_2 cancel each other out

$$P_1 V_1 = P_2 V_2$$

$$2 \times 10^6 \times V = P_2 \times \frac{V}{3}$$

Volumes cancel each other out

$$2 \times 10^6 \times 3 = P_2$$

$$P_2 = 6 \times 10^6 \text{ Pa}$$

In an adiabatic process, no heat enters or leaves the system

$$PV = \text{Constant}$$

$$P_2 V_2^\gamma = P_3 V_3^\gamma$$

$$6 \times 10^6 \times \left(\frac{V}{3}\right)^{1.3} = P_3 \times V^{1.3}$$

$$6 \times 10^6 \times \frac{V^{1.3}}{3^{1.3}} = P_3 \times V^{1.3}$$

Volumes cancel each other out

$$\frac{6 \times 10^6}{3^{1.3}} = P_3$$

$$P_3 = 1.438 \text{ MPa}$$

1.5 Question 5

A gas is contained within a well lagged cylinder with a frictionless piston. 800 J of heat are applied to the cylinder allowing the gas to expand. If the work done in expansion is 375 J, find the change in the internal energy of the gas.

From the first law of thermodynamics

$$\Delta Q = \Delta U + \Delta W$$

$$800 = \Delta U + 375$$

$$800 - 375 = \Delta U$$

$$\Delta U = 425 \text{ J}$$

1.6 Question 6

A Carnot engine has the same efficiency when working:

$$\mu \text{ efficiency} = \left(\frac{T_1 - T_2}{T_1} \right) \times 100\%$$

(a) between 1000 K and 500 K and

$$\mu = \left(\frac{1000 - 500}{1000} \right) \times 100\%$$

$$\mu = 50\%$$

(b) between 300 K and T K.

$$\mu = \left(\frac{T - 300}{T} \right) \times 100\%$$

Calculate the temperature T of the source in case (b).

If Equal

$$\frac{1}{2} \times 100\% = \left(\frac{T - 300}{T} \right) \times 100\%$$

$$T = 2(T - 300)$$

$$T = 2T - 600$$

$$600 = 2T - T$$

$$T = 600K$$

1.7 Question 7

7) Calculate the maximum efficiency of a 'Carnot' type heat engine which takes in heat energy at source of 10,000J and ejects heat to a sink with energy of 2000J.

$$Q_1 = 10,000J$$

$$Q_2 = 2,000J$$

$$\mu_{Max} = \left(\frac{Q_1 - Q_2}{Q_1} \right) \times 100\%$$

$$\mu_{Max} = \left(\frac{10000 - 2000}{10000} \right) \times 100\%$$

$$\mu_{Max} = 80\%$$

1.8 Question 8

Find the change in entropy of 10 kg of water when it is heated reversibly from 373K to 573K. The specific heat capacity of water in this temperature range is $4.20 \times 10^3 \text{ J.kg}^{-1}.\text{K}^{-1}$.

$$Mass = 10kg$$

$$T_1 = 373K$$

$$T_2 = 573K$$

$$C_w = 4.2 \times 10^3 \text{ J kg}^{-1} \text{ K}^{-1}$$

$$\Delta S = \int_1^2 \frac{\Delta Q}{T}$$

$$\Delta S = \int_{373}^{573} mcw \frac{dT}{T}$$

$$\Delta S = 10 \times 4.2 \times 10^3 \times (\ln T)$$

$$\Delta S = 4.2 \times 10^3 \times [\ln(573) - \ln(373)]$$

$$\Delta S = 18.03 \times 10^3 \text{ J K}^{-1}$$

2 Part B: Carnot Heat Engine

2.1 Introduction

The Carnot cycle, conceived by French engineer Nicolas Léonard Sadi Carnot in 1824, represents a fundamental theoretical construct in thermodynamics that establishes the maximum possible efficiency achievable by any heat engine operating between two temperature reservoirs (Pearson Learning Channels, 2022; Wikipedia, 2006). This idealized reversible cycle provides a critical benchmark against which all practical heat engines are measured, whilst simultaneously illustrating the profound constraints imposed by the second law of thermodynamics (Wikipedia, 2006). Understanding the Carnot cycle underpins the thermodynamic analysis of real engines—from conventional power plants to modern heat pumps—and demonstrates why no practical engine can achieve its theoretical efficiency limit (Fiveable, 2025a).

2.2 Concept and Structure of the Carnot Cycle

The Carnot cycle operates through four distinct reversible thermodynamic processes, connecting four equilibrium states of the working fluid (BYJUS, 2024). These processes are executed between two thermal reservoirs maintained at constant temperatures: a high-temperature reservoir at T_H and a low-temperature reservoir at T_L (Pearson Learning Channels, 2022; Chemistry LibreTexts, 2025).

2.2.1 Process 1–2: Isothermal Expansion (Heat Absorption)

The working gas expands at constant temperature T_H whilst absorbing heat Q_h from the hot reservoir. All energy converts directly to mechanical work (Pearson Learning Channels, 2022).

$$W_{12} = Q_h = \mu R T_H \ln\left(\frac{V_2}{V_1}\right)$$

where μ is the number of moles and R is the universal gas constant. The critical feature is that the temperature difference between the gas and reservoir remains infinitesimal throughout, ensuring reversibility (Galileo et al., 2016). This characteristic prevents entropy generation within the system, a hallmark of reversible processes (Wikipedia, 2006).

2.2.2 Process 2–3: Adiabatic Expansion (Work Output)

The gas continues to expand without heat exchange—the system becomes thermally insulated—while continuing to perform work on the surroundings (PhysicsPedia, 2024). This adiabatic process causes the temperature to decrease from T_H to T_L (PhysicsPedia, 2024). For a reversible adiabatic process, the relationship between temperature and volume is governed by (PhysicsPedia, 2024):

$$TV^\gamma - 1 = \text{constant}$$

2.2.3 Process 3–4: Isothermal Compression (Heat Rejection)

The gas is now compressed isothermally at temperature T_L whilst in contact with the cold reservoir (BYJUS, 2024). Work must be supplied to compress the gas, and equivalent heat Q_c is rejected to the cold reservoir at constant temperature (BYJUS, 2024). The work required is (Galileo et al., 2016):

$$W_{34} = Q_c = \mu R T_L \ln\left(\frac{V_3}{V_4}\right)$$

Again, the infinitesimal temperature difference ensures reversibility without entropy generation within the fluid (Wikipedia, 2006).

2.2.4 Process 4–1: Adiabatic Compression (Work Input)

Finally, the system is adiabatically compressed back to its initial state, with the temperature rising from T_L to T_H (PhysicsPedia, 2024). This process requires work input to be supplied, restoring the system to state 1 and completing the cycle (Wikipedia, 2006). Like process 2–3, this adiabatic compression is isentropic (Nuclear Power, 2021).

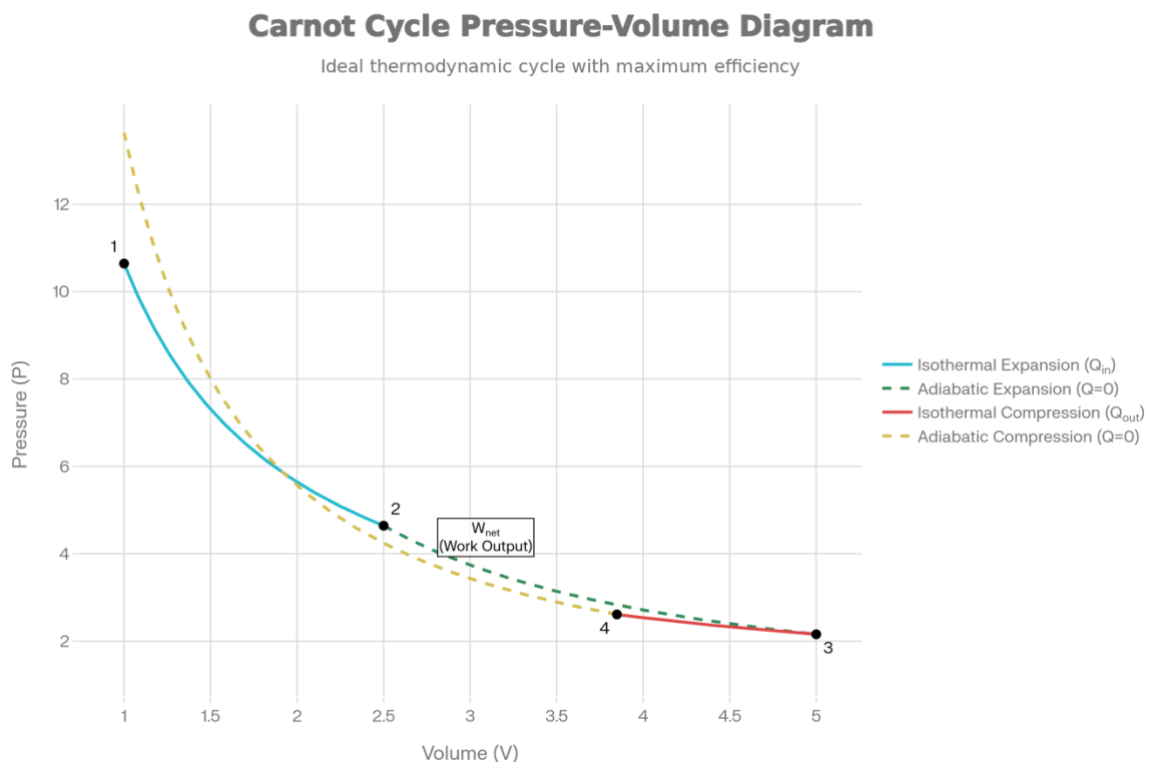


Figure 1: Carnot cycle on a pressure-volume diagram showing all four reversible processes

The pressure-volume diagram illustrates these four processes, where the enclosed area represents net work output per cycle (PhysicsPedia, 2024).

2.3 Efficiency of the Carnot Engine

Thermal efficiency is defined as the ratio of useful work output to heat input (Pearson Learning Channels, 2022):

$$\eta = \frac{W_{net}}{Q_h} = 1 - \frac{Q_c}{Q_h}$$

For a reversible cycle, entropy changes satisfy a crucial condition (Wikipedia, 2006):

$$\Delta S_{cycle} = \frac{Q_h}{T_H} - \frac{Q_c}{T_L} = 0$$

This yields the fundamental relationship (Wikipedia, 2006):

$$\frac{Q_c}{Q_h} = \frac{T_L}{T_H}$$

Substituting into the efficiency equation gives the Carnot efficiency formula (Pearson Learning Channels, 2022; TheScienceCube, 2020):

$$\eta_{Carnot} = 1 - \frac{T_L}{T_H}$$

This reveals that maximum efficiency depends exclusively on absolute temperatures of the reservoirs (Pearson Learning Channels, 2022). Efficiency can never reach 100% because T_L cannot be zero, some heat must always be rejected (Study.com, 2015).

2.4 Real Heat Engines and Deviations from Ideal Behaviour

No practical heat engine can approach Carnot efficiency because irreversibility, an inescapable feature of real processes—reduces performance (Doubtnut, 2021; Fiveable, 2025a).

2.4.1 Sources of Irreversibility

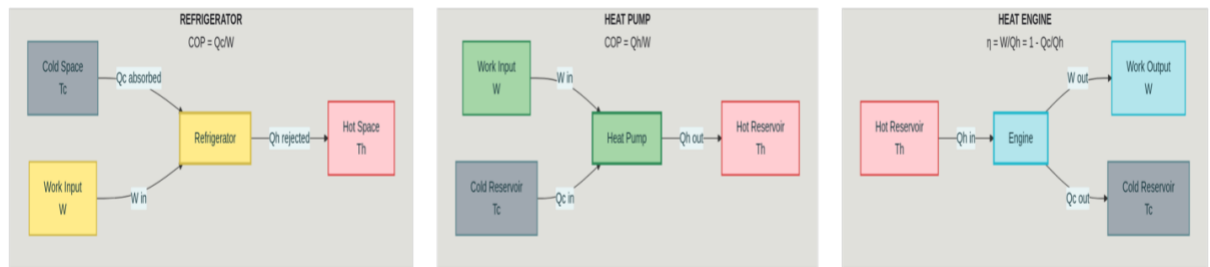
Friction and Mechanical Losses reduce available work output (Fiveable, 2025a). Finite Temperature Differences required for heat transfer across real heat exchangers violate the reversibility condition (Fiveable, 2025a). Throttling processes in expansion valves generate entropy without producing work (Fiveable, 2025a). Heat Losses through pipes and casings reduce net work (HKPHO, undated). Non-Ideal Gas Behavior introduces thermodynamic departures at high pressures (Fiveable, 2025a).

2.4.2 Practical Efficiencies

Modern combined-cycle power plants achieve ~60% efficiency, diesel engines ~45%—far below Carnot limits (Fiveable, 2025a). A conventional plant operating between 873 K and 298 K has Carnot efficiency of ~66%, yet achieves only 40–50% actual efficiency owing to accumulated irreversibilities (Fiveable, 2025a).

2.5 Comparison with Heat Pumps and Refrigerators

Heat pumps and refrigerators operate on the reversed Carnot cycle, using work input to move heat against its natural temperature gradient (Wikipedia, 2006; Fiveable, 2025b).



2.5.1 Heat Engines vs. Heat Pumps and Refrigerators

A heat engine produces work W from heat absorption, with efficiency $\eta = W/Q_h$ (Wikipedia, 2006). Heat pumps and refrigerators require work input W to transfer heat, using the Coefficient of Performance (COP) metric instead (Wikipedia, 2004; Fiveable, 2025b).

For a refrigerator (Wikipedia, 2004):

$$COP_{ref} = \frac{Q_c}{W}$$

For a heat pump (Fiveable, 2025b):

$$COP_{hp} = \frac{Q_h}{W}$$

Since $Q_h = Q_c + W$, the relationship becomes (Lumen Learning, 2010):

$$COP_{hp} = COP_{ref} + 1$$

This explains why heat pump COP exceeds refrigerator COP by unity, not a contradiction, but different metrics applied to the same device (Lumen Learning, 2010; Vedantu, 2025).

Carnot Limits:

For a Carnot refrigerator (University of Tennessee - Knoxville, undated):

$$COP_{ref, Carnot} = \frac{T_L}{T_H - T_L}$$

For a Carnot heat pump (University of Tennessee - Knoxville, undated):

$$COP_{hp, Carnot} = \frac{T_H}{T_H - T_L}$$

2.6 Conclusion

The Carnot heat engine establishes the theoretical maximum efficiency through $\eta = 1 - T_L/T_H$, derived from entropy considerations in the second law of thermodynamics (Pearson Learning Channels, 2022; Wikipedia, 2006). No practical engine approaches this limit because friction, finite temperature differences, and other irreversibilities inevitably generate entropy (Fiveable, 2025a).

Heat pumps and refrigerators demonstrate the universality of these principles: the same thermodynamic cycle, executed in reverse, serves opposite purposes with different performance metrics (Fiveable, 2025b; Lumen Learning, 2010). Understanding the Carnot cycle remains essential for engineers optimising thermal systems by identifying opportunities for irreversibility reduction through friction minimisation, enhanced heat exchanger effectiveness, and optimised operating temperatures (Fiveable, 2025a).

3 Part C: Ideal Gases

3.1 Part (i): Account of the ideal gas

3.1.1 The Ideal Gas Model

An ideal gas is a theoretical construct that assumes gas molecules are point particles with negligible volume, experience no intermolecular forces, and undergo perfectly elastic collisions (NCBI, 2024). The ideal gas law describes the relationship between pressure (P), volume (V), number of moles (n), and absolute temperature (T) (Study.com, 2024):

$$PV = nRT$$

where R is the universal gas constant (8.314 J/(K·mol)). This equation represents a fundamental state relationship, derived from Charles's law, Boyle's law, and Gay-Lussac's law (NCBI, 2024). However, this model fails to account for real gas behaviour, particularly at high pressures and low temperatures (Wikipedia, 2003).

3.1.2 Real Gases and Van der Waals Equation

Real gases deviate significantly from ideal behaviour because gas molecules have finite volume and exert attractive forces on each other (Wikipedia, 2003). Dutch physicist Johannes van der Waals addressed these limitations in 1873 by modifying the ideal gas equation (Testbook, 2019):

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

3.1.3 Pressure Correction Term (an^2/V^2)

The term an^2/V^2 accounts for intermolecular attractive forces (Shaalaa.com, 2021). Gas molecules exert attractive forces on their neighbours, reducing the speed of molecules moving toward container walls. Consequently, the measured pressure is lower than the theoretical ideal pressure (Shaalaa.com, 2021). The correction is proportional to the square of molar density $(n/V)^2$, since attractive forces increase with molecular proximity. The constant 'a' depends on the gas nature and reflects intermolecular force strength (Testbook, 2019).

3.1.4 Volume Correction Term (nb)

The term nb represents the excluded volume occupied by gas molecules themselves (BYJUS, 2023). In the ideal model, molecules are assumed as point particles with zero volume, making the entire container volume available. Real molecules occupy significant space; considering each molecule as a sphere of radius r, the excluded volume for n molecules equals nb, where $b = 4V_m$ (four times a molecule's volume) (Shaalaa.com, 2021). This correction becomes increasingly important at high pressures where molecular volume becomes comparable to container volume (BYJUS, 2023). The effective available volume becomes $(V - nb)$ rather than V.

At low pressures and high temperatures, both correction terms become negligible, and the Van der Waals equation approaches the ideal gas law (Testbook, 2019). This asymptotic behaviour validates the Van der Waals equation as a superior model bridging ideal and real gas behaviour (NCBI, 2024).

3.2 Part (ii): Temperature of gas is proportional to its kinetic theory

3.2.1 Derivation of Temperature-Kinetic Energy Proportionality

Kinetic theory models gases as collections of discrete particles in random motion (OpenStax, 2025). The pressure exerted by a gas can be derived from molecular collisions with container walls. Considering momentum transfer during elastic collisions, the kinetic theory pressure equation is (Kisembo Academy, 2018):

$$P = \frac{1}{3} \rho c^2_{rms}$$

where ρ is gas density and c_{rms} is the root mean square velocity. Rearranging using density $\rho = M/V$ (where M is total molecular mass) (Kisembo Academy, 2018):

$$PV = \frac{1}{3} M c^2_{rms}$$

Since $PV = nRT$ for an ideal gas, we can equate (Kisembo Academy, 2018):

$$nRT = \frac{1}{3} N c^2_{rms}$$

where N is the total number of molecules. Rearranging for individual molecular kinetic energy (Lumen Learning, 2010):

$$\frac{1}{3}mc^2rms = \frac{3}{2}kBT$$

where m is individual molecular mass and kB is Boltzmann's constant (1.38×10^{-23} J/K). Therefore, the average translational kinetic energy is (OpenStax, 2025):

$$KE = \frac{1}{2}m\bar{v}^2 = 23kBT$$

This fundamental relationship demonstrates that temperature is directly proportional to average kinetic energy, higher temperatures correspond to faster molecular motion (Lumen Learning, 2010). This derivation validates temperature as a measure of molecular kinetic energy (Stanford, undated).

3.3 Part (iii): At constant pressure, the root mean square speed of the ideal gas molecules are inversely proportional to the density of the gas

3.3.1 Root Mean Square Speed at Constant Pressure

From the kinetic theory pressure equation $P = (1/3)\rho c^2rms$, solving for RMS velocity at constant pressure (Doubtnut, 2021):

$$c^2rms = \frac{3P}{\rho}$$

$$c rms = \sqrt{\frac{3P}{\rho}}$$

At constant pressure and temperature, this becomes (Doubtnut, 2021):

$$c rms \propto \frac{1}{\sqrt{\rho}}$$

Therefore, root mean square speed is inversely proportional to the square root of density (GeeksforGeeks, 2022). Lighter gases have lower densities and higher RMS velocities than heavier gases at the same temperature and pressure (OpenStax, 2025).

3.3.2 Graham's Law of Diffusion

Since diffusion rate is directly proportional to molecular speed (Lumen Learning, 2015):

$$\text{diffusion rate} \propto \text{crms} \propto \frac{1}{\sqrt{\rho}}$$

This yields Graham's law of diffusion: the rate of diffusion is inversely proportional to the square root of gas density (Graham's Law, Wikipedia, 2002):

$$r \propto \frac{1}{\sqrt{\rho}}$$

Expressing density in terms of molar mass M , since $\rho \propto M$ at constant temperature and pressure (Wikipedia, 2002):

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

This relationship demonstrates that lighter gases diffuse faster than heavier gases—hydrogen molecules diffuse approximately four times faster than oxygen molecules (Chemistry LibreTexts, 2023). This principle underpins practical gas separation technologies: uranium isotope enrichment during nuclear weapons development exploited Graham's law through diffusion of UF_6 gas, selectively concentrating ^{235}U (Wikipedia, 2002). Modern applications include gas purification and isotope separation in medical and industrial contexts (Chemistry LibreTexts, 2023).

The inverse relationship between diffusion rate and molecular mass emerges directly from kinetic theory: identical temperatures produce equal average kinetic energies across all gases, but lighter molecules must move faster to achieve this energy threshold. Consequently, lighter molecules traverse any diffusion barrier more rapidly than heavier molecules, providing a quantitative basis for gas mixture separation (Chemistry LibreTexts, 2023).

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