PART 1: BASIC CONCEPTS, THERMAL EQUILIBRIUM, STATE VARIABLES AND WORK DONE IN THERMODYNAMIC PROCESSES

1.1 Learning Objectives

After studying this part, students should be able to:

1. Define thermodynamics and explain its importance in physics.
2. Identify a thermodynamic system, surroundings and boundary.
3. Distinguish between open, closed and isolated systems.
4. Explain thermodynamic equilibrium and its different forms.
5. Understand thermodynamic state variables and equations of state.
6. Explain the Zeroth Law of Thermodynamics.
7. Distinguish between heat, work and internal energy.
8. Calculate work done by a gas during expansion or compression.
9. Interpret work done using a pressure–volume (P–V) diagram.
10. Understand the significance of different thermodynamic processes.

1.2 Introduction to Thermodynamics

Thermodynamics is the branch of physics that deals with heat, temperature, work, internal energy and the conversion of energy from one form to another.

It describes how macroscopic physical systems behave when heat is supplied, work is performed or the state of a system changes.

Thermodynamics is particularly useful for studying:

- Heat engines and refrigerators.
- Expansion and compression of gases.
- Energy conversion in machines.
- Changes in temperature and pressure.
- Thermal efficiency of engines.
- Energy transfer between interacting systems.

Examples of thermodynamic systems

1. Gas enclosed in a cylinder fitted with a movable piston.
2. Water heated in a closed container.
3. Steam expanding in a turbine.
4. Air compressed inside a bicycle pump.
5. Refrigerant circulating inside a refrigerator.

Important: Classical thermodynamics generally describes macroscopic properties of matter rather than tracking the motion of individual molecules.

1.3 Thermodynamic System, Surroundings and Boundary

1.3.1 Thermodynamic System

A **thermodynamic system** is a specified quantity of matter or a region in space selected for investigation.

For example, if we study the gas enclosed in a cylinder, the gas is the thermodynamic system.

1.3.2 Surroundings

Everything outside the system that can potentially interact with it is called its **surroundings**.
For a gas enclosed in a cylinder, the cylinder, piston and external environment may form part of the surroundings, depending on the system boundary chosen.

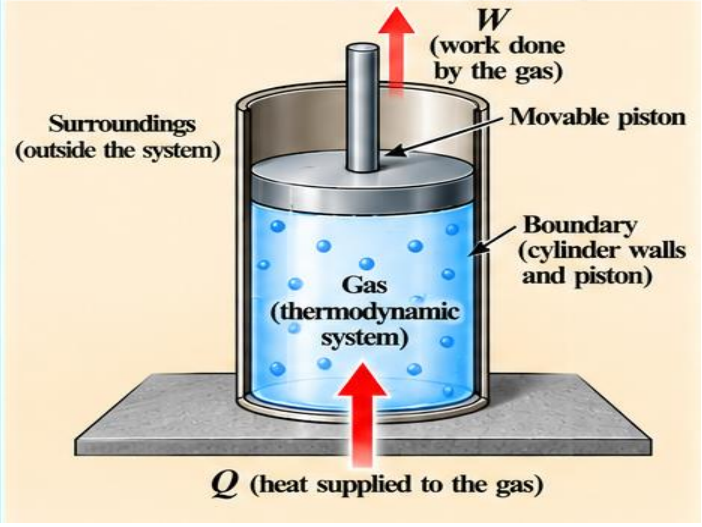
1.3.3 Boundary

The surface that separates a thermodynamic system from its surroundings is called the **boundary**.
The boundary may be:

- Real or imaginary.
- Fixed or movable.
- Thermally conducting or thermally insulating.

For example, the cylinder walls form part of the boundary of the gas system, while the movable piston allows the gas volume to change.

Figure 11.1: Thermodynamic System, Surroundings and Boundary



1.4 Types of Thermodynamic Systems

Thermodynamic systems are classified according to whether they exchange matter and energy with their surroundings.

1.4.1 Open System

An **open system** can exchange both matter and energy with its surroundings.
Examples:

- Water boiling in an open vessel.
- Steam flowing through a turbine.
- Air entering and leaving a running compressor.

Both mass and energy can cross the system boundary.

1.4.2 Closed System

A **closed system** can exchange energy with its surroundings but does not exchange matter across its boundary.
Examples:

- Gas enclosed in a sealed cylinder with a movable piston.
- Water in a sealed container being heated.

Energy may cross the boundary in the form of heat or work, but the mass of the system remains constant.

1.4.3 Isolated System

An **isolated system** exchanges neither matter nor energy with its surroundings.
An ideal isolated system has a boundary that prevents both mass transfer and energy transfer.

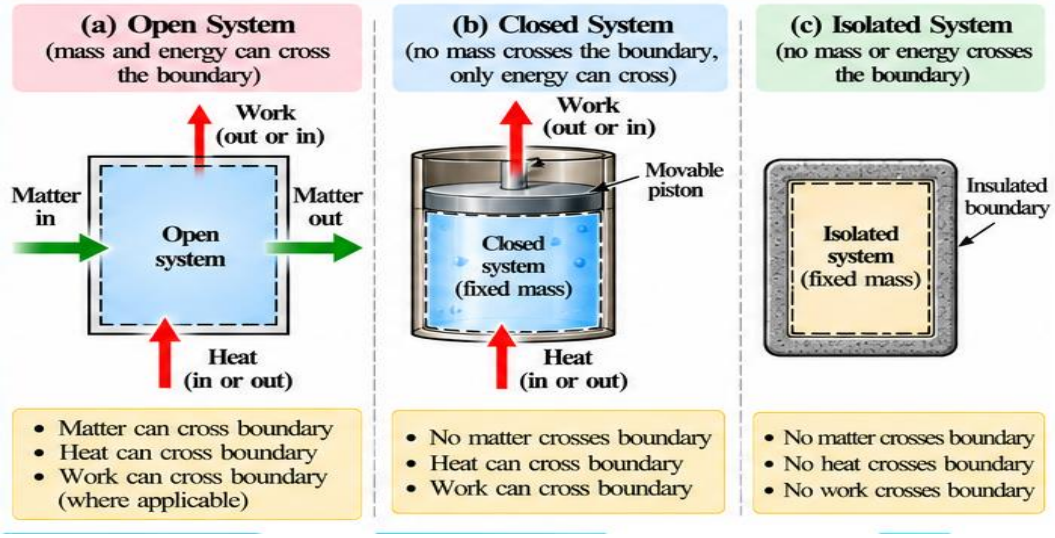
A perfectly insulated, rigid and sealed container is an idealised example.

Comparison of Thermodynamic Systems

Property	Open System	Closed System	Isolated System
Exchange of matter	Yes	No	No
Exchange of energy	Yes	Yes	No
Mass of system	May change	Constant	Constant
Example	Steam turbine	Sealed gas cylinder	Ideal insulated, rigid and sealed container

Exam Tip: A closed system is not necessarily thermally insulated. A sealed gas cylinder can receive heat from its surroundings even though matter cannot enter or leave it.

Figure 11.2: Types of Thermodynamic Systems



1.5 Thermodynamic State and State Variables

1.5.1 Thermodynamic State

The **thermodynamic state** of a system is its condition as specified by an appropriate set of macroscopic properties.

For a fixed amount of gas in equilibrium, the state can commonly be described using:

- Pressure, P
- Volume, V
- Temperature, T

These quantities are called **state variables**.

1.5.2 Pressure

Pressure is the normal force acting per unit area: $P = F/A$

Where:

- P = pressure
- F = normal force
- A = area

SI unit: pascal (Pa). 1 Pa = 1 N/m^2

For a gas, pressure results from molecular collisions with the container walls.

1.5.3 Volume

Volume is the space occupied by a system.
For a gas enclosed in a cylinder, the volume depends on the cylinder's cross-sectional area and the position of the movable piston.
For a cylinder of cross-sectional area A and gas-column length L: V = AL
SI unit: m^3.

1.5.4 Temperature

Temperature determines the direction of spontaneous heat transfer between systems in thermal contact.
Heat flows spontaneously from a system at a higher temperature to one at a lower temperature, provided no other effect reverses this transfer.
For an ideal gas, the absolute temperature is also related to the average translational kinetic energy of its molecules.
SI unit: kelvin (K).

1.5.5 Equation of State

An **equation of state** is a mathematical relationship connecting the thermodynamic state variables of a system.
For an ideal gas:

$$\boldsymbol{PV = nRT}$$

Where:

- P = absolute pressure
- V = volume
- n = number of moles
- R = universal gas constant
- T = absolute temperature

The equation of state connects pressure, volume and temperature for a fixed quantity of ideal gas.

Important Concept

For a fixed amount of ideal gas:

- At constant temperature:

$$\boldsymbol{PV = Constant}$$

- At constant pressure:

$$\boldsymbol{\frac{V}{T} = Constant}$$

- At constant volume:

$$\boldsymbol{\frac{P}{T} = Constant}$$

These relationships are valid when the gas behaves ideally and temperature is measured in kelvin.

1.6 Thermodynamic Equilibrium

A system is in **thermodynamic equilibrium** when its macroscopic properties do not change with time and it is simultaneously in thermal, mechanical and chemical equilibrium, with no relevant net driving force for change.

For the elementary gas systems studied here, the following forms of equilibrium are particularly important.

1.6.1 Thermal Equilibrium

A system is in thermal equilibrium when there is no net heat transfer between its parts or between it and another system in thermal contact.
For two systems A and B in thermal equilibrium: $T_A = T_B$
Their temperatures are equal.

1.6.2 Mechanical Equilibrium

A system is in mechanical equilibrium when there is no unbalanced mechanical force causing macroscopic motion or deformation.
For a gas in a cylinder with a frictionless movable piston, mechanical equilibrium requires the gas pressure to balance the effective external pressure, including the effects of the piston and any applied load.
In the simplest case: Pgas = Pexternal
This equality assumes that the relevant forces have been accounted for and that the piston is in mechanical equilibrium.

1.6.3 Chemical Equilibrium

Chemical equilibrium is established when there is no net progress of a chemical reaction or chemical transformation under the specified conditions.
In a system involving chemical reactions, the forward and reverse reaction rates are equal at chemical equilibrium.

1.6.4 Thermodynamic Equilibrium

A system is in thermodynamic equilibrium when it satisfies all the relevant equilibrium conditions simultaneously.
Example: A sealed gas in a rigid container may reach thermodynamic equilibrium after sufficient time if its temperature, pressure and composition become uniform and no macroscopic changes continue.

1.7 Zeroth Law of Thermodynamics

The **Zeroth Law of Thermodynamics** establishes the transitive nature of thermal equilibrium and provides the basis for temperature measurement.

Statement

If two systems A and B are separately in thermal equilibrium with a third system C, then A and B are in thermal equilibrium with each other.
If: $T_A = T_C$ and TB = T_C then: $\mathbf{T_A = T_B}$
This law allows temperature to be measured using a thermometer.

1.7.1 Explanation

Consider three systems:

- System A: an object whose temperature is to be measured.
- System B: another object.
- System C: a thermometer.

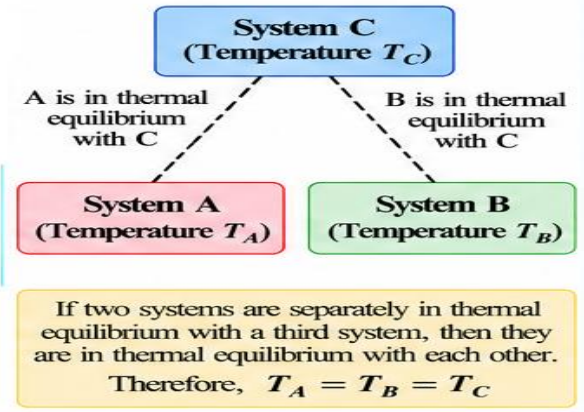
Suppose the thermometer reaches thermal equilibrium with A and then with B under the appropriate measurement conditions.
If the thermometer indicates the same temperature for both objects, the Zeroth Law establishes that A and B are in thermal equilibrium with each other.

1.7.2 Applications

The Zeroth Law is used in:

1. Designing and calibrating thermometers.
2. Measuring body temperature.
3. Measuring the temperature of liquids and gases.
4. Establishing temperature scales.
5. Determining whether two systems have the same temperature.

Figure 11.3: Zeroth Law of Thermodynamics



Exam Tip: The Zeroth Law establishes the concept of temperature and thermal equilibrium. It does not state that heat and temperature are the same physical quantity.

1.8 Heat, Work and Internal Energy

Heat, work and internal energy are closely related but represent different physical concepts.

1.8.1 Heat

Heat is energy transferred between a system and its surroundings because of a temperature difference.

Heat is not a substance stored inside a body. A system possesses internal energy; heat describes energy transfer due to a temperature difference.

Symbol: Q

SI unit: joule (J).

Using the common thermodynamic sign convention:

- Q > 0: Heat is supplied to the system.
- Q < 0: Heat is released by the system.

1.8.2 Work

Work is energy transferred when a force or other generalised driving action produces a displacement or change in the system's external constraints.

In elementary gas thermodynamics, work is commonly associated with expansion or compression against an external pressure.

Symbol: W

SI unit: joule (J).

For the sign convention used in these notes:

- W > 0: Work is done by the system on its surroundings.

- W < 0: Work is done on the system by its surroundings.

1.8.3 Internal Energy

Internal energy is the total microscopic energy associated with the constituents of a system.
It includes contributions from molecular motion and molecular interactions.
For a simple ideal gas, intermolecular potential energy is neglected, so its internal energy depends only on temperature.
For a fixed amount of ideal gas: U = U(T)
Therefore, if the temperature of an ideal gas does not change, its internal energy does not change.
For a monatomic ideal gas:

$$\boldsymbol{U = \frac{3}{2}nRT}$$

This expression applies to a classical monatomic ideal gas whose translational degrees of freedom are active."

1.8.4 Comparison of Heat, Work and Internal Energy

Property	Heat	Work	Internal Energy
Meaning	Energy transfer due to temperature difference	Energy transfer through work interactions	Microscopic energy possessed by the system
Symbol	Q	W	U
SI unit	J	J	J
State function?	No	No	Yes
Depends on the path?	Yes	Yes	No, for a specified initial and final state
Sign convention used here	Positive when supplied to system	Positive when done by system	Change may be positive or negative

Important distinction: Heat and work are path-dependent energy transfers. Internal energy is a state function.
The change in internal energy between two equilibrium states depends only on those states, not on the path taken between them.

1.9 Thermodynamic Processes

A **thermodynamic process** is a change in the state of a thermodynamic system.
During a process, one or more state variables—pressure, volume and temperature—may change.
The most important processes for the study of thermodynamics are described below.

1.9.1 Isothermal Process

An **isothermal process** takes place at constant temperature.
T = constant
For a fixed amount of ideal gas:
PV = constant
Therefore: $P_1V_1 = P_2V_2$
During an isothermal process involving an ideal gas, the internal energy change is zero because the temperature remains constant.

$$\Delta U = 0$$

1.9.2 Adiabatic Process

An **adiabatic process** is a process in which no heat is transferred between the system and its surroundings.

$$Q = 0$$

The temperature may change during an adiabatic process.
For a reversible adiabatic process of a fixed amount of ideal gas:

$$\boldsymbol{PV^{\gamma} = Constant}$$

Where:

$$\boldsymbol{\gamma = \frac{C_P}{C_V}}$$

Here, C_P and C_V are the molar heat capacities at constant pressure and constant volume, respectively.

1.9.3 Isobaric Process

An **isobaric process** takes place at constant pressure.

$$P = \text{constant}$$

For a fixed amount of ideal gas:

$$V/T = \text{constant}$$

Therefore:

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

Temperature must be measured in kelvin.

1.9.4 Isochoric Process

An **isochoric process** takes place at constant volume.

$$V = \text{constant}$$

For a fixed amount of ideal gas:

$$P/T = \text{constant}$$

Therefore:

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

Because the volume does not change, the gas does no pressure–volume work.

$$W = 0$$

1.9.5 Cyclic Process

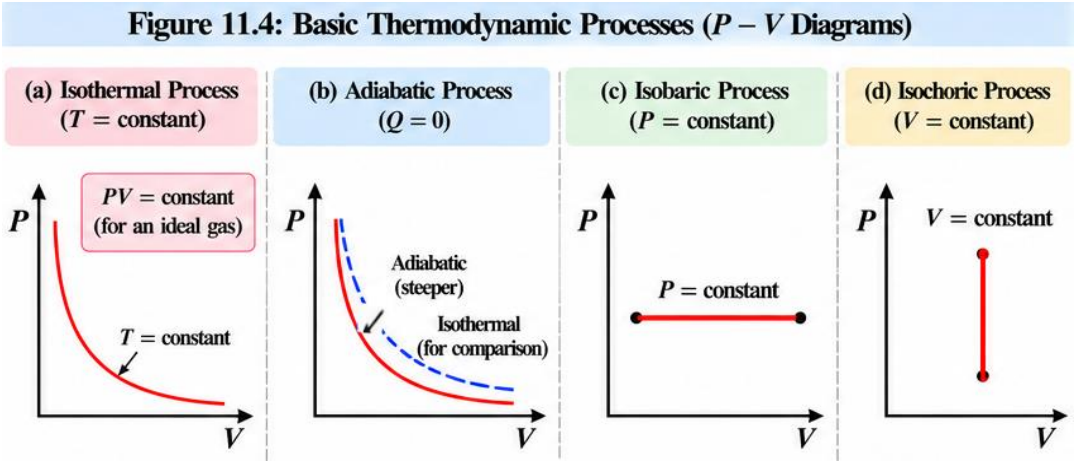
A **cyclic process** is a sequence of thermodynamic processes after which the system returns to its initial state.
For a complete cycle:

$$\boldsymbol{\Delta U_{cycle} = 0}$$

And,

$$\boldsymbol{Q_{net} = W_{net}}$$

The net heat supplied over the cycle equals the net work done by the system, using the sign convention adopted in these notes.
Note: The first law of thermodynamics, which establishes this energy relationship, will be studied in Part 2.



1.10 Work Done by a Gas

Work done during a thermodynamic process depends on the change in volume and the pressure opposing that change.

Consider a gas enclosed in a cylinder fitted with a movable piston.

Let:

- P = pressure of the gas.
- A = cross-sectional area of the piston.
- dx = small displacement of the piston.
- dV = small change in the volume of the gas.

Assume that the gas expands quasi-statically and that its pressure is well-defined throughout the process.

1.10.1 Derivation of the Expression for Work Done

The force exerted by the gas on the piston is:

$$F = PA$$

If the piston moves through a small distance dx, the small work done by the gas is:

$$dW = F\,dx$$

Substituting F = PA:

$$dW = PA\,dx$$

The corresponding change in volume is:

$$dV = A\,dx$$

Therefore:

$$\mathbf{dW = P\,dV}$$

Integrating between the initial volume V_1 and final volume V_2 gives:

$$\mathbf{W = \int P\,dV}$$

This is the general expression for pressure–volume work for a quasi-static process, with work taken as positive during expansion.

The pressure P may vary with volume, so the integral must be evaluated using the actual pressure–volume relationship.

Case 1: Expansion

When $V_2 > V_1$:

$$W > 0$$

The gas does positive work on its surroundings.

Case 2: Compression

When $V_2 < V_1$:

$$W < 0$$

The work done by the gas is negative; equivalently, work is done on the gas.

Case 3: Constant-Volume Process

When $V_1 = V_2$:

$$W = 0$$

No pressure–volume work is done because the volume does not change.

Important: A gas may exchange heat even when its volume remains constant. Zero pressure–volume work does not necessarily mean zero heat transfer.

1.11 Work Done at Constant Pressure

For an isobaric process, pressure remains constant.

Starting from: $W = \int P\, dV$

Since P is constant:

$$W = P \int dV$$

Therefore:

$$\mathbf{W = P\,(V_2 - V_1)}$$

Or

$$\mathbf{W = P\Delta V}$$

Where: $\Delta V = V_2 - V_1$

During Expansion

If $V_2 > V_1$: $W = P(V_2 - V_1) > 0$

During Compression

If $V_2 < V_1$: $W = P(V_2 - V_1) < 0$

Solved Example 1: Work Done During Expansion

Question: A gas expands at a constant pressure of 2×10^5 Pa from a volume of 0.01 m^3 to 0.03 m^3. Calculate the work done by the gas.

Given: $P = 2 \times 10^5$ Pa, $V_1 = 0.01\ m^3$, $V_2 = 0.03\ m^3$

Formula:

$$W = P(V_2 - V_1)$$

Calculation:

$$W = 2 \times 10^5 \times (0.03 - 0.01)$$
$$W = 2 \times 10^5 \times 0.02$$

Answer: $W = 4 \times 10^3$ J = 4000 J

The work done by the gas is positive because the gas expands.

1.12 Work Done in an Isothermal Process

For a fixed amount of ideal gas undergoing an isothermal process:

$$PV = nRT$$

Since T is constant:

$$P = nRT/V$$

The work done by the gas is:

$$W = \int P\, dV$$

Substituting $P = nRT/V$:

$$W = \int (nRT/V)\, dV$$

Since nRT is constant:

$$W = nRT \int (1/V)\, dV$$

Therefore, between volumes V_1 and V_2:

$$\mathbf{W = nRT \ln(V_2/V_1)}$$

Using common logarithms, the equivalent expression is:

$$W = 2.303\ nRT \log(V_2/V_1)$$

During Isothermal Expansion

During isothermal expansion, If $V_2 > V_1$, then $\ln (V_2/V_1) > 0$

Therefore: $W > 0$

During Isothermal Compression

During isothermal compression, If $V_2 < V_1$, then $\ln (V_2/V_1) < 0$

Therefore: $W < 0$

Internal Energy Change

For an ideal gas, internal energy depends only on temperature.

Since the temperature remains constant: $\mathbf{\Delta U = 0}$

Thus, during an isothermal process involving an ideal gas, the internal energy does not change.

The relationship between heat transfer and work will be derived using the first law in Part 2.

Solved Example 2: Isothermal Expansion

Question: One mole of an ideal gas expands isothermally and reversibly at 300 K from volume V_1 to volume $2V_1$. Calculate the work done. Take $R = 8.314\ J\ mol^{-1}\ K^{-1}$.

Given: $n = 1$ mol, $T = 300$ K, $V_2/V_1 = 2$, $R = 8.314\ J\ mol^{-1}\ K^{-1}$

Formula:

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

Calculation:

$$W = 1 \times 8.314 \times 300 \times \ln 2$$

Using $\ln 2 \approx 0.693$:

$$W \approx 8.314 \times 300 \times 0.693$$

Answer: $W \approx 1729$ J

The work done is positive because the gas expands.

1.13 Work Done and the P–V Diagram

A pressure–volume (P–V) diagram represents the variation of pressure with volume during a thermodynamic process.

Pressure is plotted on the vertical axis and volume on the horizontal axis.

For a quasi-static process:

$$\mathbf{W = \int P\, dV}$$

The work done by the gas is represented by the signed area under the process curve between the initial and final volumes.

1.13.1 Expansion

During expansion, the volume increases.

The area under the P–V curve represents positive work done by the gas.

1.13.2 Compression

During compression, the volume decreases.

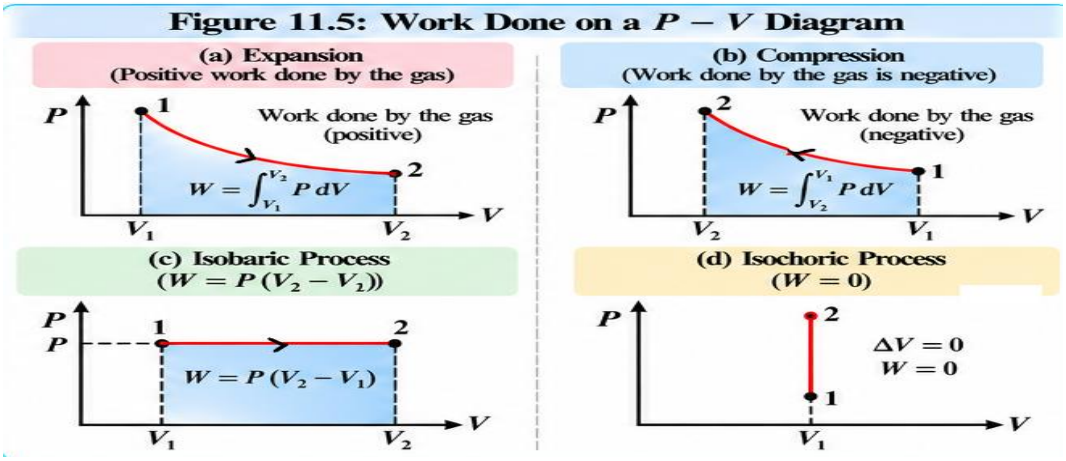
The work done by the gas is negative under the convention used here.

1.13.3 Constant-Pressure Process

For a constant-pressure process, the P–V curve is horizontal.
The work done equals the area of the rectangle between V_1 and V_2:
$W = P (V_2 - V_1)$

1.13.4 Constant-Volume Process

For a constant-volume process, the P–V curve is vertical.
Since $\Delta V = 0$: $W = 0$



1.14 Thermodynamic Path and State Functions

1.14.1 State Functions

A **state function** is a property whose value depends only on the thermodynamic state of the system, not on the process used to reach that state.
Examples include:

- Pressure P
- Volume V
- Temperature T
- Internal energy U

For internal energy: $\Delta U = U_2 - U_1$
The internal energy change depends only on the initial and final states, whereas heat transferred and work done depend on the path followed..

1.14.2 Path Functions

A path function depends on the process followed between the initial and final states.
Heat and work are path functions.
For example, a gas may expand between the same two volumes through different paths, performing different amounts of work because the pressure varies differently along each path. Therefore, the work done is not determined by the initial and final volumes alone.

1.14.3 Comparison

Feature	State Function	Path Function
Depends on	State of the system	Process followed
Examples	P, V, T, U	Heat Q, work W
Change for a specified initial and final state	Fixed	May differ for different paths
Property of the system at a state	Yes	No; represents energy transfer

NEET/JEE Insight: Internal energy change is independent of the path, but the heat transferred and work done can depend on the path.

Numerical Practice

1. A gas expands at a constant pressure of 1.5×10^5 Pa from 0.02 m^3 to 0.05 m^3. Calculate the work done by the gas.
2. One mole of an ideal gas expands reversibly and isothermally at 300 K to twice its initial volume. Calculate the work done.
3. A gas is compressed at a constant pressure of 2×10^5 Pa from 0.04 m^3 to 0.01 m^3. Calculate the work done by the gas.
4. A gas undergoes an isochoric process while its pressure increases. Calculate the pressure–volume work done by the gas.
5. A gas follows two different quasi-static paths between the same initial and final states. Explain why the work done may be different even though the change in internal energy is the same.

1.15 NEET/JEE Conceptual Insights

Concept 1: Work Done Depends on the Path

Two processes may connect the same initial and final states but produce different amounts of work.
This happens because: $W = \int P\, dV$
The pressure may vary differently along each path.

Concept 2: Isothermal Does Not Mean No Heat Transfer

For an ideal gas undergoing an isothermal process: $\Delta U = 0$
However, heat transfer and work may both be non-zero.

Concept 3: Adiabatic Does Not Mean Constant Temperature

For an adiabatic process: $Q = 0$
The temperature may change because work can be done by the gas or on the gas.

Concept 4: Equal Temperatures and Thermal Equilibrium

When two systems are in thermal equilibrium, they have equal temperatures.
However, equal temperatures alone do not establish complete thermodynamic equilibrium if other relevant driving forces remain.

Concept 5: Area Under a P–V Curve

For a quasi-static process, the signed area under the P–V curve gives the work done by the gas.
The area enclosed by a complete cycle on a P–V diagram represents the net work done during that cycle, with its sign determined by the direction of traversal.

PART 2: FIRST LAW OF THERMODYNAMICS, INTERNAL ENERGY, HEAT CAPACITY AND SPECIFIC HEAT

2.1 Learning Objectives

After studying this part, students should be able to:

1. State and explain the First Law of Thermodynamics.
2. Apply the law to different thermodynamic processes.
3. Calculate changes in internal energy, heat supplied and work done.
4. Understand the relationship between heat and work in an ideal gas.
5. Distinguish between molar heat capacities at constant volume and constant pressure.
6. Derive Mayer's relation for an ideal gas.
7. Understand the work done in isobaric, isochoric, isothermal and adiabatic processes.
8. Solve numerical problems based on the First Law.
9. Understand the significance of heat capacity in thermodynamic systems.
10. Apply these concepts to Board, NEET and JEE-level questions.

2.2 The First Law of Thermodynamics

The First Law of Thermodynamics is an expression of the **law of conservation of energy applied to thermodynamic systems**.

It states that energy cannot be created or destroyed; it can only be transferred between a system and its surroundings or converted from one form into another.

When heat is supplied to a thermodynamic system, the supplied energy may:

- Increase the internal energy of the system.
- Be used by the system to perform work on its surroundings.
- Be divided between these two effects.

2.2.1 Mathematical Statement

Using the sign convention adopted in these notes:

- Q = heat supplied to the system.
- W = work done by the system.
- ΔU = change in internal energy.

The First Law is: $$\mathbf{Q = \Delta U + W}$$

Equivalently:

$$\mathbf{\Delta U = Q - W}$$

This means that the change in internal energy equals the heat supplied to the system minus the work done by the system.

For an infinitesimal process:

$$\boldsymbol{\delta Q = dU + \delta W}$$

For pressure–volume work in a quasi-static process:

$$\boldsymbol{\delta Q = dU + P dV}$$

Here, P dV represents the infinitesimal work done by the system.

Important Sign Convention

Quantity	Positive	Negative
Heat Q	Heat enters the system	Heat leaves the system
Work W	Work is done by the system	Work is done on the system
Change in internal energy ΔU	Internal energy increases	Internal energy decreases

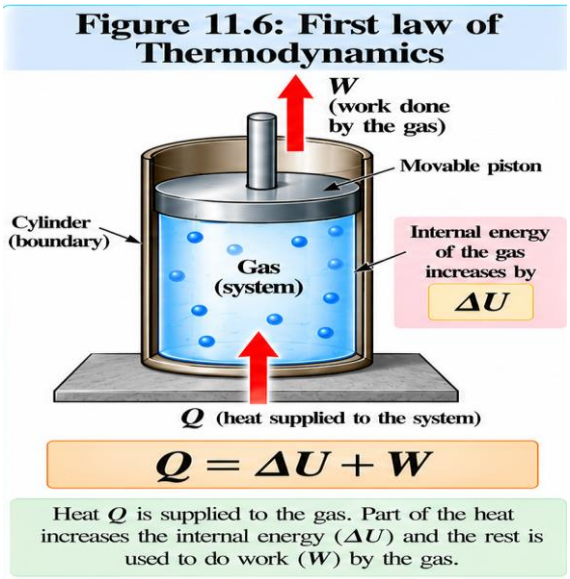
Exam Tip: Always identify the sign of Q, W and ΔU before substituting values into the First Law.

2.3 Physical Interpretation of the First Law

Consider a gas enclosed in a cylinder fitted with a movable piston.
When heat is supplied to the gas, the gas may expand and push the piston outward.
The supplied heat is divided into two parts:

1. Energy used to increase the internal energy of the gas.
2. Energy transferred to the surroundings as work done by the gas.

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



2.4 Applications of the First Law to Thermodynamic Processes

The First Law can be applied to different thermodynamic processes by considering which quantities remain constant or become zero.

2.4.1 Isochoric Process

An isochoric process occurs at constant volume.

$$V = \text{constant}$$

Since the volume does not change:

$$\Delta V = 0$$

The pressure–volume work is:

$$W = \int P\, dV$$

Therefore:

$$\mathbf{W = 0}$$

Using the First Law:

$$Q = \Delta U + W$$

Hence:

$$\mathbf{Q = \Delta U}$$

Therefore, all the heat supplied to the system increases its internal energy when no other form of work is involved.

For an Ideal Gas

For n moles of an ideal gas: $\Delta U = nC_v\Delta T$

Therefore:

$$\mathbf{Q = nC_v\Delta T}$$

Here, C_v is the molar heat capacity at constant volume.

Important Conclusion

In an isochoric process:

- Volume remains constant.
- Pressure and temperature may change.
- Pressure–volume work is zero.
- Heat supplied equals the change in internal energy.

Solved Example 1

Question: A gas receives 600 J of heat in a rigid container. Calculate the change in its internal energy.

Given: Q = +600 J, W = 0

Using the First Law:

$$\Delta U = Q - W = 600 - 0$$

Answer: $\Delta U = +600$ J

The internal energy increases by 600 J.

2.4.2 Isobaric Process

An isobaric process occurs at constant pressure.

$$P = \text{constant}$$

The work done by the gas is:

$$W = P(V_2 - V_1)$$

Therefore:

$$\mathbf{W = P\Delta V}$$

Using the First Law:

$$Q = \Delta U + W$$

Hence:

$$\mathbf{Q = \Delta U + P\Delta V}$$

For n moles of an ideal gas:

$$\Delta U = nC_v\Delta T$$

From the ideal-gas equation:

$$PV = nRT$$

At constant pressure:

$$P\Delta V = nR\Delta T$$

Therefore:

$$\mathbf{Q = nC_v\Delta T + nR\Delta T}$$

Or

$$\mathbf{Q = n(C_v + R)\Delta T}$$

As derived later in this Part: $C_P = C_v + R$

Therefore: $\mathbf{Q = nC_P\,\Delta T}$

Important Conclusion

In an isobaric process:

- Pressure remains constant.

- Volume changes when the temperature changes.
- Work is generally non-zero.
- Heat supplied is divided between increasing internal energy and doing work.

Solved Example 2

Question: A gas expands at a constant pressure of 1.5×10^5 Pa from 0.02 m³ to 0.04 m³. Calculate the work done by the gas.

Given: $P = 1.5 \times 10^5$ Pa, $V_1 = 0.02$ m³, $V_2 = 0.04$ m³

Formula:

$$W = P(V_2 - V_1)$$

Substituting:

$$W = 1.5 \times 10^5 \times (0.04 - 0.02) = 1.5 \times 10^5 \times 0.02$$

Answer: W = 3000 J

The work done by the gas is positive because the gas expands.

2.4.3 Isothermal Process

An isothermal process occurs at constant temperature.

$$T = \text{constant}$$

For an ideal gas, internal energy depends only on temperature.

Therefore:

$$\mathbf{\Delta U = 0}$$

Using the First Law:

$$Q = \Delta U + W$$

Hence:

$$\mathbf{Q = W}$$

Thus, during an isothermal process involving an ideal gas, the heat supplied to the gas equals the work done by the gas.

For a reversible isothermal process:

$$\mathbf{W = nRT \ln (V_2/V_1)}$$

Therefore:

$$\mathbf{Q = nRT \ln (V_2/V_1)}$$

During Expansion

When $V_2 > V_1$:

- $W > 0$
- $Q > 0$
- $\Delta U = 0$

The gas absorbs heat and performs an equal amount of work.

During Compression

When $V_2 < V_1$:

- $W < 0$
- $Q < 0$
- $\Delta U = 0$

The surroundings perform work on the gas, and an equal amount of energy leaves the gas as heat to maintain constant temperature.

Solved Example 3

Question: One mole of an ideal gas expands reversibly and isothermally at 300 K to twice its initial volume. Calculate the heat absorbed. Take $R = 8.314$ J mol^{-1} K^{-1}.

Given: n = 1 mol, T = 300 K, $V_2/V_1 = 2$
For a reversible isothermal process:

$$Q = nRT \ln(V_2/V_1)$$
$$Q = 1 \times 8.314 \times 300 \times \ln 2$$

Using ln 2 ≈ 0.693:

$$Q \approx 1729 \text{ J}$$

Answer: $Q \approx +1.73 \times 10^3$ J
The gas absorbs approximately 1.73 kJ of heat.

2.4.4 Adiabatic Process

An adiabatic process occurs without heat transfer between the system and its surroundings.

$$\mathbf{Q = 0}$$

Using the First Law:

$$Q = \Delta U + W$$

Therefore:

$$0 = \Delta U + W$$

Hence:

$$\mathbf{\Delta U = -W}$$

During Adiabatic Expansion

The gas performs positive work: W > 0
Therefore: ΔU < 0
For an ideal gas, its internal energy and temperature decrease.

During Adiabatic Compression

Work is done on the gas:

$$W < 0$$

Therefore:

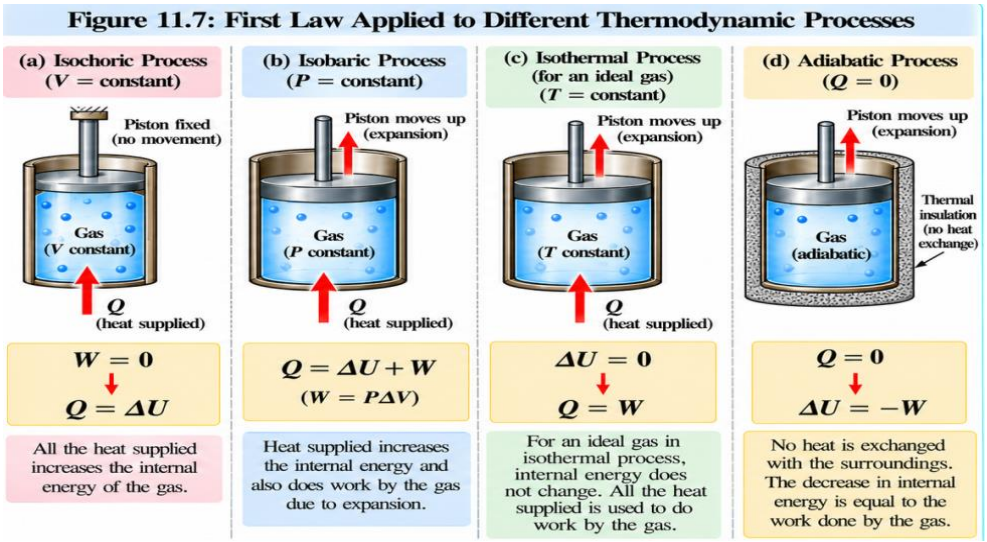
$$\Delta U > 0$$

For an ideal gas, its internal energy and temperature increase.
For a reversible adiabatic process involving a fixed amount of ideal gas:

$$\mathbf{PV^{\gamma} = constant}$$

Where: $\gamma = C_P / C_v$

Figure 11.7: First Law Applied to Different Thermodynamic Processes



Solved Example 4

Question: An ideal gas performs 500 J of work during an adiabatic expansion. Calculate the change in its internal energy.
Given: Q = 0, W = +500 J
Using: $\Delta U = Q - W = 0 - 500$
Answer: $\Delta U = -500$ J
The internal energy decreases by 500 J.

2.5 Internal Energy of an Ideal Gas

Internal energy is the microscopic energy associated with the motion and interactions of the particles of a system.
For an ideal gas, intermolecular potential energy is neglected.
Therefore, the internal energy of an ideal gas depends only on its absolute temperature.

2.5.1 Internal Energy of a Monatomic Ideal Gas

For a monatomic ideal gas, the molecules possess three translational degrees of freedom.
According to the law of equipartition of energy, each quadratic degree of freedom contributes an average energy of: $(1/2)k_\beta T$ per molecule
Where, k_β is the Boltzmann constant.
The average translational kinetic energy per molecule is:

$$E_{avg} = (3/2)\, k_\beta T$$

For N molecules:

$$U = (3/2)\, Nk_\beta T$$

Since: $Nk_\beta = nR$
Therefore: **$U = (3/2)\, nRT$**
This result applies to a classical monatomic ideal gas.

2.5.2 Change in Internal Energy

For a fixed amount of monatomic ideal gas: $U = (3/2)\, nRT$
Therefore: **$\Delta U = (3/2)\, nR\Delta T$**
The change in internal energy depends only on the temperature change.
For a general ideal gas with constant molar heat capacity over the temperature interval:

$$\mathbf{\Delta U = nC_v\Delta T}$$

Important Conclusions

1. Internal energy increases when the temperature of an ideal gas increases.
2. Internal energy decreases when its temperature decreases.
3. If an ideal gas returns to its initial temperature, its internal energy returns to its initial value.
4. For an ideal gas, an isothermal process has $\Delta U = 0$.
5. Internal energy change does not depend on the path followed between two specified equilibrium states.

2.6 Heat Capacity and Specific Heat Capacity

2.6.1 Heat Capacity

The heat capacity of a body is the amount of heat required to raise its temperature by one kelvin, under the specified conditions.
For a small temperature change: **$C = dQ/dT$**

Where, C is the heat capacity.
For a finite temperature interval with constant heat capacity: $Q = C\Delta T$
SI unit: $J\ K^{-1}$
Heat capacity depends on the amount and nature of the material and, for a gas, on the thermodynamic conditions under which heat is supplied.

2.6.2 Specific Heat Capacity

Specific heat capacity is the amount of heat required to raise the temperature of unit mass of a substance by one kelvin, under specified conditions.
For a small temperature change:

$$\boldsymbol{s = \frac{1}{m}\left(\frac{dQ}{dT}\right)}$$

For a finite temperature interval with constant specific heat capacity:

$$\mathbf{Q = ms\Delta T}$$

Where:

- Q = heat supplied.
- m = mass.
- s = specific heat capacity.
- ΔT = change in temperature.

SI unit: $J\ kg^{-1}\ K^{-1}$

Relation between Heat Capacity and Specific Heat

For a body of mass m:

$$\mathbf{C = ms}$$

This relation applies when the specific heat capacity is constant over the temperature interval.

2.6.3 Molar Heat Capacity

Molar heat capacity is the amount of heat required to raise the temperature of one mole of a substance by one kelvin under specified conditions.
For a small temperature change:

$$\boldsymbol{C_m = \frac{1}{n}\left(\frac{dQ}{dT}\right)}$$

For constant molar heat capacity over a finite temperature interval:

$$\boldsymbol{Q = nC_m\Delta T}$$

SI unit: $J\ mol^{-1}\ K^{-1}$

Comparison

Quantity	Definition	SI Unit
Heat capacity, C	Heat needed per kelvin for the entire body	$J\ K^{-1}$
Specific heat capacity, s	Heat needed per kelvin per unit mass	$J\ kg^{-1}\ K^{-1}$
Molar heat capacity, C_m	Heat needed per kelvin per mole	$J\ mol^{-1}\ K^{-1}$

Important: For gases, the heat capacity depends on the process. The two important molar heat capacities are C_v and C_P.

2.7 Molar Heat Capacity at Constant Volume (C_v)

The molar heat capacity at constant volume is the amount of heat required to raise the temperature of one mole of a gas by one kelvin while its volume remains constant.

At constant volume:

$$dV = 0$$

Therefore:

$$dW = P\,dV = 0$$

Using the First Law:

$$dQ = dU + dW$$

Hence:

$$dQ_v = dU$$

For n moles of an ideal gas:

$$\mathbf{dQ_v = nC_v dT}$$

Therefore:

$$\mathbf{dU = nC_v dT}$$

For constant C_v over a finite temperature interval: $\mathbf{\Delta U = nC_v \Delta T}$

This equation expresses the change in internal energy of an ideal gas in terms of its molar heat capacity at constant volume.

Physical Significance

At constant volume, the gas does no pressure–volume work.

Therefore, the heat supplied increases the internal energy of the gas.

For a fixed amount of ideal gas, this increases its temperature.

2.8 Molar Heat Capacity at Constant Pressure (C_P)

The molar heat capacity at constant pressure is the amount of heat required to raise the temperature of one mole of a gas by one kelvin while its pressure remains constant.

For n moles of an ideal gas:

$$\mathbf{dQ_P = nCdT}$$

Using the First Law:

$$dQ_P = dU + P\,dV$$

For an ideal gas:

$$dU = nC_v dT$$

At constant pressure, differentiating the ideal-gas equation gives:

$$P\,dV = nR\,dT$$

Substituting:

$$nC_P\,dT = nC_v dT + nR\,dT$$

Dividing by n dT:

$$\mathbf{C_P = C_v + R}$$

This is Mayer's relation for an ideal gas.

Physical Significance

At constant pressure, some of the heat supplied increases the internal energy, while the rest is used by the gas to perform expansion work.

Consequently, for an ideal gas: $\mathbf{C_P > C_v}$

2.9 Derivation of Mayer's Relation

Mayer's relation connects the molar heat capacities of an ideal gas at constant pressure and constant volume.

For one mole of an ideal gas, the First Law is:

$$dQ = dU + P\,dV$$

At Constant Volume

Since $dV = 0$:

$$dQ_v = dU$$

By definition:

$$dQ_v = C_v dT$$

Therefore:

$$dU = C_v dT$$

At Constant Pressure

At constant pressure:

$$dQ_P = dU + P\,dV$$

By definition:

$$dQ_P = C_P\,dT$$

Substituting $dU = C_v dT$:

$$C_P\,dT = C_v dT + P\,dV$$

For one mole of an ideal gas:

$$PV = RT$$

At constant pressure:

$$P\,dV = R\,dT$$

Therefore:

$$C_P\,dT = C_v dT + R\,dT$$

Dividing by dT:

$$\mathbf{C_P = C_v + R}$$

Hence:

$$\mathbf{C_P - C_v = R}$$

This is Mayer's relation.

Exam Tip: Mayer's relation applies to an ideal gas. The molar heat capacities must be used consistently with the universal gas constant R.

2.10 Heat Capacities of a Monatomic Ideal Gas

For a classical monatomic ideal gas:

$$U = (3/2)nRT$$

For a small temperature change:

$$dU = (3/2)nR\,dT$$

But:

$$dU = nC_v dT$$

Equating:

$$nC_v dT = (3/2)nR\,dT$$

Therefore:

$$\mathbf{C_v = (3/2)R}$$

Using Mayer's relation:

$$C_P = C_v + R$$
$$C_P = (3/2)R + R$$

Therefore:

$$\mathbf{C_P = (5/2)R}$$

The ratio of heat capacities is: $\gamma = C_P/C_v$

Substituting:

$$\gamma = [(5/2)R]/[(3/2)R]$$

Hence:

$$\boldsymbol{\gamma = 5/3 \approx 1.67}$$

These results apply to a classical monatomic ideal gas under the usual assumptions.

Important Values

Quantity	Formula
Molar heat capacity at constant volume	$C_v = (3/2)R$
Molar heat capacity at constant pressure	$C_p = (5/2)R$
Heat-capacity ratio	$\gamma = 5/3$
Internal energy	$U = (3/2)nRT$

2.11 Heat Capacities of a Diatomic Ideal Gas

At ordinary temperatures, a classical diatomic ideal gas is often approximated as having three translational and two rotational degrees of freedom, with vibrational modes neglected.

The total number of active quadratic degrees of freedom is then five.

According to the equipartition theorem:

$$U = (5/2)\ nRT$$

Therefore:

$$dU = (5/2)nR\ dT$$

Since:

$$dU = nC_v dT$$

We obtain:

$$\boldsymbol{C_v = (5/2)R}$$

Using Mayer's relation:

$$C_P = C_v + R$$

Therefore:

$$\boldsymbol{C_P = (7/2)R}$$

The heat-capacity ratio is:

$$\gamma = C_P/C_v$$

$$\gamma = [(7/2)R]/[(5/2)R]$$

Hence:

$$\boldsymbol{\gamma = 7/5 = 1.4}$$

Important Qualification

These values are approximate and apply when the two rotational modes are active but vibrational modes are neglected.

At higher temperatures, vibrational modes may contribute, changing the heat capacities and their ratio.

Comparison of Ideal Gases

Quantity	Monatomic Gas	Diatomic Gas at Ordinary Temperatures
C_v	(3/2)R	(5/2)R
C_P	(5/2)R	(7/2)R
$\gamma = C_P/C_v$	5/3	7/5

2.12 Solved Numerical Problems

Example 5: Change in Internal Energy

Question: Two moles of an ideal gas have a molar heat capacity at constant volume of 12.5 J mol^{-1} K^{-1}. Calculate the change in internal energy when the temperature increases by 20 K.
Given: n = 2 mol, C_v = 12.5 J mol^{-1} K^{-1}, ΔT = 20 K
Formula:

$$\Delta U = nC_v\Delta T$$

Substituting:

$$\Delta U = 2 \times 12.5 \times 20$$

Answer: ΔU = 500 J
The internal energy increases by 500 J.

Example 6: Heat Supplied at Constant Volume

Question: One mole of an ideal gas is heated at constant volume from 300 K to 350 K. If C_v = 12.5 J mol^{-1} K^{-1}, calculate the heat supplied.
Given: n = 1 mol, C_v = 12.5 J mol^{-1} K^{-1}, $\Delta T = 350 - 300 = 50$ K
At constant volume:

$$Q = nC_v\Delta T = 1 \times 12.5 \times 50$$

Answer: Q = 625 J
Since the volume is constant, the work done is zero.
Therefore, the internal energy increases by 625 J.

Example 7: Heat Supplied at Constant Pressure

Question: One mole of an ideal gas is heated at constant pressure through 40 K. If C_p = 29 J mol^{-1} K^{-1}, calculate the heat supplied.
Given: n = 1 mol, C_P = 29 J mol^{-1} K^{-1}, ΔT = 40 K
Formula:

$$Q = nC_P\,\Delta T$$

$Q = 1 \times 29 \times 40$
Answer: Q = 1160 J
The heat supplied is 1160 J.

Example 8: Finding C_P from C_v

Question: The molar heat capacity at constant volume of an ideal gas is 20.8 J mol^{-1} K^{-1}. Calculate its molar heat capacity at constant pressure. Take R = 8.314 J mol^{-1} K^{-1}.
Using Mayer's relation:

$$C_P = C_v + R = 20.8 + 8.314$$

Answer: C_P = 29.114 J mol^{-1} K^{-1}

Example 9: Work Done During Isobaric Heating

Question: Two moles of an ideal gas are heated at constant pressure through 50 K. Calculate the work done by the gas. Take R = 8.314 J mol^{-1} K^{-1}.
At constant pressure:

$$W = P\Delta V$$

For an ideal gas:

$$P\Delta V = nR\Delta T$$

Therefore:

$$W = nR\Delta T = 2 \times 8.314 \times 50$$

Answer: W = 831.4 J

The work done is positive because the gas expands during heating at constant pressure.

Example 10: First Law of Thermodynamics

Question: A gas absorbs 1000 J of heat and performs 350 J of work. Calculate the change in internal energy.

Given: Q = +1000 J, W = +350 J

Using: $\Delta U = Q - W = 1000 - 350$

Answer: ΔU = +650 J

The internal energy increases by 650 J.

Numerical Practice

1. A gas absorbs 800 J of heat and performs 300 J of work. Find ΔU.
2. A gas releases 500 J of heat while 200 J of work is done on it. Calculate ΔU.
3. Two moles of an ideal gas are heated at constant volume through 30 K. If $C_v = 12.5$ J mol^{-1} K^{-1}, calculate the heat supplied.
4. One mole of an ideal gas is heated at constant pressure through 25 K. If $C_P = 29$ J mol^{-1} K^{-1}, calculate the heat supplied.
5. A gas performs 400 J of work during an adiabatic expansion. Find the change in internal energy.
6. For an ideal gas, $C_v = 21$ J mol^{-1} K^{-1}. Calculate C_P using $R = 8.314$ J mol^{-1} K^{-1}.

2.13 NEET/JEE Conceptual Insights

Concept 1: Heat Supplied Is Not Always Equal to the Change in Internal Energy

From the First Law: $Q = \Delta U + W$

If the gas performs work, some of the supplied heat is transferred to the surroundings as work.

Concept 2: An Adiabatic Process Can Change Temperature

For an adiabatic process: Q = 0

Therefore: $\Delta U = -W$

If the gas performs positive work, its internal energy decreases. For an ideal gas, its temperature decreases.

Concept 3: Isothermal Processes of an Ideal Gas

For an isothermal process: ΔU = 0

Therefore: Q = W

This equality applies to the signed heat transfer and signed work done by the gas.

Concept 4: Why C_p Is Greater Than C_v

At constant volume, the gas does no pressure–volume work.

At constant pressure, the gas generally expands when heated and performs work.

Therefore, more heat is needed to produce the same temperature rise at constant pressure than at constant volume.

Concept 5: Mayer's Relation

For an ideal gas: $C_P - C_v = R$

The difference between the molar heat capacities is equal to the universal gas constant.

PART 3: REVERSIBLE AND IRREVERSIBLE PROCESSES, ADIABATIC EQUATIONS AND HEAT ENGINES

3.1 Learning Objectives

After studying this part, students should be able to:

1. Explain reversible and irreversible thermodynamic processes.
2. Understand quasi-static processes and their significance.
3. Distinguish between isothermal and adiabatic processes.
4. Derive the equation for a reversible adiabatic process.
5. Apply the adiabatic equations to ideal-gas problems.
6. Compare isothermal and adiabatic P–V curves.
7. Understand the concept and working principle of a heat engine.
8. Define thermal efficiency and calculate it.
9. Understand the Kelvin temperature scale in heat-engine calculations.
10. Solve numerical problems relevant to CBSE Board, NEET and JEE.

3.2 Quasi-Static Thermodynamic Process

A **quasi-static process** is an idealised thermodynamic process that proceeds through a continuous sequence of states that are arbitrarily close to thermodynamic equilibrium.
The process is sufficiently slow for the system to remain approximately in equilibrium at each stage.
For example, consider a gas enclosed in a cylinder with a movable piston.
If the external pressure is reduced by an extremely small amount, the gas expands slightly. By making a sequence of such small changes, the gas can pass through a series of near-equilibrium states.

3.2.1 Characteristics

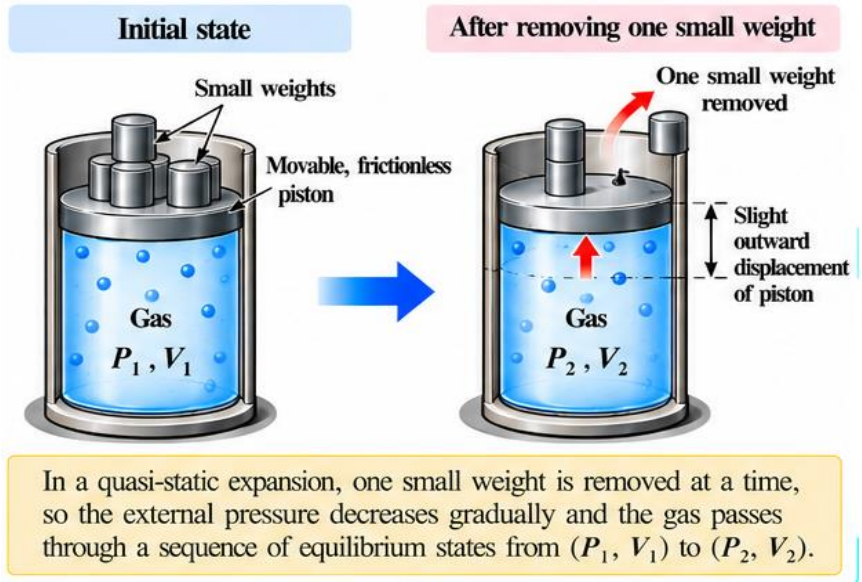
A quasi-static process:

- Proceeds through a sequence of near-equilibrium states.
- Allows pressure and temperature to be defined approximately throughout the system.
- Can be represented by a well-defined path on a P–V diagram.
- Is an idealisation used to analyse thermodynamic processes.

3.2.2 Quasi-Static Does Not Necessarily Mean Reversible

A quasi-static process is not automatically reversible.
For a process to be reversible, it must be possible to reverse it through infinitesimal changes and restore both the system and its surroundings to their original states without leaving any net change.
Friction, viscosity, turbulence or heat transfer across a finite temperature difference can make a process irreversible even when it proceeds slowly.
Exam Tip: Every reversible process is quasi-static in the usual classical thermodynamic treatment, but every quasi-static process is not necessarily reversible.

Figure 11.8: Quasi- Static Expansion of a Gas



In a quasi-static expansion, one small weight is removed at a time, so the external pressure decreases gradually and the gas passes through a sequence of equilibrium states from (P_1, V_1) to (P_2, V_2).

3.3 Reversible and Irreversible Processes

3.3.1 Reversible Process

A **reversible process** is an ideal thermodynamic process that can be reversed so that both the system and its surroundings return to their initial states without any net change elsewhere.
A reversible process requires ideal conditions, including the absence of dissipative effects such as friction and viscous dissipation.
For heat transfer to be reversible, the temperature difference driving the transfer must approach zero in the ideal limit.

Examples of Ideal Reversible Processes

- Reversible isothermal expansion or compression of an ideal gas.
- Reversible adiabatic expansion or compression of an ideal gas.
- A frictionless piston moving through a sequence of equilibrium states.

These examples are reversible only when the relevant ideal conditions are satisfied.

3.3.2 Irreversible Process

An **irreversible process** cannot be reversed in such a way that both the system and its surroundings return to their initial states without leaving any net change elsewhere.
Most real-world processes are irreversible.

Examples

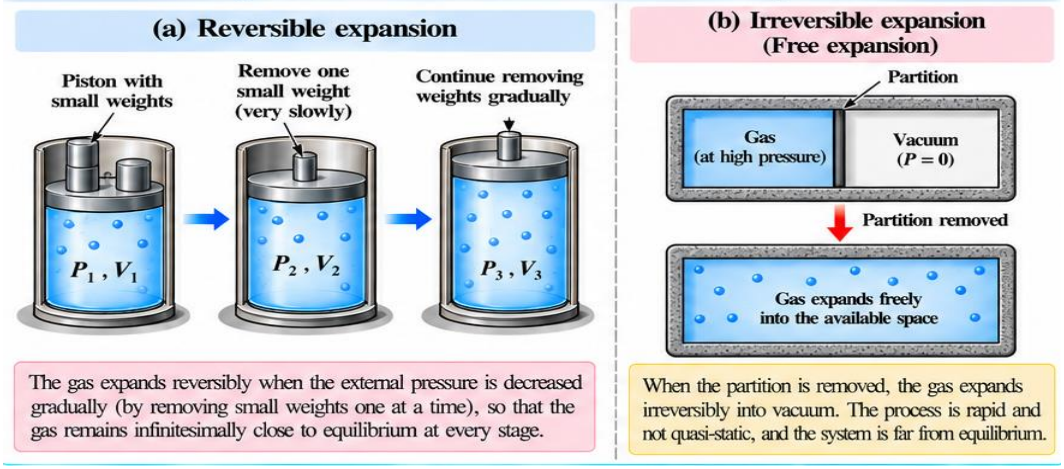
1. Free expansion of a gas into a vacuum.
2. Heat flowing spontaneously from a hot body to a cold body.
3. Gas expansion involving friction or turbulence.
4. Mixing of two different gases.
5. Rapid compression of a gas with significant dissipative effects.

3.3.3 Comparison

Feature	Reversible Process	Irreversible Process
Idealisation	Ideal limiting process	Common in real systems
Equilibrium states	Passes through equilibrium states in the standard treatment	May involve non-equilibrium states
Reversal	Can be reversed without net changes to system and surroundings	Cannot be reversed without net changes elsewhere
Dissipation	No dissipative effects in the ideal limit	Often involves friction, viscosity or other dissipation
Entropy generation	Zero for the ideal reversible process	Positive for a real irreversible process

Important: A reversible process is an ideal limit. Real processes can approach reversible behaviour but generally cannot achieve it perfectly.

Figure 11.9: Reversible and Irreversible Expansion



3.4 Work Done in Reversible and Irreversible Processes

For a quasi-static process involving pressure–volume work: $\mathbf{W = \int P\, dV}$

Here, P is the gas pressure along the path.

For a reversible process, the gas passes through equilibrium states, allowing the pressure to be specified throughout the process.

For an irreversible process, the gas may not have a uniform pressure during the process. In that case, work is calculated using the external pressure opposing the boundary motion: $\mathbf{W = \int P_{ext}\, dV}$

This expression assumes that pressure–volume boundary work is the relevant work mode.

3.4.1 Free Expansion into a Vacuum

Consider a gas expanding into a vacuum.

Since the external pressure is zero: $P_{ext} = 0$

Therefore: $W = \int 0\, dV$

Hence: $\mathbf{W = 0}$

If the container is insulated, no heat enters or leaves the gas: $Q = 0$

Using the First Law: $\Delta U = Q - W$

Therefore: $\mathbf{\Delta U = 0}$

For an ideal gas, internal energy depends only on temperature. Thus: $\mathbf{\Delta T = 0}$

This result applies to free expansion of an ideal gas in an insulated container.
Important: The conclusion that temperature remains unchanged is not generally true for real gases.

3.5 Adiabatic Process: Detailed Study

An **adiabatic process** is a thermodynamic process in which no heat is transferred between the system and its surroundings.
Therefore: **Q = 0**
Using the First Law: $Q = \Delta U + W$
Hence: $\mathbf{\Delta U = -W}$
For an ideal gas, a change in internal energy corresponds to a change in temperature.

3.5.1 Adiabatic Expansion

During expansion, the gas performs work: $W > 0$
Therefore: $\Delta U < 0$
For an ideal gas: $\Delta T < 0$
Thus, the temperature decreases.

3.5.2 Adiabatic Compression

During compression, work is done on the gas: $W < 0$
Therefore: $\Delta U > 0$
For an ideal gas: $\Delta T > 0$
Thus, the temperature increases.

3.5.3 Everyday Examples

- Air becomes warmer during rapid compression in a compression-ignition engine.
- Air may cool as it expands and rises through the atmosphere.
- Gas in a bicycle pump can become warmer during rapid compression.

These examples approximate adiabatic behaviour when heat exchange with the surroundings is small during the process.

3.6 Derivation of the Adiabatic Equation

For a fixed amount of ideal gas undergoing a reversible adiabatic process: $Q = 0$
The First Law in differential form is: $\delta Q = dU + P\,dV$
Therefore: $0 = dU + P\,dV$
For an ideal gas: $dU = nC_v dT$
Substituting: $\mathbf{nC_v dT + P\,dV = 0}$
From the ideal-gas equation: $PV = nRT$
Differentiating:

$$P\,dV + V\,dP = nR\,dT$$

Therefore:

$$dT = (P\,dV + V\,dP)/(nR)$$

Substituting this expression into the adiabatic equation:

$$nC_v(P\,dV + V\,dP)/(nR) + P\,dV = 0$$

Simplifying:

$$(C_v/R)(P\,dV + V\,dP) + P\,dV = 0$$

Multiplying by R:

$$C_v P\,dV + C_v V\,dP + RP\,dV = 0$$

Therefore:

$$C_v V\, dP + (C_v + R)P\, dV = 0$$

Using Mayer's relation:

$$C_P = C_v + R$$

We obtain:

$$C_v V\, dP + C_P\, dV = 0$$

Dividing by C_vPV:

$$dP/P + (C_p/C_v)dV/V = 0$$

Let:

$$\gamma = C_P/C_v$$

Therefore:

$$\mathbf{dP/P + \gamma\, dV/V = 0}$$

Integrating:

$$\ln P + \gamma \ln V = \text{constant}$$

Using the logarithmic identity:

$$\ln P + \ln V^{\gamma} = \text{constant}$$

Therefore:

$$\ln(PV^{\gamma}) = \text{constant}$$

Hence:

$$\mathbf{PV^{\gamma} = constant}$$

This is the equation for a reversible adiabatic process involving a fixed amount of ideal gas with constant heat capacities.

For two equilibrium states:

$$\boldsymbol{P_1 V_1^{\gamma} = P_2 V_2^{\gamma}}$$

3.7 Other Forms of the Adiabatic Equation

The adiabatic equation can be expressed in several useful forms.

3.7.1 Pressure–Volume Form

$$\mathbf{PV^{\gamma} = constant}$$

Between two states:

$$P_1 V_1^{\gamma} = P_2 V_2^{\gamma}$$

3.7.2 Temperature–Volume Form

Starting from:

$$PV^{\gamma} = \text{constant}$$

For an ideal gas:

$$P = nRT/V$$

Substituting:

$$(nRT/V)V^{\gamma} = \text{constant}$$

Therefore:

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

For a fixed amount of gas:

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

Since n and R are constant, they can be absorbed into the proportionality constant.

Between two states:

$$\mathbf{T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}}$$

3.7.3 Temperature–Pressure Form

Using:

$$PV = nRT$$

And:

$$PV^{\gamma} = constant$$

We obtain:

$$\boldsymbol{T^{\gamma} P^{1-\gamma} = constant}$$

Equivalently:

$$\boldsymbol{\frac{T^{\gamma}}{P^{\gamma-1}} = constant}$$

Between two states:

$$\boldsymbol{T_1{}^{\gamma} P_1{}^{1-\gamma} = T_2{}^{\gamma} P_2{}^{1-\gamma}}$$

An equivalent and often convenient form is:

$$\boxed{\boldsymbol{\frac{T_1}{T_2} = \left(\frac{P_1}{P_2}\right)^{\frac{\gamma-1}{\gamma}}}}$$

The last expression gives the ratio of absolute temperatures for two equilibrium states on the same reversible adiabatic path.

Important assumptions: The gas behaves ideally, the process is reversible and adiabatic, and the heat capacities are constant over the temperature range.

3.8 Isothermal and Adiabatic Processes: Comparison

Both isothermal and adiabatic processes are important in thermodynamics, but they differ in their thermal conditions.

Feature	Isothermal Process	Adiabatic Process
Temperature	Constant	Generally changes
Heat transfer	May be non-zero	Zero
Ideal-gas internal energy change	Zero	Generally non-zero
Equation	PV = constant	PV^{γ} = constant
During expansion	Heat may enter the gas	Temperature decreases for an ideal gas
During compression	Heat may leave the gas	Temperature increases for an ideal gas
Reversible form	Requires reversible conditions for the reversible isothermal model	Requires reversible conditions for PV^{γ} = constant

3.8.1 Why Is the Adiabatic Curve Steeper?

For a reversible isothermal process: PV = constant

Differentiating: $P\,dV + V\,dP = 0$

Therefore: $dP/dV = -P/V$

For a reversible adiabatic process: PV^{γ} = constant

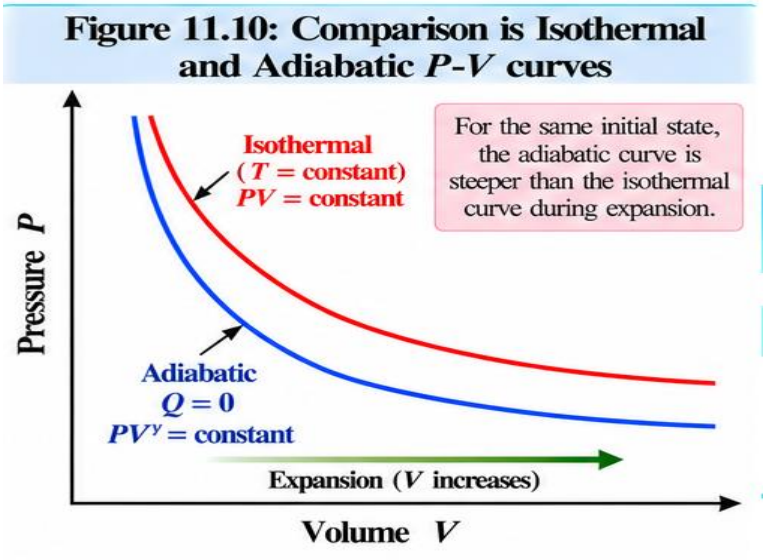
Differentiating: $V^{\gamma}\,dP + \gamma PV^{\gamma-1}\,dV = 0$

Therefore: $dP/dV = -\gamma P/V$

Since $\gamma > 1$ for an ordinary ideal gas: $|-\gamma P/V| > |-P/V|$

Hence, at the same state, the adiabatic curve has a greater magnitude of slope than the isothermal curve.

Conclusion: The reversible adiabatic P–V curve is steeper than the reversible isothermal P–V curve at the same state for an ideal gas with $\gamma > 1$.



3.9 Solved Numerical on Adiabatic Processes

Example 1: Final Pressure During Adiabatic Expansion

Question: An ideal gas expands reversibly and adiabatically from a volume of 2 L to 4 L. Its initial pressure is 8×10^5 Pa. If $\gamma = 1.4$, calculate the final pressure.

Given: $P_1 = 8 \times 10^5$ Pa, $V_1 = 2$ L, $V_2 = 4$ L, $\gamma = 1.4$

Using:

$$P_1 V_1^{\gamma} = P_2 V_2^{\gamma}$$

Therefore:

$$P_2 = P_1 \left(\frac{V_1}{V_2}\right)^{\gamma}$$

Substituting:

$$P_2 = 8 \times 10^5 \times (2/4)^{1.4} = 8 \times 10^5 \times (0.5)^{1.4}$$

Since:

$(0.5)^{1.4} \approx 0.379$

Therefore:

$$P_2 \approx 8 \times 10^5 \times 0.379$$

Answer: $P_2 \approx 3.03 \times 10^5$ Pa

The final pressure is approximately 3.03×10^5 Pa.

Example 2: Final Temperature During Adiabatic Expansion

Question: An ideal gas expands reversibly and adiabatically from 2 L to 4 L. Its initial temperature is 400 K and $\gamma = 1.4$. Calculate the final temperature.

Using:

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$$

Therefore:

$$T_2 = T_1 \left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

Substituting: $T_2 = 400 \times (2/4)^{0.4}$ $T_2 = 400 \times (0.5)^{0.4}$
Since: $(0.5)^{0.4} \approx 0.758$
Therefore: $T_2 \approx 400 \times 0.758$
Answer: $T_2 \approx 303$ K
The temperature decreases during adiabatic expansion.

Example 3: Work Done During Adiabatic Expansion

Question: An ideal gas undergoes an adiabatic expansion. Its internal energy decreases by 700 J. Calculate the work done by the gas.
Given: Q = 0, $\Delta U = -700$ J
Using the First Law: $\Delta U = Q - W$
Therefore: $-700 = 0 - W$
Hence: **W = +700 J**
The gas performs 700 J of work.

3.10 Heat Engines

A **heat engine** is a device that operates cyclically to convert part of the heat absorbed from a high-temperature source into useful work while rejecting the remaining heat to a lower-temperature sink.
A heat engine cannot convert all the heat absorbed into work in a cyclic operation.

3.10.1 Main Components

A simple heat engine consists of:

1. **Hot reservoir:** Supplies heat to the engine.
2. **Working substance:** A gas or another substance that undergoes thermodynamic processes.
3. **Cold reservoir:** Receives the heat rejected by the engine.
4. **Mechanical arrangement:** Allows the engine to deliver useful work.

3.10.2 Working Principle

During a complete cycle:

- The engine absorbs heat Q_H from the hot reservoir.
- It converts part of that energy into useful work W.
- It rejects heat Q_C to the cold reservoir.
- It returns to its initial thermodynamic state.

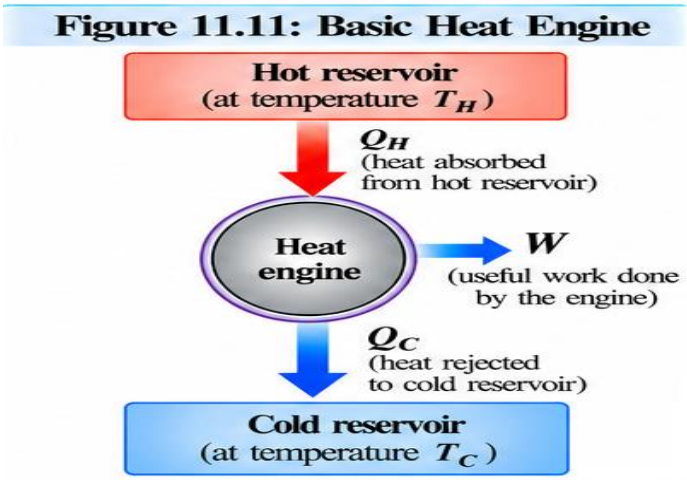
Here, Q_H and Q_C are positive magnitudes of the heat absorbed and rejected, respectively.
Since the engine returns to its initial state:

$$\Delta U_{cycle} = 0$$

From the First Law:

$$\mathbf{W = Q_H - Q_C}$$

Thus, the net work output equals the heat absorbed minus the heat rejected.



3.11 Thermal Efficiency of a Heat Engine

Thermal efficiency measures the fraction of the heat absorbed by an engine that is converted into useful work.

It is defined as:

$$\eta = W/Q_H$$

Since:

$$W = Q_H - Q_C$$

Therefore:

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

If efficiency is expressed as a percentage:

Efficiency (%) = η × 100

3.11.1 Important Conclusions

1. Efficiency is a dimensionless quantity.
2. For a heat engine, useful work is produced from part of the heat absorbed.
3. Some heat must be rejected to the cold reservoir in a cyclic heat engine.
4. A heat engine cannot achieve 100% efficiency when operating cyclically between reservoirs under the Second Law of Thermodynamics.
5. Efficiency depends on the operating cycle and the temperatures of the reservoirs.

Solved Example 4: Efficiency of a Heat Engine

Question: A heat engine absorbs 2000 J of heat from a hot reservoir and rejects 1200 J to a cold reservoir. Calculate the work output and thermal efficiency.

Given: $Q_H = 2000$ J, $Q_C = 1200$ J

Work output: $W = Q_H - Q_C = 2000 - 1200 = 800$ J

Efficiency: $\eta = W/Q_H = 800/2000 = 0.4$

Therefore: **Efficiency = 40%**

3.12 The Kelvin–Planck Statement and Heat Engines

The Kelvin–Planck statement is one formulation of the Second Law of Thermodynamics.

It states that no cyclic heat engine can convert all the heat absorbed from a single thermal reservoir completely into work without producing any other effect.

In practical terms, a cyclic heat engine operating between a hot reservoir and a cold reservoir must reject some heat to the cold reservoir.

Therefore: $Q_C > 0$ and: $\eta < 1$
Thus, a heat engine cannot have 100% thermal efficiency.
Important: This conclusion follows from the Second Law, not from the First Law alone. The First Law expresses energy conservation. The Second Law places restrictions on the possible direction and efficiency of energy conversion.

Numerical Practice

1. An ideal gas expands reversibly and adiabatically from 3 L to 6 L. Its initial pressure is 6×10^5 Pa. If $\gamma = 1.4$, calculate the final pressure.
2. An ideal gas undergoes reversible adiabatic expansion from 500 K to a larger volume. If $V_2/V_1 = 4$ and $\gamma = 1.4$, calculate the final temperature.
3. A heat engine absorbs 5000 J of heat and rejects 3000 J during each cycle. Calculate its work output and efficiency.
4. A heat engine operates with an efficiency of 25% and absorbs 8000 J of heat per cycle. Calculate the work output and heat rejected.
5. A gas undergoes adiabatic compression, and 900 J of work is done on it. Calculate the change in internal energy, assuming no other work interactions.

3.13 NEET/JEE Conceptual Insights

Concept 1: Reversibility Is an Ideal Limit

A slow process is not necessarily reversible. Friction and finite temperature differences can generate entropy even when a process proceeds slowly.

Concept 2: Adiabatic Expansion

For an ideal gas undergoing adiabatic expansion: $Q = 0$
If the gas performs work: $\Delta U = -W < 0$
Its internal energy decreases, and so does its temperature.

Concept 3: Adiabatic Curve

For a reversible adiabatic process: $PV^\gamma = \text{constant}$
For an ordinary ideal gas with $\gamma > 1$, the adiabatic P–V curve is steeper than the isothermal curve at the same state.

Concept 4: Heat Engine Efficiency

The thermal efficiency of an engine is the ratio of useful work output to heat absorbed:
$\eta = W/Q_H$
It is not the ratio of work output to heat rejected.

Concept 5: Energy Conservation and the Second Law

The First Law ensures that energy is conserved.
The Second Law explains why the complete conversion of heat into work in a cyclic heat engine is impossible.

PART 4: SECOND LAW OF THERMODYNAMICS, CARNOT ENGINE, REFRIGERATOR AND HEAT PUMP

4.1 Learning Objectives

After studying this part, students should be able to:

1. State and explain the Second Law of Thermodynamics.
2. Understand the limitations of the First Law.
3. Explain the Kelvin–Planck and Clausius statements.
4. Understand the working principle of a heat engine.
5. Explain the Carnot cycle and its four thermodynamic processes.
6. Derive the expression for the efficiency of a Carnot engine.
7. Understand the working principle of a refrigerator.
8. Define and calculate the coefficient of performance (COP).
9. Distinguish between a heat engine, refrigerator and heat pump.
10. Solve numerical problems relevant to Board, NEET and JEE examinations.

4.2 The Second Law of Thermodynamics

The First Law of Thermodynamics expresses the conservation of energy. However, it does not determine the natural direction of a process or the maximum efficiency with which heat can be converted into work.

For example, the First Law alone does not explain why heat flows spontaneously from a hot body to a cold body rather than in the opposite direction.

4.2.1 Limitations of the First Law

The First Law states: $Q = \Delta U + W$

It accounts for the energy supplied to a system, the change in its internal energy and the work performed.

However, the First Law alone cannot explain:

- Why heat flows spontaneously from hot to cold.
- Why a gas expands spontaneously into an available vacuum.
- Why friction converts mechanical energy into thermal energy.
- Why a cyclic heat engine cannot convert all absorbed heat into useful work.
- Why natural thermodynamic processes generally have a preferred direction.

These limitations are addressed by the Second Law.

4.2.2 Natural Direction of Heat Flow

Suppose a hot object at temperature T_H is placed in contact with a cold object at temperature T_C,
Where: $T_H > T_C$

Heat flows spontaneously from the hot object to the cold object until thermal equilibrium is approached.

The reverse transfer—from cold to hot without any external effect—is not spontaneous.

A refrigerator can transfer heat from a colder region to a warmer region, but it requires external work.

Important: The Second Law does not prohibit heat transfer from cold to hot under all circumstances. It prohibits such a transfer as the sole effect of a cyclic process without the necessary external intervention.

4.3 Kelvin–Planck Statement of the Second Law

The Kelvin–Planck statement concerns the limitations of heat engines.

Statement

It is impossible to construct a cyclic heat engine whose sole effect is to absorb heat from a single thermal reservoir and convert that heat completely into work.

In simpler terms, **a cyclic heat engine cannot convert all the heat absorbed from a hot reservoir into useful work without rejecting some heat to another reservoir or producing another effect.**

For a heat engine:

Q_H = Heat absorbed from the hot reservoir.

Q_C = Magnitude of heat rejected to the cold reservoir.

W = Net work output.

The First Law gives: $W = Q_H - Q_C$

For a heat engine operating cyclically, the Second Law requires heat rejection: $Q_C > 0$

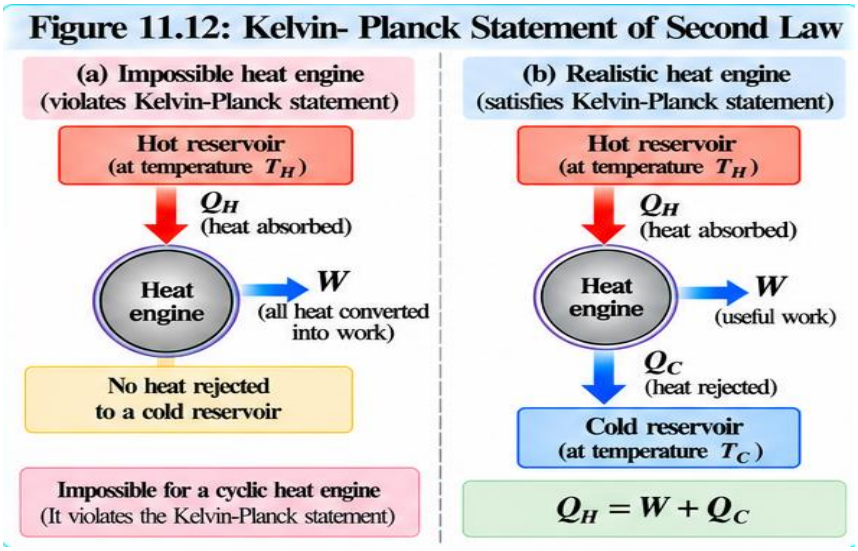
Therefore: $W < Q_H$

Hence, the thermal efficiency must be less than 100%.

Important Conclusion

A heat engine cannot have 100% thermal efficiency when operating cyclically between thermal reservoirs.

This limitation arises from the Second Law, not from the First Law alone.



4.4 Clausius Statement of the Second Law

The Clausius statement concerns the direction of heat transfer.

Statement

It is impossible to construct a cyclic device whose sole effect is to transfer heat from a colder body to a hotter body without external work or another compensating effect.

In simpler terms, heat does not spontaneously flow from a cold object to a hot object.

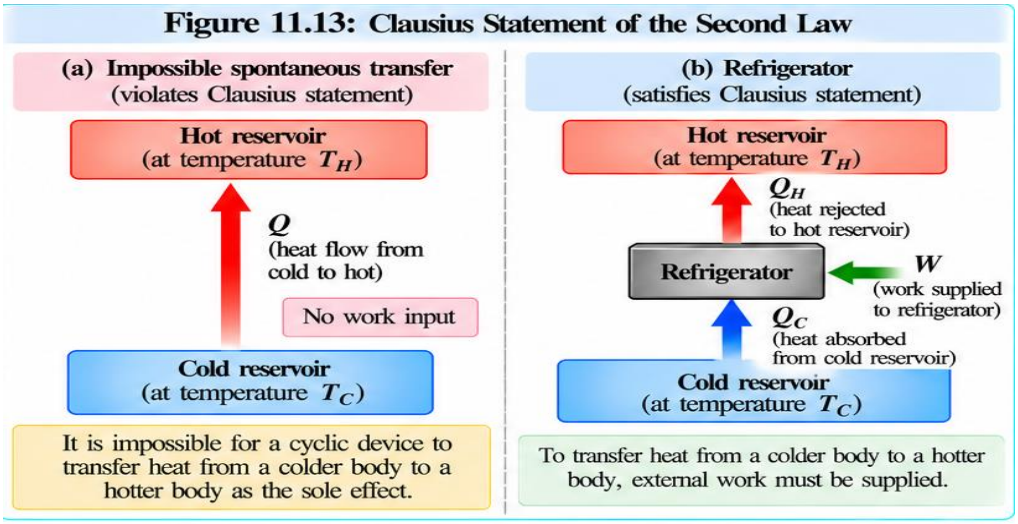
To transfer heat from a cold region to a warmer region, a refrigerator requires an external energy supply.

4.4.1 Example: Refrigerator

Inside a refrigerator:

- The evaporator absorbs heat from the cold compartment.
- The compressor consumes electrical energy.
- The condenser releases heat into the warmer surroundings.

Thus, heat is transferred from a colder region to a warmer region with the help of external work.



4.5 Equivalence of Kelvin–Planck and Clausius Statements

The Kelvin–Planck and Clausius statements are two equivalent formulations of the Second Law of Thermodynamics.

Although they describe different situations, a violation of one would imply a violation of the other.

4.5.1 If the Kelvin–Planck Statement Were Violated

Suppose an idealised engine could absorb heat from a single hot reservoir and convert all of it into work.

That work could be used to operate a refrigerator.

The refrigerator could then transfer heat from a cold reservoir to the hot reservoir without requiring any additional external work.

The combined device would transfer heat from cold to hot without an external work input.

This would violate the Clausius statement.

4.5.2 If the Clausius Statement Were Violated

Suppose a refrigerator could transfer heat from cold to hot without external work.

Such a device could be combined with an ordinary heat engine operating between the same reservoirs.

The refrigerator could return the engine's rejected heat to the hot reservoir without consuming work.

The combined device would convert heat taken from a single reservoir completely into work.

This would violate the Kelvin–Planck statement.

Therefore, the two statements are equivalent formulations of the Second Law.

Exam Tip: Remember the distinction:

- Kelvin–Planck: No cyclic heat engine can convert all absorbed heat into work.
- Clausius: Heat cannot be transferred from cold to hot as the sole effect of a cyclic device without external work.

4.6 Carnot Engine

A **Carnot engine** is an ideal reversible heat engine operating between two thermal reservoirs at fixed temperatures.
It operates through a reversible thermodynamic cycle known as the **Carnot cycle**.
A Carnot engine provides the maximum possible efficiency for an engine operating between two specified reservoir temperatures.

4.6.1 Main Components

A simplified Carnot engine consists of:

1. A hot reservoir at absolute temperature T_H
2. A cold reservoir at absolute temperature T_C
3. An ideal gas acting as the working substance.
4. A cylinder with a frictionless, insulating piston.
5. Thermal contacts that allow reversible heat transfer when required.

4.6.2 Working Principle

The Carnot cycle contains four reversible processes:

1. Reversible isothermal expansion at T_H
2. Reversible adiabatic expansion from T_H to T_C
3. Reversible isothermal compression at T_C
4. Reversible adiabatic compression from T_C to T_H

During the cycle, the gas absorbs heat from the hot reservoir, performs net work and rejects heat to the cold reservoir.
At the end of the cycle, the gas returns to its initial state.

4.7 The Four Processes of the Carnot Cycle

The Carnot cycle consists of two isothermal processes and two adiabatic processes.
Let the four equilibrium states be A, B, C and D.

4.7.1 Process A → B: Reversible Isothermal Expansion

The gas expands reversibly while remaining in thermal contact with the hot reservoir.
Temperature: $T = T_H$
Since the gas expands, it performs positive work.
To maintain constant temperature, the gas absorbs heat Q_H from the hot reservoir.
For an ideal gas undergoing reversible isothermal expansion: $\Delta U_{AB} = 0$
Therefore: $Q_H = W_{AB}$
For n moles of ideal gas: $\mathbf{W_{AB} = nRT_H \ln(V_B / V_A)}$
Here, V_A and V_B are the volumes at states A and B.

4.7.2 Process B → C: Reversible Adiabatic Expansion

The gas is thermally insulated from the surroundings and expands reversibly.
Therefore: $Q_{BC} = 0$
The gas performs work, and its internal energy decreases.
For an ideal gas, the temperature falls from T_H to T_C.
The adiabatic relation is: $\mathbf{PV^{\gamma} = constant}$

4.7.3 Process C → D: Reversible Isothermal Compression

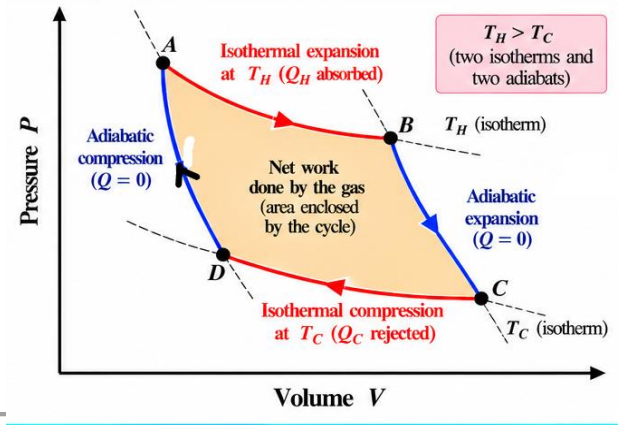
The gas is placed in thermal contact with the cold reservoir at T_C.
The gas is compressed reversibly at constant temperature.

Work is done on the gas, and heat Q_C is rejected to the cold reservoir.
For the gas: $\Delta U_{CD} = 0$
The work done by the gas is negative.
For n moles of ideal gas: $\mathbf{W_{CD} = nRT_C \ln (V_D / V_C)}$
Since $V_D < V_C$, the logarithm is negative.

4.7.4 Process D → A: Reversible Adiabatic Compression

The gas is thermally insulated and compressed reversibly.
No heat is transferred: $Q_{DA} = 0$
Work is done on the gas, increasing its internal energy.
For an ideal gas, its temperature rises from T_C to T_H.
The adiabatic relation is: $\mathbf{PV^{\gamma} = constant}$
The gas returns to its initial state, completing the cycle.

Figure 11.14: *P*–*V* Diagram of the Carnot Cycle



4.8 Efficiency of a Carnot Engine

The thermal efficiency of a heat engine is defined as: $\eta = W/Q_H$
For one complete cycle, the First Law gives: $W = Q_H - Q_C$
Therefore: $\eta = (Q_H - Q_C)/Q_H$
Hence: $\mathbf{\eta = 1 - Q_C / Q_H}$
For a reversible Carnot engine operating between two reservoirs at absolute temperatures T_H and T_C: $\mathbf{Q_C / Q_H = T_C / T_H}$
Therefore: $\mathbf{\eta\ (Carnot) = 1 - T_C / T_H}$
This is the efficiency of a reversible Carnot engine.
Where:

- T_H = absolute temperature of the hot reservoir.
- T_C = absolute temperature of the cold reservoir.

Both temperatures must be expressed in kelvin.

4.8.1 Important Conclusions

Case 1: Hot Reservoir Temperature Increases

If T_C remains constant and T_H increases, the efficiency increases.

Case 2: Cold Reservoir Temperature Decreases

If T_H remains constant and T_C decreases, the efficiency increases.

Case 3: Both Reservoir Temperatures Are Equal

If $T_H = T_C$:

$$\eta = 1 - 1 = 0$$

No net work can be obtained from a reversible cyclic engine operating between reservoirs at the same temperature.

Case 4: Cold Reservoir Temperature Approaches Absolute Zero

If T_C approaches 0 K: η approaches 1 mathematically.
However, absolute zero cannot be attained by a finite sequence of ordinary thermodynamic processes, so this limiting efficiency is not achievable by a real engine.

Important: The Carnot efficiency is the maximum theoretical efficiency for a heat engine operating between two specified reservoir temperatures.

4.9 Solved Numerical Problems on Carnot Engines

Example 1: Carnot Engine Efficiency

Question: A Carnot engine operates between a hot reservoir at 600 K and a cold reservoir at 300 K. Calculate its efficiency.

Given: $T_H = 600$ K, $T_C = 300$ K

Formula: $\eta = 1 - T_C / T_H$

Substituting:

$$\eta = 1 - 300/600 = 1 - 0.5 = 0.5$$

Therefore: **Efficiency = 50%**

Example 2: Work Output

Question: A Carnot engine absorbs 4000 J of heat from a reservoir at 800 K and rejects heat to a reservoir at 400 K. Calculate the work output per cycle.

Given: $Q_H = 4000$ J, $T_H = 800$ K, $T_C = 400$ K

Efficiency: $\eta = 1 - 400/800 = 0.5$

Since: $\eta = W/Q_H$

Therefore: $W = \eta Q_H = 0.5 \times 4000$

Answer: W = 2000 J

The heat rejected is: $Q_C = Q_H - W = 4000 - 2000$ **= 2000 J**

Example 3: Finding the Cold Reservoir Temperature

Question: A Carnot engine has an efficiency of 40%. If the hot reservoir temperature is 500 K, calculate the cold reservoir temperature.

Given: $\eta = 0.40$, $T_H = 500$ K

Formula: $\eta = 1 - T_C / T_H$

Therefore: $T_C / T_H = 1 - \eta$

Or: $T_C = T_H (1 - \eta) = 500 \times (1 - 0.40) = 500 \times 0.60$

Answer: $T_C = 300$ K

4.10 Refrigerator

A **refrigerator** is a device that uses external work to transfer heat from a low-temperature region to a high-temperature region.

It operates cyclically and commonly uses a refrigerant as the working substance.

4.10.1 Main Energy Transfers

Let:

Q_C = Heat absorbed from the cold region.

Q_H = Heat released to the hot surroundings.

W = Work supplied to the refrigerator.

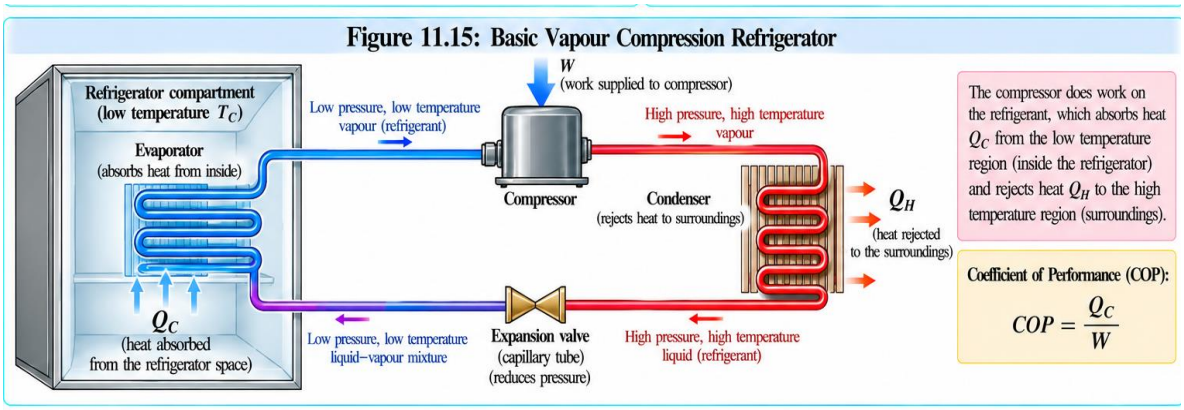
Using the First Law for a complete cycle: $\mathbf{Q_H = Q_C + W}$

The refrigerator absorbs heat from its cold compartment and releases a larger amount of heat to the surroundings because the supplied work also becomes part of the rejected energy.

4.10.2 Basic Working Principle

In a typical vapour-compression refrigerator:

1. The evaporator absorbs heat from the refrigerated space.
2. The compressor raises the refrigerant pressure and temperature using external work.
3. The condenser releases heat to the surroundings.
4. The expansion device reduces the refrigerant pressure.
5. The refrigerant returns to the evaporator, and the cycle repeats.



4.11 Coefficient of Performance of a Refrigerator

The performance of a refrigerator is measured using its **coefficient of performance (COP)**.
It is defined as the heat removed from the cold region divided by the work supplied.
Therefore: **COP (R) = Q_C /W**
Using: W = $Q_H - Q_C$
We obtain: **COP (R) = Q_C /($Q_H - Q_C$)**
COP is dimensionless.
Unlike thermal efficiency, COP is not restricted to values below 1.

4.11.1 COP of a Reversible Refrigerator

For a reversible refrigerator operating between reservoirs at temperatures T_C and T_H:

$$Q_C / T_C = Q_H / T_H$$

Therefore: $Q_H / Q_C = T_H / T_C$
Using: COP (R) = Q_C /($Q_H - Q_C$)
Divide the denominator by Q_C:

$$COP_R = \frac{1}{\frac{Q_H}{Q_C} - 1}$$

Substituting: COP (R) = 1/(T_H /T_C − 1)
Hence: **COP (R) = T_C /($T_H - T_C$)**
Where:

- T_C = absolute temperature of the cold reservoir.
- T_H = absolute temperature of the hot reservoir.

Both temperatures must be expressed in kelvin.

Important Conclusions

1. COP increases when the temperature difference between the reservoirs decreases.
2. COP decreases when the temperature difference increases, all other ideal conditions being equal.

3. A reversible refrigerator has the maximum possible COP for the specified reservoir temperatures.
4. A real refrigerator has a lower COP than the reversible ideal limit under comparable conditions.

4.12 Solved Numerical Problems on Refrigerators

Example 4: Refrigerator COP

Question: A refrigerator removes 600 J of heat from its cold compartment while consuming 200 J of work. Calculate its COP.
Given: $Q_C = 600$ J, $W = 200$ J
Formula: COP (R) = $Q_C / W = 600/200$
Answer: COP_R = 3

Example 5: Heat Rejected by a Refrigerator

Question: A refrigerator removes 800 J of heat from its cold compartment and consumes 300 J of work. Calculate the heat rejected to the surroundings.
Given: $Q_C = 800$ J, $W = 300$ J,
Using: $Q_H = Q_C + W = 800 + 300$
Answer: Q_H = 1100 J

Example 6: Ideal Refrigerator COP

Question: A reversible refrigerator operates between a cold reservoir at 270 K and a hot reservoir at 300 K. Calculate its maximum COP.
Given: $T_C = 270$ K, $T_H = 300$ K
Formula: COP (R) = $T_C / (T_H - T_C)$
Substituting:
COP (R) = $270/(300 - 270) = 270/30$
Answer: COP_R = 9
This is the ideal maximum COP for the specified reservoir temperatures.

4.13 Heat Pump

A **heat pump** is a device that uses external work to transfer heat from a colder region to a warmer region, with the primary objective of supplying useful heat to the warmer region.
A refrigerator and a heat pump can operate using the same basic thermodynamic cycle.
The difference lies mainly in the intended useful output:

- A refrigerator is used to remove heat from a cold space.
- A heat pump is used to supply heat to a warm space.

4.13.1 Coefficient of Performance of a Heat Pump

The coefficient of performance of a heat pump is defined as: **COP (HP) = Q_H / W**
Since: $Q_H = Q_C + W$
We obtain: COP (HP) = $(Q_C + W)/W$
Therefore: **COP (HP) = COP (R) + 1**
This relation applies when the refrigerator and heat pump operate between the same reservoirs and use the same energy-transfer definitions.
For a reversible heat pump: **COP (HP) = $T_H / (T_H - T_C)$**

Solved Example 7: Heat Pump COP

Question: A heat pump supplies 1500 J of heat to a room while consuming 300 J of work. Calculate its COP.
Given: Q_H = 1500 J, W = 300 J
Formula: COP (HP) = Q_H / W = 1500/300
Answer: COP (HP) = 5

4.14 Comparison of Heat Engine, Refrigerator and Heat Pump

Feature	Heat Engine	Refrigerator	Heat Pump
Primary purpose	Produce work	Remove heat from a cold space	Supply heat to a warm space
Heat absorbed	From hot reservoir	From cold reservoir	From cold reservoir
Work interaction	Produces work	Requires work	Requires work
Heat rejected	To cold reservoir	To hot surroundings	To hot surroundings
Performance measure	Thermal efficiency	COP of refrigerator	COP of heat pump
Formula	η = W/Q_H	COP_R = Q_C/W	COP_HP = Q_H/W

Exam Tip: The COP of a refrigerator or heat pump can exceed 1 because the device transfers heat using work rather than converting the supplied work entirely into heat at the desired location.

4.15 Important Conceptual Questions

Question 1: Why can a heat engine not have 100% efficiency?
Answer: The Second Law of Thermodynamics requires a cyclic heat engine to reject some heat rather than converting all absorbed heat into work.

Question 2: Can a refrigerator transfer heat from cold to hot?
Answer: Yes. It does so by consuming external work.

Question 3: Why is the Carnot engine considered ideal?
Answer: It operates through a fully reversible cycle and represents the maximum theoretical efficiency possible between two specified reservoir temperatures.

Question 4: Can the COP of a refrigerator exceed 1?
Answer: Yes. COP is the ratio of heat removed to work supplied, so it can exceed 1.

Question 5: What happens to Carnot efficiency if the hot reservoir temperature increases while the cold reservoir temperature remains constant?
Answer: The efficiency increases because: $\eta = 1 - T_C / T_H$

Question 6: What is the difference between the First and Second Laws of Thermodynamics?
Answer: The First Law expresses energy conservation. The Second Law specifies restrictions on the direction of thermodynamic processes and on the conversion of heat into work.
