Chapter 1

Heat and Thermodynamics

Thermometers

The instruments with which we may conveniently record temperature are called thermometers. The following types of thermometers are in common use:

(1) **Liquid thermometers:** They are based on the expansion of liquids, such as mercury, alcohol, etc.

(2) **Gas thermometers:** They work on the thermal expansion of gases like hydrogen, air, etc. These are more sensitive than liquid thermometers.

(3) **Resistance thermometers:** The electrical resistance of metals varies with temperature, and this property of metals is used for measuring temperature.

(4) **Thermo-electric thermometers:** These are based on the development of e.m.f. due to the difference in temperature between the junctions of two dissimilar metals.

(5) **Vapour pressure thermometers:** These are based on the change of vapour pressure with temperature, and are used for measuring very low temperatures.

(6) **Radiation thermometers:** By measuring the thermal radiation emitted by a body, its temperature can be determined.

Resistance Thermometry: Platinum Resistance Thermometer (PRT)

When the temperature of a metal wire increases, its electrical resistance also increases. This increase is gradual, almost uniform, and valid over a wide temperature range. Because of this property, metal wires can be used to measure temperature. Such instruments are called resistance thermometers.

Clausius Relation (Linear Approximation)

Clausius first proposed a simple relation between resistance and temperature: $R_\theta = R_0 (1 + \alpha\theta)$. Where R_0 = resistance at 0°C, R_θ = resistance at temperature θ°C, and α = temperature coefficient of resistance.

Limitations:

- It predicts that resistance becomes zero at absolute zero, which is not true experimentally.
- It does not fit experimental results accurately at ordinary temperatures

Callendar's Parabolic Relation

Callendar showed that pure platinum wire, free from impurities and mechanical strain, has a unique resistance at each temperature. He proposed a parabolic relation:

$$R_\theta = R_0 (1 + \alpha\theta + \beta\theta^2)$$

Where α and β are constants of the material. For pure platinum: $\alpha = 3.94 \times 10^{-3}$ and $\beta = -5.8 \times 10^{-7}$. This equation is much more accurate than the linear relation.

Platinum Resistance Scale of Temperature

Since β is very small compared to α, the $\beta\theta^2$ term is often neglected. The linear form becomes:

$$R_\theta = R_0 (1 + \alpha\theta p)$$

Here, θp is the platinum resistance temperature. At 100°C: $R_{100} = R_0 (1 + 100\alpha)$

Therefore: $\alpha = (R_{100} - R_0) / (100R_0)$

Expression for Platinum Temperature

$$\theta p = (R_\theta - R_0) / (R_0\, \alpha)$$

Substituting α: $$\theta p = (R_\theta - R_0) / (R_{100} - R_0) \times 100.$$

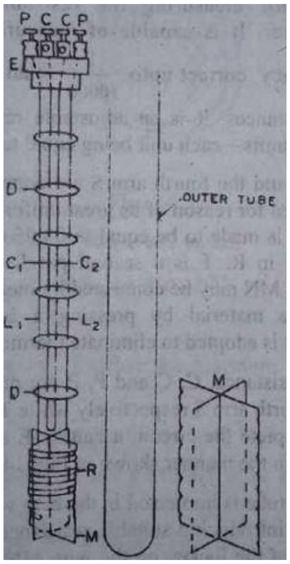
The quantity $(R_{100} - R_0)$ is called the fundamental interval of the thermometer.

Difference between True Temperature and Platinum Temperature

The true temperature θ is not exactly equal to θp because resistance variation is not perfectly linear. Callendar showed:

$$\theta - \theta p = \delta \left[(\theta/100)^2 - (\theta/100) \right]$$

Where δ is a constant depending on the platinum wire. For highly pure platinum, $\delta \approx 1.5$. Higher purity platinum gives a larger α and smaller δ.



Deduction of the Callendar Formula

Using the parabolic resistance relation, Callendar showed that $\theta - \theta p$ depends on a quadratic function of temperature.

$$\delta = -(100^2 \beta) / (\alpha + 100\beta)$$

Since $\beta < 0$ and $\alpha > 0$, δ is positive.

Experimental Determination of δ

To determine δ, the resistance of the platinum wire is measured at: 0°C, 100°C, and 444.6°C (melting point of Sulphur). Once δ is known, θp is measured, and true temperature θ is calculated.

Construction of Platinum Resistance Thermometer

Historical Note: First constructed by Sir William Siemens in 1871, and later improved by Callendar and Griffiths.

Construction:

- Pure platinum wire is used.
- The wire is doubled to reduce induced currents.
- It is wound on a mica sheet.
- Placed inside a hard glass or glazed porcelain tube.

- The tube is evacuated and sealed to prevent oxidation.

Leads and Compensation:

i. Platinum leads connect the wire to the binding screws.
ii. Compensating leads are used to eliminate lead resistance effects.

Temperature Range:

i. Up to 700°C: copper leads and glass tube.
ii. High temperatures: platinum leads and porcelain tube.

Callendar and Griffiths Bridge

This is a highly precise form of Wheatstone bridge used to measure very small resistance changes.

Features:

i. Accuracy up to 1/10,000 ohm.
ii. Ratio arms P and Q are equal.
iii. Adjustable resistance arm R.
iv. Platinum thermometer wire in arm S.
v. Uniform bridge wire MN for fine adjustment.
vi. This bridge allows extremely accurate resistance and temperature measurement.

Advantages of Platinum Resistance Thermometer (PRT)

1. High accuracy: Platinum resistance thermometers are very accurate and provide reliable temperature measurements over a wide range. Hence, they are used as standard thermometers in laboratories.
2. Good reproducibility: For pure platinum, the resistance at a given temperature is always the same. Therefore, PRTs give highly reproducible results.
3. Nearly linear resistance–temperature relation: The variation of resistance with temperature is almost linear, especially over a large temperature range, making calculations simple and reliable.
4. Wide temperature range: Platinum resistance thermometers can be used from about −200°C to nearly 1000°C.
5. Chemical stability of platinum: Platinum does not oxidize or corrode easily at high temperatures, ensuring long life and stability of the thermometer.
6. High sensitivity: A small temperature change produces a measurable change in resistance, allowing precise temperature determination.
7. Suitable for calibration purposes: Due to their accuracy and stability, PRTs are widely used for calibrating other thermometers.

Disadvantages of Platinum Resistance Thermometer (PRT)

1. High cost: Platinum is an expensive metal, making PRTs costlier compared to thermocouples and liquid thermometers.
2. Delicate construction: The platinum wire is very thin and fragile, so the thermometer must be handled carefully.
3. Slow response time: Because of its larger thermal mass, a PRT responds slowly to rapid temperature changes.
4. Unsuitable for very high temperatures: Above about 1000°C, platinum wire may deform or evaporate, limiting its use at extremely high temperatures.
5. Requires electrical measuring instruments: Accurate resistance measurement needs a Wheatstone bridge or potentiometer, increasing experimental complexity.
6. Affected by mechanical strain: Any strain or deformation of the platinum wire changes its resistance permanently, leading to measurement errors.
7. Not suitable for rapidly varying temperatures: Due to slow response and thermal inertia, PRTs are not ideal for fluctuating or transient temperatures.

Thermo-Electric Thermometry

Introduction

Temperature is a fundamental physical quantity that indicates the degree of hotness or coldness of a body. It can be measured using various physical properties that change predictably with temperature. Common methods include liquid expansion, electrical resistance variation, thermoelectric e.m.f., vapour pressure changes, and thermal radiation.

A thermo-electric thermometer operates on the principle that a temperature difference between two junctions of dissimilar metals produces an electrical voltage. This method is particularly useful for measuring high temperatures and temperatures at inaccessible locations.

Thermo-Couple Thermometer

A thermocouple thermometer consists of two different metal wires joined together at two points, forming two junctions. One junction is called the hot junction, and the other is called the cold or reference junction. The temperature difference between these two junctions produces a measurable electrical signal.

Thermocouples are widely used in industrial and laboratory temperature measurements because of their simple construction and wide operating range.

Principle (Seebeck Effect)

When two dissimilar metals are connected to form a closed circuit and the two junctions are maintained at different temperatures, an electromotive force (e.m.f.) is generated in the circuit. This effect was discovered by Seebeck in 1821 and is known as the Seebeck effect.

The magnitude of the thermo-e.m.f. depends on:

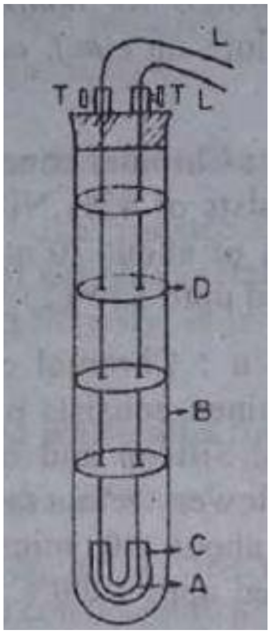
i. The temperature difference between the junctions
ii. The nature of the metals used
iii. The average temperature of the junctions
iv. This e.m.f. causes a current to flow when the circuit is closed.

Construction of a Thermo-Electric Thermometer

A thermocouple is constructed by welding or soldering two dissimilar metal wires at one end to form the hot junction. The other ends form the cold junction. The wires are insulated using glass, ceramic, or fire-clay tubes to prevent electrical contact and chemical contamination. The thermocouple is connected to a sensitive measuring instrument such as a galvanometer or potentiometer. The entire assembly is designed to withstand high temperatures and harsh industrial environments.

Measurement Using a Potentiometer

The thermo-e.m.f. generated signal in a thermocouple is very small, usually of the order of microvolts. Therefore, a sensitive potentiometer is used for accurate measurement. By adjusting an external resistance, a uniform potential gradient is maintained along the potentiometer wire, typically between 5 and 10 microvolts per centimeter. The balancing length corresponding to the thermo-e.m.f. is measured, allowing accurate determination of the generated voltage.



Calibration of the Thermo-Electric Thermometer

Calibration is essential for accurate temperature measurement. The cold junction is maintained at a known reference temperature, usually 0°C, using melting ice. The hot junction is then placed at several known temperatures. The corresponding thermo-e.m.f. values are measured, and a calibration curve of e.m.f. versus temperature is plotted. Once calibrated, the thermocouple can be used to determine unknown temperatures directly from this curve.

Empirical Relation Between e.m.f. and Temperature

Experimentally, the relationship between thermo-e.m.f. (E) and temperature (θ) of the hot junction is found to be approximately:

$$E = a\theta + b\theta^2$$

where a and b are constants depending on the thermocouple materials. This empirical relation provides a convenient mathematical method for calculating temperature from measured e.m.f.

Applications of the Thermo-Electric Thermometer

Thermo-electric thermometers are extensively used in:

- Industrial furnaces and kilns
- Boilers and steam plants
- Metallurgical and glass industries
- Power plants
- Chemical processing units
- Research laboratories for high-temperature experiments

Advantages and Disadvantages of the Thermoelectric Thermometer

Advantages

i. Wide Temperature Range: A thermoelectric thermometer can measure a very large range of temperatures, from very low cryogenic temperatures up to about 1600°C, depending on the type of thermocouple used.
ii. Simple Construction: It consists of two dissimilar metal wires joined at one end. The construction is simple and relatively inexpensive.
iii. Quick Response: The junction can be made very small and light, allowing it to respond quickly to temperature changes.
iv. Remote Measurement: The generated emf can be measured at a distance using a galvanometer or digital voltmeter, making it suitable for hazardous locations.
v. No External Power Required: The thermocouple generates its own emf due to temperature difference, so no external power supply is needed.
vi. Rugged and Durable: It can withstand vibration, mechanical shock, and harsh industrial environments.

Disadvantages

i. Lower Accuracy: It is generally less accurate compared to platinum resistance thermometers.
ii. Non-Linear Relationship: The relationship between emf and temperature is not perfectly linear, so calibration tables are required.
iii. Reference Junction Required: The cold junction temperature must be known or compensated for accurate measurement.
iv. Drift and Aging: At high temperatures, oxidation or material changes may occur, causing measurement errors.
v. Small Output Voltage: The generated emf is very small (in millivolts), requiring sensitive measuring instruments.

Platinum Resistance Thermometer (PRT)

Q1. A platinum resistance thermometer has a resistance R_0 = 100 ohm at 0°C and R_{100} = 138.5 ohm at 100°C. If the resistance at an unknown temperature is R_θ = 119.25 ohm, calculate the platinum temperature θ_p.

Q1 Solution

Given: $R_0 = 100\ \Omega$, $R_{100} = 138.5\ \Omega$, $R_\theta = 119.25\ \Omega$

Use: $\theta_p = [(R_\theta - R_0) / (R_{100} - R_0)] \times 100$

$\theta_p = [(119.25 - 100) / (138.5 - 100)] \times 100$

$\theta_p = (19.25 / 38.5) \times 100 = 50\ °\text{C}$

Q2. For a platinum resistance thermometer, R_0 = 50 ohm and the temperature coefficient of resistance $\alpha = 3.9 \times 10^{-3}\ °\text{C}^{-1}$. Calculate the resistance of the thermometer at 200°C.

Q2 Solution

Given: $R_0 = 50\ \Omega$, $\alpha = 3.9 \times 10^{-3}\ °\text{C}^{-1}$, $\theta = 200\ °\text{C}$

Use linear relation: $R_\theta = R_0(1 + \alpha\theta)$

$R_\theta = 50[1 + (3.9 \times 10^{-3})(200)]$

$= 50[1 + 0.78] = 50 \times 1.78 = 89\ \Omega$

Q3. For a platinum wire used in a resistance thermometer, the constants are: $\alpha = 3.94 \times 10^{-3}$ and $\beta = -5.8 \times 10^{-7}$. Calculate the Callendar constant δ.

Q3 Solution

Given: $\alpha = 3.94 \times 10^{-3}$, $\beta = -5.8 \times 10^{-7}$

Use: $\delta = -(100^2\beta)/(\alpha + 100\beta)$

$\delta = -(10000 \times (-5.8\times10^{-7})) / (3.94\times10^{-3} + 100\times(-5.8\times10^{-7}))$

$\delta = 0.0058 / 0.003882 \approx 1.494 \approx 1.49$

Q4. A platinum resistance thermometer has R_0 = 25 ohm and R_{100} = 34.63 ohm. (a) Calculate the temperature coefficient of resistance α. (b) If the resistance at an unknown temperature is R_θ = 31.0 ohm, calculate the platinum temperature θ_p.

Q4 Solution

Given: $R_0 = 25\ \Omega$, $R_{100} = 34.63\ \Omega$

(a) Find α

Use: $\alpha = (R_{100} - R_0) / (100R_0)$

$\alpha = (34.63 - 25) / (100 \times 25) = 9.63 / 2500 = 0.003852\ °C^{-1}$

(b) Given $R_\theta = 31.0\ \Omega$, find θ_p

Use: $\theta_p = [(R_\theta - R_0) / (R_{100} - R_0)] \times 100$

$\theta_p = [(31.0 - 25) / (34.63 - 25)] \times 100$

$\theta_p = (6.0 / 9.63) \times 100 \approx 62.3\ °C$

Q5. In a platinum resistance thermometer, the platinum temperature is θ_p = 300°C. If the Callendar constant is δ = 1.5, use Callendar's relation to calculate the true temperature θ.

Q5 Solution

Given: $\theta p = 300\ °C$, $\delta = 1.5$

Callendar relation: $\theta - \theta_p = \delta[(\theta/100)^2 - (\theta/100)]$

$\theta - 300 = 1.5[(\theta/100)^2 - (\theta/100)]$

Let $x = \theta/100$, so $\theta = 100x$

Then: $100x - 300 = 1.5(x^2 - x)$

$\Rightarrow 1.5x^2 - 101.5x + 300 = 0$

Solve quadratic: $x = [101.5 \pm \sqrt{(101.5^2 - 4\times1.5\times300)}] / (2\times1.5)$

Smaller (physical) root $x \approx 3.0975$

$\theta = 100x \approx 309.75\ °C \approx 310\ °C$

Thermo-Electric Thermometer (Thermocouple)

Q6. A copper–constantan thermocouple has a sensitivity of 45 microvolts per degree Celsius. If the measured thermo-emf is 2.25 millivolts and the cold junction is maintained at 0°C, calculate the temperature of the hot junction.

Q6 Solution

Given: Sensitivity $S = 45\ \mu V/°C$, $E = 2.25\ mV = 2250\ \mu V$, cold junction at 0°C

Use: $\theta = E / S$ (since $T_c = 0°C$)

$\theta = 2250 / 45 = 50\ °C$

Q7. In a thermocouple–potentiometer arrangement, the potential gradient along the potentiometer wire is 8 microvolts per centimeter. If the balancing length is 250 centimeters, calculate the thermo-emf generated by the thermocouple.

Q7 Solution

Given: Potential gradient $k = 8\ \mu V/cm$, balancing length $l = 250$ cm

Thermo-emf: $E = k\,l = 8 \times 250 = 2000\ \mu V = 2.0\ mV$

Q8. For a thermocouple, the relation between thermo-emf and temperature is given by: $E = a\theta + b\theta^2$ where a = 40 microvolts per degree Celsius and b = 0.02 microvolts per degree Celsius squared. If the measured thermo-emf is 6.0 millivolts, calculate the temperature of the hot junction.

Q8 Solution

Given: $E = a\theta + b\theta^2$, $a = 40\ \mu V/°C$, $b = 0.02\ \mu V/°C^2$, $E = 6.0\ mV = 6000\ \mu V$

Equation: $0.02\theta^2 + 40\theta - 6000 = 0$

Divide by 0.02: $\theta^2 + 2000\theta - 300000 = 0$

$\theta = [-2000 + \sqrt{(2000^2 + 4\times300000)}] / 2$ (positive root)

$\theta = [-2000 + \sqrt{(5,200,000)}] / 2 \approx [-2000 + 2280.35] / 2 \approx 140.18\ °C$

So, $\theta \approx 140\ °C$

Q9. An iron–constantan thermocouple has a sensitivity of 55 microvolts per degree Celsius. The cold junction is maintained at 25°C, and the measured thermo-emf is 4.4 millivolts. Using cold junction compensation, calculate the hot junction temperature.

Q9 Solution

Given: S = 55 μV/°C, Tc = 25°C, measured E = 4.4 mV = 4400 μV

Assuming linear behavior: $E = S(T_h - T_c)$

Th − Tc = 4400 / 55 = 80 °C

Th = 25 + 80 = 105 °C

Q10. For a thermocouple, the emf–temperature relation is: $E = a\theta + b\theta^2$, where a = 50 microvolts per degree Celsius and b = −0.02 microvolts per degree Celsius squared. Calculate the neutral temperature of the thermocouple.

Q10 Solution

Given: $E = a\theta + b\theta^2$, a = 50 μV/°C, b = −0.02 μV/°C²

Neutral temperature occurs at maximum emf: $dE/d\theta = a + 2b\theta = 0$

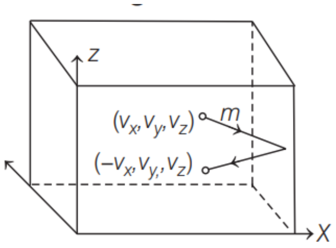
$\theta n = -a/(2b) = -50 / [2(-0.02)] = 50/0.04 = 1250$ °C

Expression for Pressure Exerted by a Gas

In the kinetic theory of gases, a gas is assumed to consist of a very large number of identical molecules that are in continuous random motion. These molecules move freely in all directions and frequently collide with one another and with the walls of the container. The pressure exerted by a gas on the walls of its container arises due to these repeated elastic collisions of gas molecules with the container walls.

Consider an ideal gas enclosed in a cubical container of side l and volume $V = l^3$. Let the total number of molecules be n, and let each molecule have mass m. The motion of a molecule can be resolved into three mutually perpendicular velocity components c_x, c_y and c_z. The square of the speed of a molecule is given by $c^2 = c_x^2 + c_y^2 + c_z^2$.

Consider a single molecule moving with velocity component c_x towards the wall perpendicular to the x-axis. During an elastic collision with the wall, the velocity component along the x-direction reverses from c_x to $-c_x$. The change in momentum of the molecule along the x-direction is therefore $2mc_x$. The molecule travels a distance $2l$ between successive collisions with the same wall, and hence the time interval between collisions is $2l/c_x$. The force exerted by the molecule on the wall is the rate of change of momentum and is given by $F = mc_x{}^2/l$.



The area of the wall is l^2. Hence, the pressure exerted by a single molecule on the wall is $P = mc_x^2/V$. Considering all n molecules, the total pressure exerted by the gas is $P = (m \Sigma c_x^2/V)$. Taking the average value, we obtain $P = mnc_x^2/V$.

Since molecular motion is random, the average values of the squares of the velocity components are equal, that is $c_x^2 = c_y^2 = c_z^2$. Therefore, $c^2 = 3c_x^2$, giving $c_x^2 = c^2/3$. Substituting this result, the expression for pressure becomes

$$P = mnc^2/3V$$

Multiplying both sides by V, we obtain

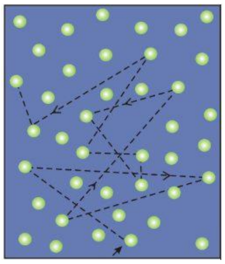
$$PV = mnc^2/3$$

If $M = mn$, then

$$PV = Mc^2/3$$

This equation establishes a direct connection between the macroscopic pressure of a gas and the microscopic motion of its molecules.

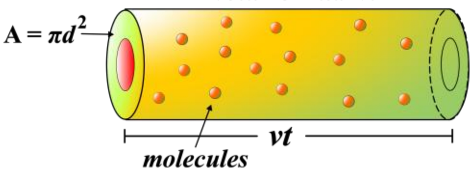
Mean Free Path of Gas Molecules



In the kinetic theory of gases, gas molecules are in continuous random motion and frequently collide with one another. The distance travelled by a molecule between successive collisions is not fixed and varies from collision to collision. Therefore, the concept of mean free path is introduced.

The mean free path, denoted by λ (=S/N), is defined as the average distance travelled by a gas molecule between two successive collisions with other molecules. It is a statistical quantity and plays an important role in explaining transport properties of gases.

To derive an expression for mean free path, consider a gas of identical spherical molecules, each having an effective diameter d. A collision occurs when the distance between the centers of two molecules becomes equal to d. For simplicity, assume that one molecule moves with an average speed $\bar{c}$ while the others remain at rest.



In time t, the molecule travels a distance $\bar{c}t$ and sweeps out a cylindrical volume with cross-sectional area πd^2. The volume swept out is $\pi d^2 \bar{c}t$. If n is the number of molecules per unit volume, the number of collisions in time t is $\pi d^2 \bar{c} t n$.

The mean free path λ is defined as the distance travelled per collision. Hence,

$$\lambda = \bar{c}t / (\pi d^2 \bar{c} t n) = 1 / (\pi d^2 n).$$

In reality, all molecules are in motion. To account for the increased collision frequency due to relative motion, a factor of $\sqrt{2}$ is introduced, giving the more accurate expression

$$\lambda = 1 / (\sqrt{2}\, \pi\, d^2\, n).$$

Using the ideal gas equation, the number density *n* can be expressed as $n = p/(kT)$, where *P* is the pressure, *T* is the absolute temperature, and *k* is the Boltzmann constant. Substituting this value, the mean free path becomes

$$\lambda = kT / (\sqrt{2}\, \pi\, d^2\, p)$$

This expression shows that the mean free path is directly proportional to temperature and inversely proportional to pressure, and it explains the behavior of gases under different physical conditions.

Pressure Exerted by a Gas (Kinetic Theory)

Q1. A gas contains 2.5×10^{25} molecules in a volume of $0.02\ m^3$. The mass of each molecule is 4.65×10^{-26} kg, and the mean-square speed is c2 = 4.0 × 105 $m^2\ s^{-2}$. Calculate the pressure *P*.

Use: $P = mn\, c^2/3V$

$mn = (4.65\times10^{-26})(2.5\times10^{25}) = 1.16$ kg.

$mn/V = 1.16 / 0.02 = 5.81 \times 10^1\ kgm^{-3}$.

$P = (1/3)(5.81 \times 10\text{^}1)(4.0\times10\text{^}5) = 7.75 \times 10^6$ Pa.

Therefore, $P = 7.75 \times 10^6$ Pa.

Q2. The density of a gas is 1.2 kgm^{-3} and the rms speed is 500 ms^{-1}. Find the pressure *P*.

Use: $P = P = mn\, c^2/3V$ and $c^2 = c_{rms}^2$

$\langle c^2\rangle = (500)^2 = 250000\ m^2s^{-2}$

$P = (1/3)(1.2)(250000) = 10^5$ Pa.

Therefore, $P = 10^5$ Pa

Q3. A gas has a pressure of 1.5×10^5 Pa and a density of 0.9 kgm^{-3}. Calculate the rms speed c_{rms}.

Use $P = (1/3)\rho\, c_{rms}^2 \Rightarrow c_{rms} = \sqrt{(3P/\rho)}$.

$3P/\rho = 3(1.5\times10^5)/0.9 = 5\times10^5$

$c_{rms} = \sqrt{(5\times10^5)} = 707\ ms^{-1}$

Therefore $c_{rms} = 707\ ms^{-1}$

Q4. The pressure of a gas is $P = 2.0 \times 10^5$ Pa. If the density is doubled while the rms speed remains constant, find the new pressure.

From $P = (1/3)\rho c_{rms}^2$, if c_{rms} is constant, then $P \propto \rho$.

Doubling ρ doubles P.

New pressure $= 2 \times (2.0\times10^5) = 4.0 \times10^5$ Pa.

Q5. For a gas, all quantities remain constant except the rms speed. If c_{rms} is increased by 20%, find the percentage change in pressure.

Using $P = (1/3)\rho c_{\text{rms}}^2$, pressure is proportional to c_{rms}^2

New $c_{\text{rms}} = 1.20\ c_{\text{rms}}$

$\Rightarrow$ New pressure factor = $(1.20)^2 = 1.44$

Percentage increase = $(1.44 - 1) \times 100\% = 44.0\%$

Q6. A gas has pressure $P = 1.01 \times 10^5$ Pa and rms speed $c_{\text{rms}} = 420\ \text{ms}^{-1}$. Find the mass density ρ of the gas.

Use: $P = (1/3)\rho\, c_{\text{rms}}^2 \ \Rightarrow\ \rho = 3P / c_{\text{rms}}^2$.

$c_{\text{rms}}^2 = (420)^2 = 176400$.

$\rho = 3(1.01\times10^5) / 176400 = 1.72\ \text{kgm}^{-3}$.

Therefore, $\rho \approx 1.718\ \text{kg/m}^3$.

Q7. A gas has number density $n = 2.5 \times 10^{25}\ \text{m}^{-3}$ at temperature $T = 300$ K. Using kinetic theory, show numerically that the pressure equals n k T and calculate P. (Take $k = 1.38 \times 10^{-23}\ \text{J K}^{-1}$.)

From kinetic theory: $P = (1/3)\ n\ mc^2$, and for an ideal gas $c^2 = 3kT/m$.

Substitute: $P = (1/3)\ n\ m\ (3kT/m) = n\ k\ T$.

$P = (2.5\times10^{25})(1.38\times10^{-23})(300)$.

$P = 1.04 \times 10^5$ Pa

Q8. A gas has pressure $P = 1.0 \times 10^5$ Pa in volume $V = 0.05\ \text{m}^3$. It contains $n = 1.2 \times 10^{25}$molecules, each of mass $m = 5.31 \times 10^{-26}$ kg. Calculate the mean square speed $\langle c^2 \rangle$.

Use $PV = (1/3)\ m\ n\ \langle c^2\rangle \ \Rightarrow\ \langle c^2\rangle = 3PV / (mn)$.

3PV = 3(1.0×10^5)(0.05) = 1.5×10^4.

$mn = (5.31\times10^{-26})(1.2\times10^{25}) = 6.37 \times 10^{-1}$ kg.

$\langle c^2\rangle = 1.5\times 10^4 / 6.37 \times 10^{-1} = 2.35 \times$ 10^4 m^2s^{-2}

Q9. For a gas, the average value of the square of the x-component of molecular speed is $c_x^2 = 1.5 \times 10^5$ m²s^{-2}. If $m = 4.8 \times 10^{-26}$ kg, n = 3.0 × 10^{25} molecules, and V = 0.03 m^3, calculate the pressure P.

Use $P = mnc_x^2/V$

mn = $(4.8\times10^{-26})(3.0\times1010^{25}) = 1.44$ kg.

mn/V = 1.44 / 0.03 = 4.80×10^1 kgm^{-3}.

$P = (4.80 \times 10^1)(1.5\times10^5) = 7.20 \times 10^6$ Pa

Q10. Two gases A and B are at the same temperature T = 300 K. Their molecular masses are $m_A = 4.65 \times 10^{-26}$ kg and $m_B = 2.32 \times 10^{-26}$ kg. Find the ratio of their rms speeds c_{rms} (B)/ c_{rms} (A).

Use $c_{rms} = \sqrt{(3kT/m)}$.

c_{rms} (B)/ c_{rms} (A) = $\sqrt{(m_A / m_B)} = \sqrt{((4.65\times10^{-26})/(2.32\times10^{-26}))}$.

$= \sqrt{(2)} = 1.42$.

Therefore, c_{rms} (B) = 1.42 × c_{rms} (A).

Mean Free Path of Gas Molecules

Key relations used: $\lambda = 1/(\sqrt{2}\ \pi\ d^2\ n)$ and $\lambda = kT/(\sqrt{2}\ \pi\ d^2\ p)$. (Take $k = 1.38 \times 10^{-23}$ J K^{-1}.)

Q11. Calculate the mean free path λ of air molecules at T = 300 K and p = 1.01 × 10^5 Pa. Take molecular diameter $d = 3.7 \times 10^{-10}$ m.

Use $\lambda = kT/(\sqrt{2}\ \pi\ d^2\ p)$.

$d^2 = (3.7\times10^{-10})^2 = 1.37 \times 10^{-19}$ m².

Denominator = $\sqrt{2}\ \pi\ d^2\ p = (1.414)(\pi)(1.37 \times 10^{-19})(1.01\times10^5)$.

$\lambda = (1.38\times10^{-23} \times 300) / [\sqrt{2}\ \pi\ d^2\ p] = 6.74 \times 10^{-8}$ m

Therefore, $\lambda = 6.74 \times 10^{-8}$ m

Q12. A gas has number density $n = 2.5 \times 10^{25}$ m^{-3} and molecular diameter $d = 4.0 \times 10^{-10}$ m. Find the mean free path λ.

Use $\lambda = 1/(\sqrt{2}\ \pi\ d^2\ n)$.

$d^2 = (4.0\times 10^{-10})^2 = 1.60 \times 10^{-19}$ m²

$\sqrt{2}\ \pi\ d^2\ n = (1.414)(\pi)(1.60 \times 10^{-19})(2.5\times10^{25})$

$\lambda = 5.63 \times 10^{-8}$ m

Q13. At constant temperature, the pressure of a gas is reduced to one-fourth of its original value. By what factor does the mean free path change?

From $\lambda = kT/(\sqrt{2}\,\pi\, d^2\, p)$, $\lambda \propto 1/p$ when T and d are constant.

If p becomes p/4, then λ becomes 4λ.

Therefore, the mean free path increases by a factor of 4.

Q14. If the absolute temperature of a gas is doubled while pressure remains constant, by what factor does the mean free path change?

From $\lambda = kT/(\sqrt{2}\,\pi\, d^2\, p)$, $\lambda \propto T$ when p and d are constant.

If T becomes 2T, then λ becomes 2λ.

Therefore, mean free path doubles.

Q15. A gas has molecular diameter $d = 2.0 \times 10^{-10}$ m at T = 300 K and $P = 2.0 \times 10^{5}$ Pa. Calculate the mean free path λ.

Use $\lambda = kT/(\sqrt{2}\,\pi\, d^2\, p)$.

$d^2 = (2.0\times 10^{-10})^2 = 4.0 \times 10^{-20}\ \text{m}^2$.

$\lambda = 1.17 \times \times 10^{-7}$ m

Q16. At T = 300 K, the mean free path is $\lambda = 1.0 \times 10^{-6}$ m for a gas with molecular diameter $d = 3.0 \times 10^{-10}$ m. Find the pressure p.

Use $p = kT/(\sqrt{2}\,\pi\, d^2\, \lambda)$.

$d^2 = (3.0\times10^{-10})^2 = 9.00 \times 10^{-20}\ \text{m}^2$.

$p = (1.38\times10^{-23}\times 300) / [\sqrt{2}\,\pi\, d^2\, \lambda] = 1.04 \times 10^{4}$ Pa.

Therefore, $p = 1.04 \times 10^{4}$ Pa.

Q17. If the molecular diameter of a gas is doubled while temperature and pressure remain constant, how does the mean free path change?

From $\lambda = kT/(\sqrt{2}\,\pi\, d^2\, p)$, $\lambda \propto 1/d^2$.

If d becomes 2d, then d^2 becomes $4d^2$, so λ becomes $\lambda/4$. Therefore, mean free path becomes one-fourth.

Q18. A gas has mean free path $\lambda = 7.0 \times 10^{-8}$ m and molecular diameter $d = 3.5 \times 10^{-10}$ m. Calculate the number density n.

Use $n = 1/(\sqrt{2}\,\pi\, d^2\, \lambda)$.

$d^2 = (3.5\times10^{-10})^2 = 1.23 \times 10^{-19}$ m².

$n = 2.62 \times 10^{25}$ m^{-3}

Q19. For a gas at T = 300 K with molecular diameter $d = 3.2 \times 10^{-10}$ m, calculate λ at (i) $p_1 = 1.0 \times 10^5$ Pa and (ii) $p_2 = 5.0 \times 10^5$Pa. Also verify the scaling with pressure.

Use $\lambda = kT/(\sqrt{2}\,\pi\, d^2\, p)$.

At $p_1 = 1.0\times10^5$ Pa: $\lambda_1 = 9.10 \times 10^{-8}$ m

At $p_2 = 5.0\times10^5$ Pa: $\lambda_2 = 1.82 \times 10^{-8}$ m

Since $p_2 = 5p_1$, λ_2 should be $\lambda_1/5$.

$\lambda_1/5$ = 1.82e-08 m, which matches λ_2.

Q20. A gas has a molecular diameter d = 3.7 × 10–10 m at a pressure $p = 1.01 \times 10^{5}$ Pa. At what temperature T is the mean free path required to be $\lambda = 1.0 \times 10^{-7}$ m?

Use $\lambda = kT/(\sqrt{2}\,\pi\, d^2\, p) \Rightarrow T = \lambda(\sqrt{2}\,\pi\, d^2\, p)/k$.

$d^2 = (3.7\times10^{-10})^2 = 1.37 \times 10^{-19}$ m².

$T = (1.0\times10^{-7})(\sqrt{2}\,\pi\, d^2\, p) / (1.38\times10^{-23})$.

T = 445 K.

Equipartition of Energy

The equipartition of energy theorem is a fundamental principle of classical statistical mechanics that establishes a direct connection between temperature and molecular energy. According to this theorem, each independent quadratic degree of freedom contributes an average energy of 1/2 kT per molecule, where k is Boltzmann’s constant and T is the absolute temperature.

For a monatomic ideal gas, molecules have three translational degrees of freedom corresponding to motion along three perpendicular directions. Therefore, the average energy per molecule is 3/2 kT. For one mole of gas, replacing Nk with the universal gas constant R, the internal energy becomes U = 3/2 RT.

For a diatomic gas at ordinary temperatures, in addition to three translational degrees of freedom, two rotational degrees of freedom are active. Thus, the average energy per molecule is 5/2 kT, and the molar internal energy is U = 5/2 RT. At higher temperatures, vibrational modes may also contribute, further increasing the internal energy.

Significance of Equipartition of Energy:

1. It provides a direct connection between microscopic molecular motion and macroscopic thermodynamic quantities such as internal energy and temperature.

2. It gives a physical meaning of temperature as a measure of average molecular energy.

3. It explains why the internal energy of an ideal gas depends only on temperature.

4. It helps calculate internal energy using molecular degrees of freedom.

5. It explains the difference in heat capacities between monatomic and diatomic gases.

6. It forms the theoretical basis of the kinetic theory of gases.

7. Its limitations at low temperatures led to the development of quantum theory.

Specific Heat of Gases

Specific heat is defined as the amount of heat required to raise the temperature of a substance by one degree. For gases, two specific heats are defined: the specific heat at constant volume, C_v, and the specific heat at constant pressure, C_p. At constant volume, no external work is done, and therefore dQ equals dU. Hence $Cv = (dU/dT)_v$.

For a monatomic gas, since U = 3/2 RT, we obtain C_v = 3/2 R. For a diatomic gas without vibrational contribution, C_v = 5/2 R. At constant pressure, heat must supply both internal energy increase and external work; C_p is always greater than C_v.

Significance of Specific Heat of Gases:

1. Specific heat determines how much heat is required to raise the temperature of a gas.

2. The existence of two specific heats shows that gases can perform external work during heating.

3. *Cv* represents the change in internal energy only.

4. *Cp* represents the change in internal energy plus work done during expansion.

5. The value of specific heat reveals molecular structure and degrees of freedom.

6. Specific heats are essential in studying heat engines, refrigerators, and thermodynamic cycles.

7. They are important in atmospheric physics and gas dynamics.

Relation between the Two Specific Heats

Using the first law of thermodynamics and the ideal gas equation PV = RT for one mole, it can be shown that $C_p - C_v = R$. This important thermodynamic relation holds for all ideal gases.

For a monatomic gas, C_v = 3/2 R and C_p = 5/2 R. For a diatomic gas, C_v = 5/2 R and C_p = 7/2 R. The ratio $\gamma = C_p/Cv$ plays an important role in adiabatic processes and determines the behavior of gases under compression and expansion.

Significance:

1. The relation $Cp - Cv = R$ connects thermodynamics with the ideal gas law.

2. It shows that the difference between specific heats is due to work done during expansion.

3. It is valid for all ideal gases.

4. It leads to the important ratio $\gamma = Cp/Cv$.

5. The value of γ determines adiabatic relations such as PV^{γ} = constant.

6. It is essential in calculating the speed of sound in gases.

7. It plays a crucial role in thermodynamics and engineering applications.

Mathematical Problems

Constants used:

$k = 1.38 \times 10^{-23}$ J K^{-1}

$R = 8.314$ J mol^{-1} K^{-1}

$N_A = 6.022 \times 10^{23}$ mol^{-1}

Question 1: A monatomic ideal gas is at T = 350 K. (a) Find the average translational energy per molecule. (b) Find the internal energy of 1 mole.

Solution:

Average energy per molecule $= (3/2)kT$

$= (3/2)(1.38 \times 10^{-23})(350)$

$= 7.25 \times 10^{-21}$ J per molecule

Internal energy for 1 mole: $U = (3/2)RT$

$= (3/2)(8.314)(350)$

$= 4.36 \times 10^{3}$ J

Question 2: A diatomic gas (rotationally active) is at T = 400 K. (a) Find the average energy per molecule. (b) Find molar internal energy. (c) Compare with a monatomic gas at the same temperature.

Solution:

Average energy per molecule $= (5/2)kT$

$= (5/2)(1.38 \times 10^{-23})(400)$

$= 1.38 \times 10^{-20}$ J

Molar internal energy: $U = (5/2)RT$

$= 2.5(8.314)(400)$

$= 8.314 \times 10^{3}$ J

Ratio with monatomic gas at the same T = 5/3

Question 3: A gas has 4 degrees of freedom. (a) Write the expression for molar internal energy. (b) Find internal energy at T = 500 K. (c) Find C_v.

Solution:

$U = (f/2)RT = 2RT$

At T = 500 K: $U = 2(8.314)(500) = 8.314 \times 10^{3}$ J

$C_v = (f/2)R = 2R = 16.63$ J mol^{-1} K^{-1}

Question 4: Given $C_v = 16.6$ J mol^{-1} K^{-1}. (a) Determine degrees of freedom. (b) Identify the nature of the gas.

Solution:

$f = (2C_v)/R$

$= (2 \times 16.6)/8.314$

≈ 4

Gas behaves approximately as a 4-degree-of-freedom system.

Question 5: Find the rms velocity of helium at T = 300 K using the equipartition theorem, and verify that (1/2) mvrms^2 = (3/2) kT.

Solution:

$(1/2)mv_{rms}^{2} = (3/2)kT$

$v_{rms} = (3kT/m)^{1/2}$

Mass of He atom = 6.64×10^$^{-27}$ kg

$v_{rms} = [(3 \times 1.38 \times 10^{-23} \times 300) / (6.64 \times 10^{-27})]^{1/2}$

$v_{rms} \approx 1.37 \times 10^{3}$ m/s

Review of the First Law of Thermodynamics and Its Applications

Thermodynamics deals with the relations between heat, work, temperature, and energy in macroscopic systems. The First Law of Thermodynamics is essentially the principle of conservation of energy applied to thermal systems.

The internal energy of a system, denoted by U, represents the total microscopic energy of molecules, including translational, rotational, vibrational, and interaction energies. For an ideal gas, internal energy depends only on temperature.

The First Law of Thermodynamics states that the heat supplied to a system is equal to the increase in internal energy plus the work done by the system. In differential form, it is written as:

$$\delta Q = dU + \delta W$$

For a quasi-static process, the work done by the system is given by:

$$\delta W = P\,dV$$

Therefore, the First Law can also be written as:

$$\delta Q = dU + P\,dV$$

For an isochoric process (constant volume), $dV = 0$, and hence no work is done. Therefore:

$$\delta Q = dU$$

For an isothermal process of an ideal gas, the temperature remains constant and hence $\Delta U = 0$. Thus heat supplied is completely converted into work:

$$Q = W$$

The work done during the isothermal expansion of an ideal gas is:

$$W = nRT\,\ln(V_2 / V_1)$$

For an adiabatic process, no heat is exchanged with the surroundings, so $Q = 0$ and:

$$dU = -\delta W$$

For an ideal gas undergoing a reversible adiabatic process, the relation is:

$$P\,V^{\gamma} = constant$$

In a cyclic process, the system returns to its initial state, so the change in internal energy is zero:

$$\Delta U = 0$$

Hence, for a cyclic process:

$$Q = W$$

Thus, the First Law establishes conservation of energy in thermodynamics and provides the foundation for analyzing heat engines, refrigerators, and all thermodynamic processes.

Reversible and Irreversible Processes

A reversible process is an ideal process carried out infinitely slowly so that the system remains in thermodynamic equilibrium at every stage. It can be reversed without leaving any net change in the system and surroundings. Reversible processes yield maximum work output.

An irreversible process occurs when the system is not in equilibrium during the transformation. Examples include free expansion, frictional effects, and heat flow across a finite temperature difference. Irreversible processes always produce less work than reversible processes between the same states.

For expansion between the same initial and final states:

$$W_{rev} > W_{irr}$$

Reversible processes define the maximum possible efficiency, while irreversible processes represent real natural processes.

Second Law of Thermodynamics

The First Law of Thermodynamics establishes conservation of energy but does not determine the direction of natural processes. The Second Law of Thermodynamics explains why heat flows spontaneously from a hot body to a cold body and why complete conversion of heat into work is impossible.

Kelvin–Planck Statement: It is impossible to construct a heat engine that operates in a cycle and converts all the heat absorbed from a single reservoir completely into work. If Q_1 is the heat absorbed from a hot reservoir and Q_2 is the heat rejected to a cold reservoir, then the work done is:

$$W = Q_1 - Q_2$$

Since Q_2 cannot be zero, total heat cannot be completely converted into work.

Clausius Statement: Heat cannot flow spontaneously from a colder body to a hotter body without external work being done. This principle explains the operation of refrigerators and heat pumps.

The efficiency of a heat engine operating between temperatures T_H and T_C is defined as:

$$\eta = W / Q_H$$

Using energy conservation:

$$\eta = 1 - (Q_C / Q_H)$$

For a reversible Carnot engine operating between T_H and T_C, the maximum efficiency is:

$$\eta_{Carnot} = 1 - (T_C / T_H)$$

Entropy is introduced to express the Second Law mathematically. For a reversible process:

$$dS = \delta Q_{rev} / T$$

For a finite change:

$$\Delta S = \int (\delta Q_{rev} / T)$$

For an isolated system:

$$\Delta S \geq 0$$

For a reversible process, $\Delta S = 0$. For an irreversible process, $\Delta S > 0$. Thus, the entropy of the universe always increases in spontaneous processes.

For an ideal gas undergoing a reversible process, the entropy change is:

$$\Delta S = nC_V \ln(T_2 / T_1) + nR \ln(V_2 / V_1)$$

For an isothermal process:

$$\Delta S = nR \ln(V_2 / V_1)$$

A reversible process proceeds infinitely slowly and maintains thermodynamic equilibrium throughout. It produces the maximum possible work. An irreversible process involves friction, turbulence, or finite temperature differences and always produces less work than a reversible process between the same states.

The Second Law therefore determines the direction of natural processes, introduces entropy as a state function, limits the efficiency of heat engines, and distinguishes between reversible and irreversible processes.

1) Question: One mole of an ideal gas expands isothermally at 300 K from 10 L to 20 L. Find the work done.
Solution:

$W = nRT \ln(V_2/V_1)$
$= (1)(8.314)(300) \ln(2)$
$= 1728$ J

2) Question: Two moles of a monatomic ideal gas are heated from 300 K to 500 K at constant volume. Find heat supplied and change in internal energy.
Solution:

$\Delta T = 200$ K
$\Delta U = nC_v\Delta T = 2(3/2\ R)(200)$
$= 4988$ J
$Q = \Delta U = 4988$ J

3) Question: One mole of an ideal gas expands at constant pressure 2×10^5 Pa from 0.01 m^3 to 0.03 m^3.
Solution:

$\Delta V = 0.02$ m^3
$W = P\Delta V = 4000$ J
$\Delta T = P\Delta V/(nR) \approx 481$ K
$\Delta U = (3/2)R\Delta T \approx 5998$ J
$Q = \Delta U + W \approx 9998$ J

4) Question: One mole expands adiabatically from 10 L to 20 L, γ=1.4, T1=400 K. Find T2.
Solution:

$T_2 = T_1(V_1/V_2)^{\gamma-1}$
$= 400(1/2)$^0.4 ≈ 303 K

5) Question: A gas absorbs 500 J and does 300 J of work in a complete cycle. Find ΔU.
Solution:

For a complete cycle, $\Delta U = 0$

6) Question: Ideal gas free expansion into a vacuum (insulated). Find W, Q, and ΔU.
Solution:

$W = 0, Q = 0, \Delta U = 0$

7) Question: A system receives 1200 J of heat and does 900 J of work. Find ΔU.
Solution:

$\Delta U = Q - W = 1200 - 900 = 300$ J

8) Question: Gas does 500 J work and loses 200 J heat. Find ΔU.
Solution:

$\Delta U = Q - W = (-200) - 500 = -700$ J

9) Question: One mole of monatomic gas is heated at constant pressure from 300 K to 450 K. Find W, ΔU, and Q.
Solution:

$\Delta T = 150$ K
$W = nR\Delta T = 1247$ J
$\Delta U = (3/2)R\Delta T = 1871$ J
$Q = (5/2)R\Delta T = 3118$ J

10) Question: Heat engine absorbs 2000 J and rejects 1200 J. Find W and efficiency.
Solution:

$W = 800$ J
$\eta = 800/2000 = 0.40$

11) Question: Carnot engine between 500 K and 300 K. Find efficiency.
Solution:

$\eta = 1 - 300/500 = 0.40$

12) Question: Carnot engine absorbs 1000 J at 600 K, rejects to 300 K. Find W and efficiency.
Solution:

$\eta = 1 - 300/600 = 0.5$
$W = 500$ J
$Q_c = 500$ J

13) Question: Two moles expand isothermally at 400 K from 5 L to 15 L. Find ΔS.
Solution:

$\Delta S = nR \ln(V2/V1)$
$= 2(8.314) \ln 3$
≈ 18.27 J/K

14) Question: One mole monatomic gas is heated from 300 K to 600 K at constant volume. Find ΔS.

Solution:

$\Delta S = nC_v \ln(T2/T1)$

$= (3/2\ R) \ln 2$

≈ 8.64 J/K

15) Question: 1000 J heat flows from 400 K to 300 K. Find entropy changes.

Solution:

$\Delta S_{hot} = -1000/400 = -2.5$ J/K

$\Delta S_{cold} = +1000/300 = +3.33$ J/K

Total $\Delta S = +0.83$ J/K