

CHAPTER

11

Thermodynamics

Basic Concepts and the Zeroth Law • Heat, Work and the First Law •
Thermodynamic Processes • Second Law and Carnot Engine

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READING KEY

DEFINITION

NOTE

REMEMBER

DERIVATION

STRATEGY

Formulas sit on graph paper • coloured words are the key terms

Thermodynamics is the branch of physics that studies **heat**, **work** and the changes they cause in a **working substance**. It is a **macroscopic science**. It uses a few large-scale variables and does not describe molecules. The state of a gas is given by its **pressure**, **volume**, **temperature**, **mass** and **composition**.

1.1 System, Surroundings and Boundary

DEFINITION

Thermodynamic System

A **thermodynamic system** is a collection of a **very large number of particles** (atoms or molecules). It has definite values of **pressure**, **volume** and **temperature**.

It may be a **solid**, a **liquid**, a **gas**, or a mix of these states.

DEFINITION

Surroundings

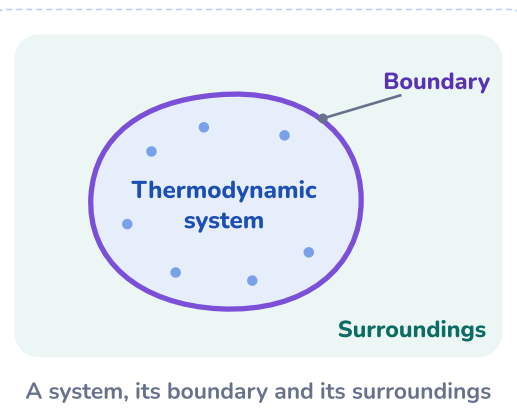
The **surroundings** of a system are everything outside it that has a **direct effect** on it. All the space in the universe outside the system is its surroundings.

e.g. The **environment** around a system.

DEFINITION

System Boundary

A **system boundary** is a closed two-dimensional surface, **real or imaginary**, around the space filled by the system. It keeps the system apart from its surroundings. Energy may or may not pass through it. Work can be done **on** or **by** the system across it.



1.2 Classification of Thermodynamic Systems

Systems are classified by **what can cross the boundary**. A system may be **open**, **closed** or **isolated**.

i Open System

An **open system** exchanges **both energy and matter** with its surroundings.

ii Closed System

A **closed system** exchanges **only energy** with its surroundings, not matter.

iii Isolated System

An **isolated system** exchanges **neither energy nor matter** with the outside.

1.3 Thermodynamic Equilibrium

DEFINITION

A system is in **thermodynamic equilibrium** when its **macroscopic variables do not change with time**. These variables are pressure, volume, temperature, mass, composition, etc.

EXAMPLE

A gas is kept in a **closed, rigid container**. The container is **fully insulated** from its surroundings. The pressure, volume, temperature, mass and composition of the gas stay the same with time. So the gas is in **thermodynamic equilibrium**.

WHETHER A SYSTEM IS IN EQUILIBRIUM DEPENDS ON

i The surroundings

What lies **around** the system.

ii Nature of the wall

The kind of **wall** that separates the system from its surroundings.

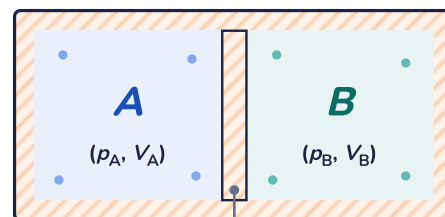
• TWO SYSTEMS WITH AN ADIABATIC WALL BETWEEN THEM

Take **two gases A and B** in two separate containers. Let their pressures and volumes be (p_A, V_A) and (p_B, V_B) .

DEFINITION

An **adiabatic wall** is an **insulating wall**. It does not let energy (heat) flow from one side to the other.

The two systems are placed close together with an **adiabatic wall** between them. Similar adiabatic walls also insulate them from the rest of the surroundings.



Adiabatic wall

A and B separated by an adiabatic wall

KEY In this case, any pair of values (p_A, V_A) is in equilibrium with any pair of values (p_B, V_B) .

1.4 Thermal Equilibrium

DEFINITION

Two systems are in **thermal equilibrium** with each other when they are at the **same temperature**.

Now replace the adiabatic wall between gases A and B with a **diathermic wall**.

DEFINITION

A **diathermic wall** is a **conducting wall**. It lets energy (heat) flow from one side to the other.

Heat now flows through the wall. So the **macroscopic variables** of both gases change by themselves. The pressure, the volume, or both may change.

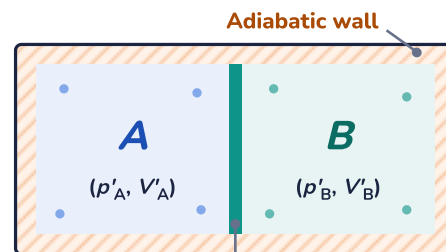
After the change, let the values be (p'_A, V'_A) and (p'_B, V'_B) . These **new states** of A and B are in equilibrium with each other.

Energy flow from one gas to the other

Stops

KEY

So the temperatures of the two gases become equal.
The gases are now in thermal equilibrium.



Diathermic wall

A and B in thermal equilibrium

• TYPES OF EQUILIBRIUM

i Mechanical

A system is in **mechanical equilibrium** when **no unbalanced force and no unbalanced torque** acts on it.

ii Chemical

A system is in **chemical equilibrium** when its internal structure has **no spontaneous change** due to chemical reaction, diffusion, etc.

iii Thermal

Two systems are in **thermal equilibrium** when **no net heat flows** between them after they are put in thermal contact.

1.5 Zeroth Law of Thermodynamics

This law was stated by

R. H. Fowler in 1931

LAW

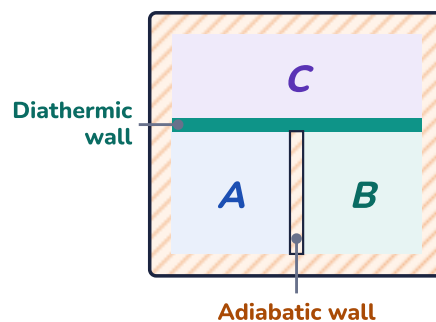
Zeroth Law of Thermodynamics

If two systems A and B are **each in thermal equilibrium** with a third system C , then A and B are also in **thermal equilibrium with each other**.

• EXPERIMENTAL PROOF

a Experiment (a)

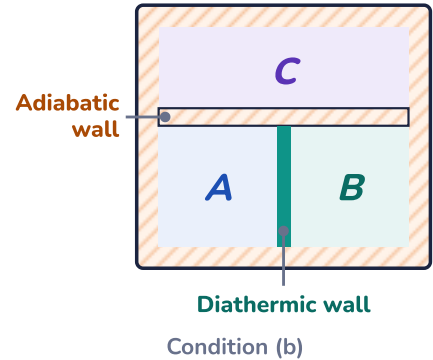
A and B are separated by a fixed **adiabatic wall**. Each one touches a third system C through a **diathermic wall**. The variables of A and B change until each reaches thermal equilibrium with C . So A and B are **each in thermal equilibrium with C** .



Condition (a)

b Experiment (b)

Now the wall between A and B is changed to a **diathermic wall**. An **adiabatic wall** now separates C from A and B . No further change takes place in A and B . They are found to be **in thermal equilibrium with each other**.



KEY Experiments (a) and (b) together prove the zeroth law.

• CONCEPT OF TEMPERATURE

CONCEPT

What the Zeroth Law Tells Us

The zeroth law shows that **temperature** is a **physical quantity**. It has the **same value** for all systems that are in **thermal equilibrium** with each other.

So, if A and B are each in thermal equilibrium with C , then $T_A = T_C$ and $T_B = T_C$. $\therefore T_A = T_B$. So A and B are in **thermal equilibrium** too.

• SOME DEFINITIONS OF TEMPERATURE

- 1 **Temperature** is the thermodynamic variable that decides **whether two systems in contact are in thermal equilibrium** or not.
- 2 The **temperature** of a body is the quantity that tells the **degree of hotness or coldness** of the body.
- 3 The **temperature** of a body is the quantity that decides the **direction of heat flow** when it touches another body.

02 PART 2 Heat, Work and the First Law

2.1 Internal Energy

DEFINITION

The **internal energy** of a system is the total energy of its molecules due to their **motion** and their **configuration** (arrangement). It is written as U .

i Internal Kinetic Energy U_K

It comes from the **motion of the molecules**. This motion is of three kinds: **translational**, **rotational** and **vibrational**.

ii Internal Potential Energy U_P

It comes from the **configuration** of the molecules, that is, how they are arranged.

INTERNAL ENERGY

$$U = U_K + U_P$$

where, U_K = internal kinetic energy, U_P = internal potential energy

NOTE

So internal energy is the **sum of the kinetic and potential energies** of the molecules. These energies are measured in a frame where the system's **centre of mass** does **not move**.

• IDEAL GAS

The molecules of an **ideal gas** do **not attract each other**. So:

$$\text{Intermolecular force} = 0 \rightarrow \text{No intermolecular potential energy} \rightarrow U_P = 0$$

So the internal energy of an ideal gas is **only the sum of the kinetic energies** of its molecules. These come from their random **translational, rotational and vibrational** motions.

KEY The internal energy of an ideal gas depends only on its temperature.

• REAL GAS

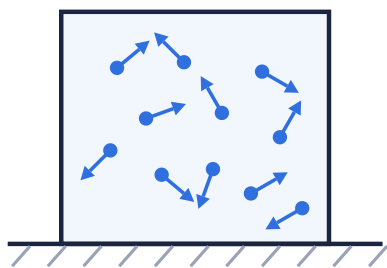
The molecules of a **real gas** pull on one another. These intermolecular forces **cannot be neglected**. So some **work must be done** to change the distance between the molecules.

$$\text{Internal energy of a real gas} = \text{Internal kinetic energy} + \text{Internal potential energy}$$

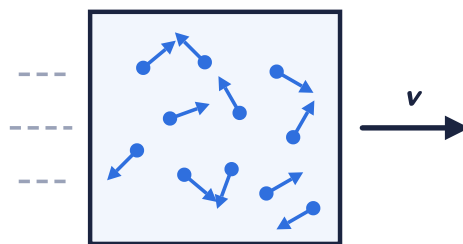
KEY So the internal energy of a real gas depends on both its temperature and its volume.

• KEY POINTS ABOUT INTERNAL ENERGY

- ◆ Internal energy is a **macroscopic state variable**. It depends on the state of the system, that is, on its pressure, volume, temperature, mass, composition, etc. Here the container is **at rest** (Fig. a).
- ◆ It depends **only on the state** of the system. It **does not depend on the path** taken to reach that state.
- ◆ The internal energy of a gas can change when its **macroscopic state variables** change.
- ◆ The kinetic energy of the **system as a whole** does not count in thermodynamics. Suppose the gas container moves with some velocity (Fig. b). Then the KE of the container is **not included** in the internal energy.



(a) Container at rest



(b) Container moving with velocity v

2.2 Heat

DEFINITION

Heat is the energy that flows between a **system** and its **surroundings** because of a **temperature difference** between them.

SI unit of heat

joule (J)

The heat Q needed to raise the temperature of a body from T_i to T_f depends on three things:

i Mass

The **mass** of the body.

ii Nature of substance

What the body is **made of**.

iii Temperature change

How much its **temperature changes**.

$$\text{i.e. } \Delta Q \propto m \Delta T \quad \text{or} \quad \Delta Q \propto m (T_f - T_i)$$

HEAT SUPPLIED

$$\Delta Q = m s (T_f - T_i)$$

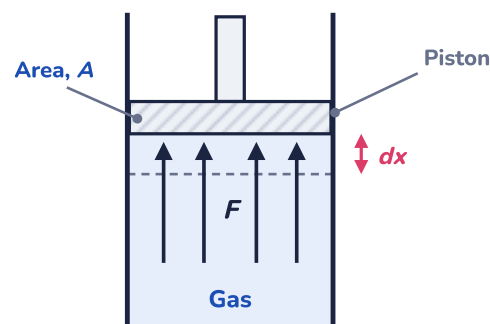
where, m = mass of the body, T_i = initial temperature, T_f = final temperature, s = specific heat of the material

2.3 Work Done by a Gas

In thermodynamics, **work** means work done **by the system** or work done **on the system**.

SETUP – GIVEN INFORMATION

- ◆ A gas is enclosed in a **cylinder with a movable piston**.
- ◆ p = pressure of the gas on the piston.
- ◆ A = area of the piston.



Gas in a cylinder with a movable piston

DERIVATION

- 1 Force of the gas on the piston:

$$F = pA$$

- 2 The piston moves out by a tiny distance dx . Work done by the gas:

$$dW = F dx = pA dx = p dV \quad [\because A dx = dV]$$

- 3 For a finite change in volume from V_i to V_f :

$$W = \int_{V_i}^{V_f} dW$$

WORK DONE BY A GAS

$$W = \int_{V_i}^{V_f} p dV$$

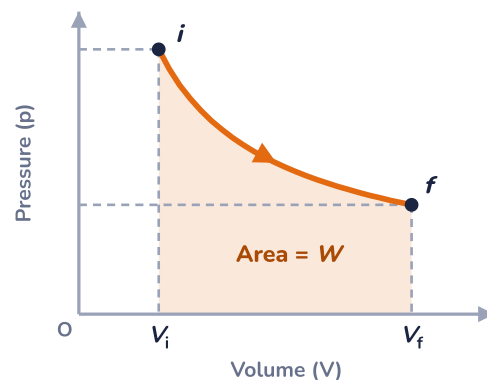
Here, p may stay **constant** or may **change** during the process.

INDICATOR DIAGRAM

DEFINITION

An **indicator diagram** is a graph of the **pressure (p)** of a gas against its **volume (V)**. A gas can change its state in many ways. Each way gives its own p - V graph.

On an indicator diagram, the **area under the p - V graph** gives the **work done**.



Area under the p - V curve = work done

$$\text{Work} = \int_{V_i}^{V_f} p dV = \text{area under } p\text{-}V \text{ graph} \Rightarrow \Delta W = \int_{V_i}^{V_f} p dV$$

The system **expands**: $V_f > V_i$

W is positive

The system **contracts**: $V_f < V_i$

W is negative

REMEMBER**Work Depends on the Path**

Like heat, work done **depends on the path**. So work is **not a state function**. In a **cyclic process**, the work done equals the **area enclosed** by the p - V loop.

- ◆ Cycle goes **clockwise**: work done is **positive**.
- ◆ Cycle goes **anticlockwise**: work done is **negative**.

2.4 Sign Convention for Heat and Work

The **internal energy** of a system can be changed in **four ways**. Each way gives a sign to ΔW or ΔQ .

(i) Work is done **on** the system

$\Delta W = \text{negative}$

(ii) The system **does** work

$\Delta W = \text{positive}$

(iii) Heat is **given to** the system

$\Delta Q = \text{positive}$

(iv) Heat is **taken out** of the system

$\Delta Q = \text{negative}$

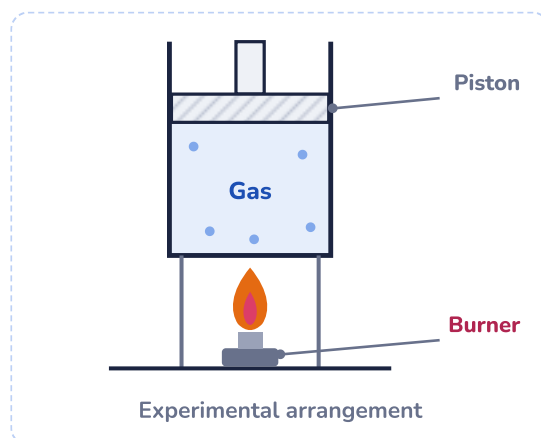
IMPORTANT**Sign Convention Used in These Notes**

- ◆ ΔQ is **positive** when heat **enters** the system. It is **negative** when heat **leaves** it.
- ◆ ΔW is **positive** when the system **does work** (it expands). It is **negative** when work is **done on** the system (it is compressed).
- ◆ These signs are used in **every topic** of this chapter. With them, the first law is $\Delta Q = \Delta U + \Delta W$.

2.5 Heat and Work as Energy Transfer

A simple experiment shows how heat and work change the internal energy of a gas.

- I Place a **cylinder containing some gas** over a **burner**.
Heat flows from the burner into the gas. So the **internal energy** of the gas **increases**.
- II The gas pushes the piston **upward**. So the gas **does work**. Because of this work, the **internal energy** of the gas **decreases**.



Both of these changes can also happen in the **opposite direction**:

i Gas Touches a Colder Body

Heat flows **from the gas to the colder body**. The temperature of the gas falls. So its internal energy **decreases**.

ii Piston Pushed Down

Now **work is done on the gas**. So the internal energy of the gas **increases**.

KEY Heat and work are two separate ways to change both the state and the internal energy of a system.

CONCEPT

Heat Is Energy in Transit

Heat is energy on the move from one body to another. Heat is **not a state variable**. The state of a system is described by its **internal energy**.

So **neither heat nor work is a state variable**. Both are ways of **transferring energy**, and each can change the internal energy of a system.

2.6 First Law of Thermodynamics

LAW

First Law of Thermodynamics

The **first law of thermodynamics** is the **law of conservation of energy** applied to a system. It takes into account the energy that flows between the system and its surroundings.

Statement: Heat given to a system **raises its internal energy, does external work**, or both.

FIRST LAW

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

where, ΔQ = heat given to the system, ΔU = change in its internal energy, ΔW = work done by the system

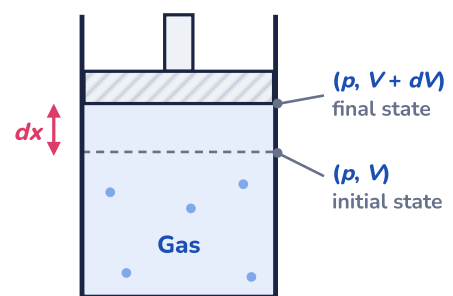
ΔU is decided only by

the starting and final states

• EXPERIMENTAL ARRANGEMENT TO PROVE THE FIRST LAW

SETUP – GIVEN INFORMATION

- ◆ A gas is in a cylinder with a **massless, frictionless piston**. It expands by a **very small volume dV** .
- ◆ p = pressure and V = volume of the gas.
- ◆ A = area of cross-section of the piston, dx = distance moved by the piston.



Arrangement to prove the first law

DERIVATION

1 Work done by the gas:

$$dW = \text{force} \times dx$$

2 Force = pA . So:

$$dW = pA \times dx = p(A dx) = p dV \quad [\because A dx = dV]$$

$$\therefore dW = p dV$$

For the small displacement dx , the pressure is taken as constant.

3 So, from the first law:

$$\Delta Q = \Delta U + p dV$$

ΔQ

heat exchanged between the system and surroundings

ΔU

change in internal energy of the system

2.7 Heat Capacity and Specific Heat

Suppose an amount of heat ΔQ changes the temperature of a body by ΔT . Then its heat capacity is:

HEAT CAPACITY

$$S = \frac{\Delta Q}{\Delta T}$$

DEFINITION

The **heat capacity** of a body is numerically equal to the **heat needed to change its temperature by one unit** (1 K).

Unit of heat capacity

J K^{-1} (J/K)

NOTE

The heat needed for a **1-unit rise** in temperature may be **different** at different temperatures.

• SPECIFIC HEAT CAPACITY

DEFINITION

The **specific heat capacity** of a substance is the heat needed to change the temperature of **unit mass** of the substance **by one unit**.

$$s = \frac{S}{m} = \frac{1}{m} \frac{\Delta Q}{\Delta T}$$

SPECIFIC HEAT CAPACITY

$$s = \frac{1}{m} \frac{\Delta Q}{\Delta T}$$

where, s = specific heat capacity of the substance, m = mass

IT DEPENDS ON

i Nature of the substance

What the substance **is**.

ii Its temperature

The **temperature** at which it is heated.

Unit of specific heat capacity

$$\text{J kg}^{-1} \text{K}^{-1}$$

KEY Heat capacity per kilogram is called the specific heat capacity.

2.8 Molar Specific Heat Capacity

DEFINITION

The **molar specific heat capacity** of a substance is its **heat capacity for one mole**. It is the heat that raises the temperature of **one gram mole** of the substance **by one unit**.

$$C = \frac{S}{\mu} = \frac{1}{\mu} \left(\frac{\Delta Q}{\Delta T} \right)$$

MOLAR SPECIFIC HEAT CAPACITY

$$C = \frac{1}{\mu} \frac{\Delta Q}{\Delta T}$$

where, μ = number of moles

i Nature of the substance

ii Its temperature

iii How heat is supplied

Unit of molar specific heat capacity

$\text{J mol}^{-1} \text{K}^{-1}$

• MOLAR SPECIFIC HEAT OF SOLIDS – LAW OF EQUIPARTITION

The **law of equipartition of energy** can predict the molar specific heat capacity of a solid.

DERIVATION

Take a solid made of N atoms. Each atom **vibrates about its mean position**.

1 The average energy for vibration in **one dimension** is:

$$2 \times \frac{1}{2} k_B T = k_B T \quad \dots (i)$$

2 In **three dimensions**, the average energy is $3k_B T$. For **one mole** of the solid, the total energy is:

$$U = 3k_B T \times N_A = 3RT \quad [\because k_B N_A = R] \quad \dots (ii)$$

3 At **constant pressure**:

$$\Delta Q = \Delta U_{\text{int}} + p \Delta V \approx \Delta U_{\text{int}}$$

For a solid, ΔV is negligible.

4 So, using Eq. (ii):

$$C = \frac{\Delta Q}{\Delta T} = \frac{\Delta U_{\text{int}}}{\Delta T} = 3R$$

SUBSTANCE	SPECIFIC HEAT ($\text{J kg}^{-1} \text{K}^{-1}$)	MOLAR SPECIFIC HEAT ($\text{J mol}^{-1} \text{K}^{-1}$)
Aluminium	900.0	24.4
Carbon	506.5	6.1
Copper	386.4	24.5
Lead	127.7	26.5
Silver	236.1	25.5
Tungsten	134.4	24.9

Values for some solids, measured at room temperature and normal atmospheric pressure

2.9 Specific Heat Capacity of Water

In earlier times, the **calorie** was used as the **unit of heat**.

GOOD TO KNOW

Calorie — Old Definition

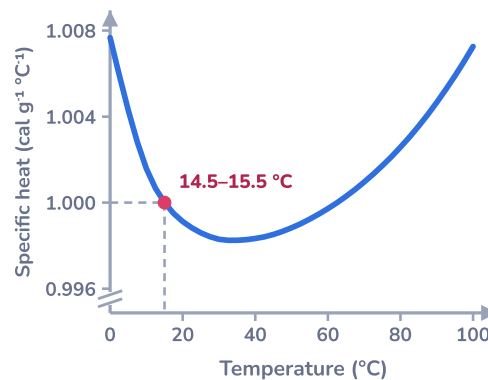
One calorie was the heat that makes **1 g of water** warmer by **1 °C**.

Later it was found that the **specific heat of water changes slightly with temperature**. The graph shows this change.

DEFINITION

One Calorie — Exact Definition

One calorie is the heat that warms **1 g of water** from **14.5 °C to 15.5 °C**.



Specific heat of water vs temperature

NOTE

Heat is a form of energy. So the **joule (J)** is the preferred unit of heat in the SI system.

SPECIFIC HEAT CAPACITY OF WATER

$$s_{\text{water}} = 4186 \text{ J kg}^{-1} \text{ K}^{-1} \quad \text{or} \quad 4.186 \text{ J g}^{-1} \text{ K}^{-1}$$

MECHANICAL EQUIVALENT OF HEAT

DEFINITION

The **mechanical equivalent of heat** is the **work that must be done** to produce **1 calorie of heat**.

It is only a

conversion factor

CONVERSION

$$1 \text{ calorie (heat energy)} = 4.186 \text{ J} \approx 4.2 \text{ J}$$

2.10 Specific Heat Capacities of Gases

The specific heat capacity of a gas **depends on the process**. That is, it depends on the **conditions** under which heat flows between the gas and its surroundings.

A gas has **two main** molar heat capacities:

i At Constant Volume, C_V

The **molar heat capacity at constant volume** is the heat that warms **one mole** of a gas by **1 °C (or 1 K)** at **constant volume**. It is written as C_V .

ii At Constant Pressure, C_p

The **molar heat capacity at constant pressure** is the heat that warms **one mole** of a gas by **1 °C (or 1 K)** at **constant pressure**. It is written as C_p .

REMEMBER

For a gas, $C_p > C_V$ **always**. One mole of a gas needs **more heat** for a 1 °C (1 K) rise at constant pressure than at constant volume.

2.11 Mayer's Formula

For an **ideal gas**, C_p and C_V are related as:

$$C_p - C_V = R \quad \dots (i)$$

This relation is called

Mayer's formula

DERIVATION

Start with the **first law** for **1 mole** of the gas: $\Delta Q = \Delta U + p \Delta V$.

- 1** Heat ΔQ is taken in at **constant volume**, so $\Delta V = 0$.

$$\therefore p \Delta V = 0 \quad \text{and} \quad \Delta Q = C_V \Delta T \quad (\text{for one mole})$$

- 2** Then:

$$C_V = \left(\frac{\Delta Q}{\Delta T} \right)_V = \left(\frac{\Delta U}{\Delta T} \right)_V = \left(\frac{\Delta U}{\Delta T} \right) \quad \dots (ii)$$

The subscript V is dropped in the last step. The U of an ideal gas depends only on temperature, not on volume.

- 3** Now heat ΔQ is taken in at **constant pressure**, so $\Delta Q = C_p \Delta T$.

$$C_p = \left(\frac{\Delta Q}{\Delta T} \right)_p = \left(\frac{\Delta U}{\Delta T} \right)_p + p \left(\frac{\Delta V}{\Delta T} \right)_p$$

The subscript p is dropped from the first term. The U of an ideal gas depends only on T , not on pressure.

- 4** Using Eq. (ii):

$$C_p = C_V + p \left(\frac{\Delta V}{\Delta T} \right)_p \quad \dots (iii)$$

5 For one mole of an ideal gas, $pV = RT$. At constant pressure:

$$p \left(\frac{\Delta V}{\Delta T} \right)_p = R \quad \dots \text{(iv)}$$

6 From Eqs. (iii) and (iv):

$$C_p - C_V = R$$

MAYER'S FORMULA

$$C_p - C_V = R$$

where, C_p = molar specific heat of an ideal gas at **constant pressure**, C_V = its molar specific heat at **constant volume**,
 R = universal gas constant

• HEAT CAPACITY RATIO γ

The ratio of C_p to C_V is written as γ . It is called the **heat capacity ratio**.

$$\gamma = C_p / C_V$$

MOLAR HEAT AT CONSTANT VOLUME

$$C_V = \frac{R}{\gamma - 1}$$

MOLAR HEAT AT CONSTANT PRESSURE

$$C_p = \gamma \frac{R}{\gamma - 1}$$

03 PART 3 Thermodynamic Processes

3.1 Thermodynamic State Variables

DEFINITION

The macroscopic variables whose values **fully describe an equilibrium state** of a system are called **state variables**.

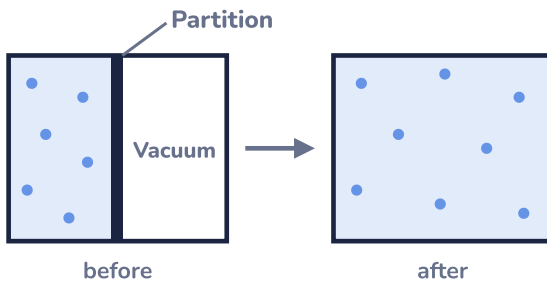
e.g. **Pressure, volume, temperature** and **mass**.

• EQUILIBRIUM STATE

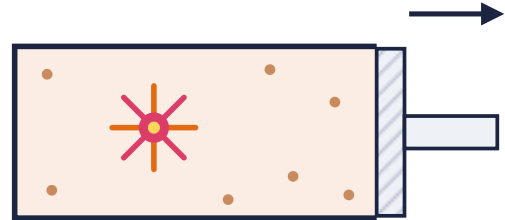
A system need not be in equilibrium at every moment. Given enough time, it **settles** into **mechanical** and **thermal equilibrium**.

EXAMPLE

Petrol vapour and air are mixed and lit by a **spark**. This gas mixture goes through an **explosive chemical reaction**. It is **not in an equilibrium state**. With time, the gas gets a **uniform temperature and pressure**. It then reaches **thermal and mechanical equilibrium** with its surroundings.



(a) Partition removed suddenly: free expansion



(b) A gas mixture in an explosive chemical reaction

• EXTENSIVE AND INTENSIVE VARIABLES

State variables are of **two types**: **extensive** and **intensive**. To tell them apart, imagine a system in equilibrium **divided into two equal parts**.

i Extensive Variables

Variables whose values **become half** in each part are called **extensive variables**. They show the **size** of the system.

e.g. Internal energy (U), volume (V), total mass (M).

ii Intensive Variables

Variables whose values **stay the same** in each part are called **intensive variables**. They **do not depend on the size** of the system.

e.g. Pressure (p), temperature (T), density (ρ).

NOTE

Extensive variables change when the size of the system changes. **Intensive variables** do not change with size.

3.2 Equation of State

The state variables of a system are **not always independent** of each other.

DEFINITION

The **equation of state** of a system is the equation that gives the **relation between its state variables**.

E.G. EQUATION OF STATE OF AN IDEAL GAS (IDEAL GAS EQUATION)

$$pV = \mu RT$$

So, for a **fixed amount** of gas, only **two variables are independent**. For example, p and V , or T and V .

DEFINITION

An **isotherm** is the **pressure–volume curve** of a gas at a **fixed temperature**.

3.3 Quasi-static Process

DEFINITION

Thermodynamic Process

A **thermodynamic process** is a change in the **state of a system**. In it, the **state variables change with time**.

DEFINITION

Quasi-static Process

A **quasi-static process** is an **infinitely slow** process. In it, the system stays in **thermal and mechanical equilibrium** with its surroundings at every stage. Its variables (p, T, V) change only in tiny steps.

It is an **imagined (ideal) idea**. In practice, processes that are **slow enough** are treated as quasi-static.

At every stage of a quasi-static process:

Difference between the pressure of the system and the outside pressure

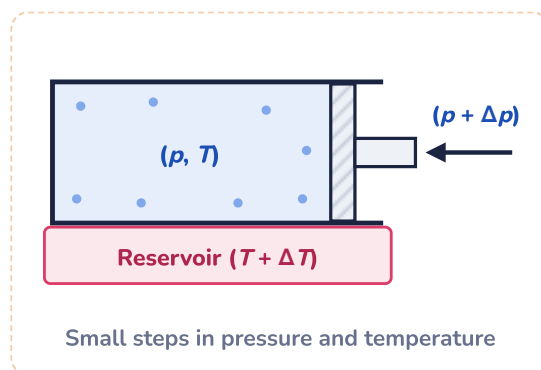
Infinitely small

Temperature difference between the system and its surroundings

Infinitely small

To take a gas from state (p, T) to state (p', T') by a **quasi-static process**:

- 1 Change the **outside pressure** by a very small amount.
- 2 Let the system **make its pressure equal** to that of the surroundings.
- 3 Repeat this **infinitely slowly** until the pressure of the system becomes p' .



To change the **temperature**, keep a **very small temperature difference** between the system and a reservoir. Use a series of reservoirs whose temperatures change **step by step** from T to T' . In the end, the system reaches the temperature T' .

NOTE

A process is **quasi-static** when it has **no accelerated motion of the piston**, **no large temperature gradient** and **no large pressure gradient**.

3.4 Types of Thermodynamic Processes

i Isothermal Process

An **isothermal process** is a process in which the **temperature stays constant**.

e.g. Water at 0 °C freezing into ice at 0 °C.

ii Isobaric Process

An **isobaric process** is a process in which the **pressure stays constant**.

e.g. Water boiling in an open vessel.

iii Isochoric Process

An **isochoric process** is a process in which the **volume stays constant**. So the system does **zero work**.

e.g. Heating a gas kept in a closed, rigid container (fixed walls).

iv Adiabatic Process

An **adiabatic process** is a process in which **no heat flows** into or out of the system.

e.g. Fast compression, like filling a bicycle tube with a hand pump.

(V) CYCLIC AND NON-CYCLIC PROCESSES

Cyclic Process

The initial and final states are the **same**.

Non-cyclic Process

The initial and final states are **different**.

3.5 Isothermal Process

In an **isothermal process**, the **temperature stays constant**. For an ideal gas, the equation of state then gives $pV = \text{constant}$. So the gas obeys **Boyle's law**.

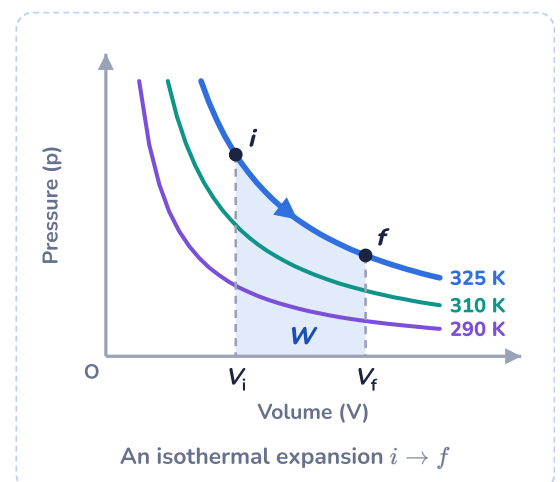
$$p_i V_i = p_f V_f \quad (\text{isothermal process})$$

● P - V DIAGRAM

On a p - V diagram, an **isotherm** is a curve that joins **points at the same temperature**.

The curve $i \rightarrow f$ shows an **isothermal expansion** from V_i to V_f . The arrow shows the direction of the process.

The **shaded area** under $i \rightarrow f$ is the **work done** by the gas.



DERIVATION

The work done in an isothermal process is the **area under the p - V graph**.

1

$$W = \int_{V_i}^{V_f} p \, dV = \mu RT \int_{V_i}^{V_f} \frac{dV}{V} \quad \left[\because pV = \mu RT, \therefore p = \frac{\mu RT}{V} \right]$$

2

$$= \mu RT \left[\ln V \right]_{V_i}^{V_f} = \mu RT [\ln V_f - \ln V_i]$$

3

$$W_{\text{iso}} = \mu RT \ln \left(\frac{V_f}{V_i} \right)$$

WORK DONE IN AN ISOTHERMAL PROCESS

$$W_{\text{iso}} = 2.303 \mu RT \log_{10} \left(\frac{V_f}{V_i} \right)$$

where, μ = number of moles, R = gas constant, T = temperature, V_i and V_f = initial and final volumes of the gas

The temperature of the ideal gas stays constant

$$\therefore \Delta U = 0$$

So, from the first law $\Delta Q = \Delta U + \Delta W$:

$$\Rightarrow \Delta Q = \Delta W = \mu RT \ln \left(\frac{V_f}{V_i} \right)$$

NOTE

In an isothermal change, all the **heat supplied** is used to **do work on the surroundings**. If work is **done on the system**, the system gives out an **equal amount of heat**.

The **sign of the work** depends on the change in volume. There are two cases:

I $V_f > V_i$, so $W > 0$

This is an **isothermal expansion**. The gas **absorbs heat**.

II $V_f < V_i$, so $W < 0$

This is an **isothermal compression**. The surroundings do **work on the gas**, and the gas **releases heat**.

3.6 Adiabatic Process

DEFINITION

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

By the first law, $\Delta Q = \Delta U + \Delta W$... (i). For an adiabatic process, $\Delta Q = 0$.

$$\therefore \Delta U = -\Delta W$$

ADIABATIC PROCESS

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

$$\text{where, } \gamma = \frac{C_p}{C_v}$$

So, when an ideal gas goes adiabatically from (p_i, V_i) to (p_f, V_f) :

$$p_i V_i^\gamma = p_f V_f^\gamma = \text{constant}$$

EXAMPLE

Sound in Air

When **sound travels in air**, the air goes through **compressions and rarefactions**. These are **adiabatic**. The air particles oscillate **very fast**. So heat has no time to enter or leave the region of the oscillating particles.

In an adiabatic process, p and T , and also V and T , are related as:

RELATION BETWEEN P AND T

$$p^{1-\gamma} \cdot T^\gamma = \text{constant}$$

RELATION BETWEEN V AND T

$$V^{\gamma-1} \cdot T = \text{constant}$$

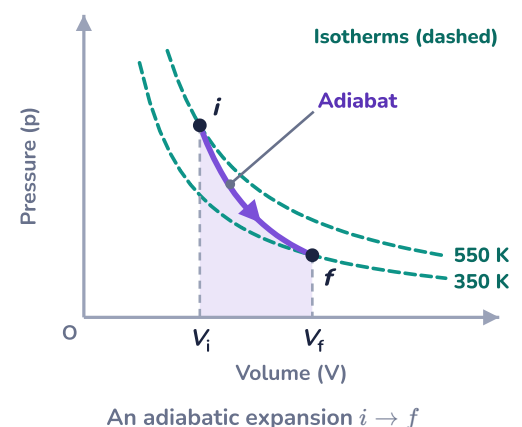
• P - V DIAGRAM

On a p - V diagram, an adiabatic process is shown by an **adiabatic curve**.

DEFINITION

An **adiabat** is a curve that represents an **adiabatic process** on a p - V diagram.

The gas expands from i to f (see the arrow). Its temperature falls from 550 K to 350 K. The adiabat is **steeper** than the isotherms it crosses.



• SLOPE OF AN ADIABAT

Differentiate $pV^\gamma = \text{constant}$:

$$dp V^\gamma + p \gamma V^{\gamma-1} dV = 0$$

$$\Rightarrow \frac{dp}{dV} = -\gamma \left(\frac{p}{V} \right)$$

REMEMBER

Slope of an adiabat $= -\gamma \left(\frac{p}{V} \right)$. This is γ **times the slope of an isotherm** through the same point. Since $\gamma > 1$, an **adiabat is always steeper** than an isotherm.

• SPECIFIC HEAT IN AN ADIABATIC PROCESS

By the definition of specific heat:

$$C = \frac{\Delta Q}{m \Delta T} = \frac{Q}{m \Delta T}, \quad \text{and } \Delta Q = 0 \text{ in an adiabatic process} \Rightarrow C = 0$$

KEY So, during adiabatic expansion or compression, a gas has zero specific heat.

• WORK DONE

DERIVATION

Since $pV^\gamma = K$ (constant), we have $p_i V_i^\gamma = p_f V_f^\gamma = K$.

1 Work done in an adiabatic process:

$$W = \int_{V_i}^{V_f} p dV = \int_{V_i}^{V_f} \frac{K}{V^\gamma} dV$$

2 Integrate:

$$= K \left[\frac{V^{-\gamma+1}}{-\gamma+1} \right]_{V_i}^{V_f} = \frac{K}{1-\gamma} \left[\frac{1}{V_f^{\gamma-1}} - \frac{1}{V_i^{\gamma-1}} \right]$$

3 Put $K = p_f V_f^\gamma$ in the first term and $K = p_i V_i^\gamma$ in the second:

$$W = \frac{1}{1-\gamma} \left[\frac{p_f V_f^\gamma}{V_f^{\gamma-1}} - \frac{p_i V_i^\gamma}{V_i^{\gamma-1}} \right] = \frac{p_i V_i - p_f V_f}{\gamma - 1}$$

4 Since $pV = \mu RT$, we have $p_i V_i = \mu RT_i$ and $p_f V_f = \mu RT_f$.

WORK DONE IN AN ADIABATIC PROCESS

$$W = \frac{\mu R (T_i - T_f)}{\gamma - 1}$$

By the first law, $\Delta Q = \Delta U + \Delta W$. Since $\Delta Q = 0$, we get $\Delta U = -\Delta W$.

i Work Done by the System

$W > 0$, so $T_f < T_i$. The internal energy, and so the **temperature, falls**.

ii Work Done on the System

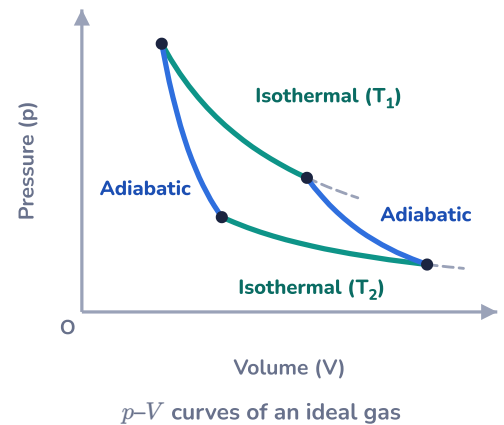
$W < 0$, so $T_f > T_i$. The internal energy, and so the **temperature, rises**.

NOTE

Nearly all real adiabatic processes happen **very fast**. So **no heat can flow** between the system and its surroundings.

e.g. **Sudden bursting** of a bicycle tube, and **sound waves** travelling in air.

The figure shows p - V curves of an ideal gas. **Two adiabats join two isotherms**.



3.7 Isochoric Process

DEFINITION

An **isochoric process** is a process in which the **volume of the system stays constant**.

i Heat added to the system

The **pressure increases**.

ii Heat taken out of the system

The **pressure decreases**.

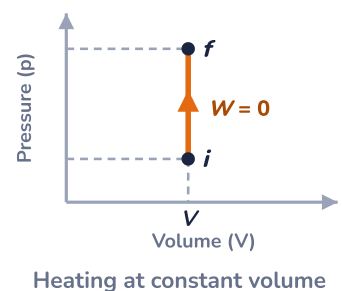
EQUATION OF STATE

Here p and T change, but V stays constant. The gas obeys **Gay-Lussac's law**: $p \propto T \Rightarrow p_1/T_1 = p_2/T_2$ (where $V = \text{constant}$).

$$\Rightarrow \Delta W = p \Delta V = 0 \quad [\because \Delta V = 0]$$

KEY So the work done is zero: $\Delta W = 0$.

The first law then gives $\Delta Q = \Delta U$. So in an isochoric process, the heat given or taken changes **only** the **internal energy and temperature**.



$$\Delta U = \mu C_V \Delta T$$

3.8 Isobaric Process

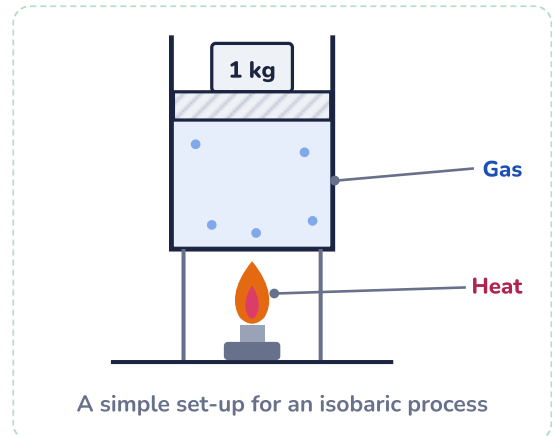
DEFINITION

An **isobaric process** is a thermodynamic process in which a system goes through a physical change at **constant pressure**.

EXAMPLE

A gas is **heated** in a piston–cylinder. A **fixed weight** rests on the piston, so the pressure stays the same.

Let the **pressure** p of a gas stay constant while its volume changes from V_i to V_f . The work done by the gas is:



$$W = \int_{V_i}^{V_f} p dV = p \int_{V_i}^{V_f} dV = p(V_f - V_i)$$

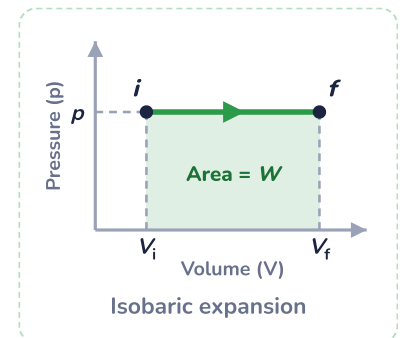
WORK DONE IN AN ISOBARIC PROCESS

$$W = \mu R (T_f - T_i)$$

$[\because pV = \mu RT]$

NOTE

Here the gas temperature does not stay fixed. So its **internal energy changes too**. In an isobaric process, the heat absorbed goes **partly into internal energy** and **partly into doing work**.



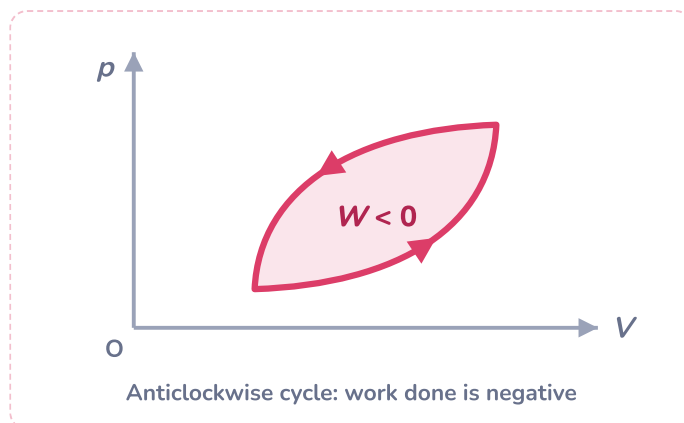
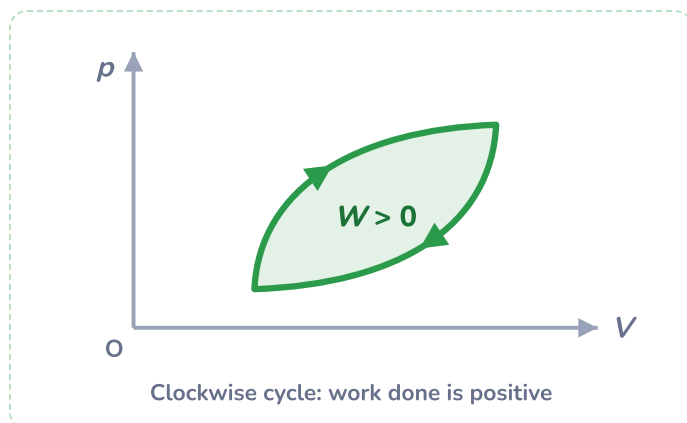
3.9 Cyclic Process

DEFINITION

A **cyclic process** is a process, or a series of processes, that brings the system **back to its initial state**. Heat and work are exchanged on the way.

The initial and final states of a cyclic process are the **same**. So:

$$\Delta U = U_f - U_i = 0$$



For a cyclic process, the p - V graph is a **closed curve**. The **area enclosed** by the curve equals the **work done**. The first law is $\Delta Q = \Delta U + \Delta W$. For a cyclic process:

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

KEY The heat supplied to the system is turned into work done, and work into heat.

• CALCULATION OF WORK DONE

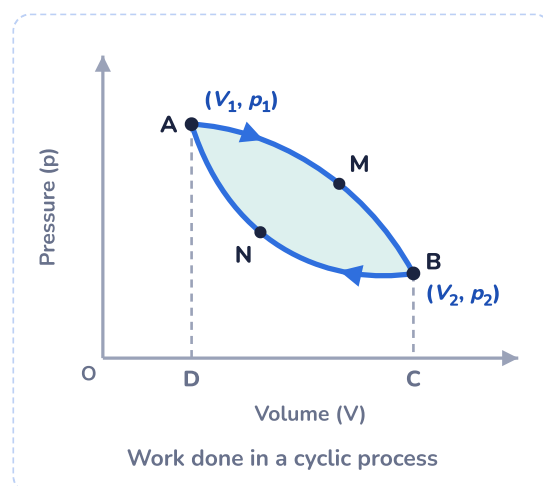
Let $A(V_1, p_1)$ be the **initial state** of a gas and $B(V_2, p_2)$ its **final state**. The gas goes from A to B by the upper path AMB . It comes back from B to A by the lower path BNA .

Work done by the gas in the **expansion** from A to B :

$$W_1 = \text{area } AMBCDA$$

Work done in the **compression** from B to A is $W_2 = -\text{area } BNADCB$. So the **net work done** by the gas in the cycle is:

$$\begin{aligned} W_{A \rightarrow B \rightarrow A} &= W_1 + W_2 \\ &= \text{area } AMBCDA - \text{area } BNADCB \\ &= \text{area } AMBNA \end{aligned}$$



KEY The work done in a cyclic process equals the area enclosed by the loop.

Cycle goes **clockwise**

Work done is positive

Cycle goes **anticlockwise**

Work done is negative

NOTE

Cyclic processes are very important. **Engines and refrigerators** work in cycles. In each cycle, the system uses **incoming heat** to do work and then **returns to its initial state**.

DEFINITION

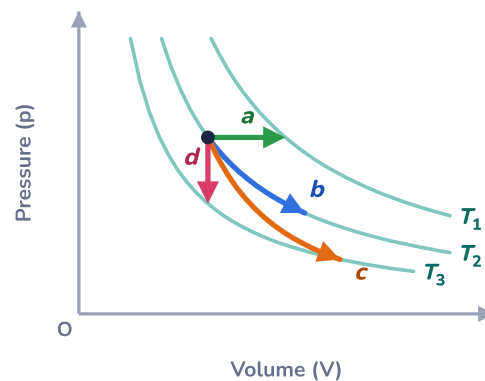
Non-cyclic Process

A **non-cyclic process** is a process whose **final state differs from its starting state** after a series of changes.

3.10 Summary of Thermodynamic Processes

All four processes can be drawn together on a **single p - V diagram**. Each path starts from the same point on isotherm T_2 :

- ◆ Path **a**: **isobaric** (pressure constant)
- ◆ Path **b**: **isothermal** (along isotherm T_2)
- ◆ Path **c**: **adiabatic** (steeper than the isotherm)
- ◆ Path **d**: **isochoric** (volume constant)



PROCESS	CONSTANT QUANTITY	PATH	HEAT / WORK / INTERNAL ENERGY
Isobaric	p	a	$\Delta Q = \mu C_p \Delta T$, $\Delta W = p \Delta V$, $\Delta U = \mu C_V \Delta T$
Isochoric	V	d	$\Delta Q = \Delta U = \mu C_V \Delta T$, $\Delta W = 0$
Isothermal	T	b	$\Delta Q = \Delta W = \mu RT \ln(V_f/V_i)$, $\Delta U = 0$
Adiabatic	pV^γ	c	$\Delta Q = 0$, $\Delta W = -\Delta U$

Thermodynamic processes at a glance (μ = number of moles)

04

PART 4

Second Law and Carnot Engine

4.1 Second Law of Thermodynamics

Many processes obey **energy conservation** but **never happen in nature**.

EXAMPLE

A **ball lies on the floor**. In principle, it could take some heat from the ground and **jump up by itself**. The **first law** (energy conservation) allows this. But it **never happens** in nature.

So some **other basic law of nature** must forbid such a process, even though it conserves energy.

DEFINITION

The **second law of thermodynamics** is the law of nature that **limits what the first law allows**.

THE SECOND LAW SETS A BASIC LIMIT ON

i Heat engine

The **efficiency** of a heat engine.

ii Refrigerator

The **coefficient of performance** of a refrigerator.

The **Kelvin–Planck** and **Clausius** statements rule out a **perfect heat engine** and a **perfect refrigerator**, respectively.

• KELVIN–PLANCK STATEMENT

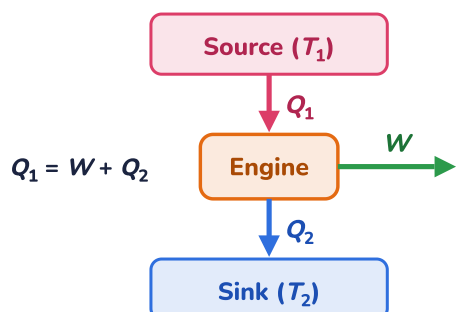
LAW

No process is possible whose only result is to take heat from a reservoir and **change all of it into work**.

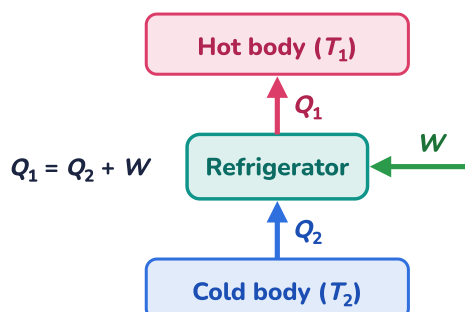
• CLAUSIUS STATEMENT

LAW

No process is possible in which the only result is that heat **flows from a colder body to a hotter body**.



Heat engine: by Kelvin–Planck, Q_2 can never be zero



Refrigerator: by Clausius, W can never be zero

• PMM1 AND PMM2

i PMM1

A **perpetual motion machine of the first kind (PMM1)** is a device that breaks the **first law**, because it creates energy.

ii PMM2

A **perpetual motion machine of the second kind (PMM2)** is a device that breaks the **second law**.

4.2 Reversible Process

DEFINITION

A **reversible process** is a process that can be run backwards so that **both the system and its surroundings** return exactly to their initial states. **No other change** is left anywhere in the universe.

i Heat

If heat is **absorbed** in the direct process, the **same amount of heat** is **given out** in the reverse process.

ii Work

Suppose the direct process needs work to be done **on** the working substance. Then, in the reverse process, the substance does the **same amount of work** (work is done **by** it).

• CONDITIONS FOR REVERSIBILITY

- I There must be **no dissipative forces** at all, such as **friction, viscosity and electrical resistance**.
- II The direct and reverse processes must take place **infinitely slowly**.
- III The temperature of the system must **never differ much** from that of its surroundings.

• EXAMPLES OF REVERSIBLE PROCESSES

- ◆ All **isothermal** and **adiabatic** changes, when they are done **very slowly**.
- ◆ Ice **absorbs some heat and melts**. When the same heat is removed, the water formed **freezes back** into ice.
- ◆ A spring is stretched or compressed **extremely slowly**, so that no oscillations start.
- ◆ A **perfectly elastic ball** falls on a **perfectly elastic horizontal floor**. It rises back to its starting height.
- ◆ **Very slow** evaporation or condensation.

REMEMBER

The conditions for a reversible process can **never be fully met** in practice. So a reversible process is only an **ideal idea**. Real processes always **lose some heat** through friction, conduction, radiation, etc.

• WHY AN IDEAL ENGINE IS NOT POSSIBLE

CONCEPT

Rule of Nature

Irreversibility is the rule of nature. A change that has taken place in the universe **can never be exactly undone**.

KEY That is why no engine can have **100% efficiency**.

If **all resistive forces** could be removed, the efficiency of an engine would be as **high as possible**.

GOOD TO KNOW

Some **trains have been proposed** that will run inside **vacuum tunnels**. This removes **air friction** and so raises the efficiency of the engine.

4.3 Irreversible Process

DEFINITION

An **irreversible process** is any process that **cannot be reversed exactly**.

All Natural Processes

Conduction, radiation and radioactive decay are **irreversible**.

All Practical Processes

Free expansion, Joule–Thomson expansion and electrical heating of a wire are also **irreversible**.

• TWO MAIN CAUSES OF IRREVERSIBILITY

i Non-equilibrium States

Many processes take the system to **non-equilibrium states**. **e.g.** Diffusion of gases, decay of organic matter.

ii Dissipative Forces

Many processes involve **dissipative forces**, such as **friction, viscosity and inelasticity**.

• EXAMPLES OF IRREVERSIBLE PROCESSES

- I** A **steel ball** falls on an **inelastic lead sheet**. Its **kinetic energy changes into heat**, and this heat warms the lead sheet. The heat **never changes back** into kinetic energy of the ball.
- II** A spring is stretched **suddenly and fast**. This sets up **vibrations** in it, and part of the energy is **dissipated** (lost).
- III** **Sudden** expansion or contraction, and **fast** evaporation or condensation.
- IV** An **electric current** flowing through a **resistor**.
- V** **Heat flow** between bodies at **different temperatures**.
- VI** The **Joule–Thomson effect**. If the gas flow is reversed, the same **cooling or heating effect is not seen**.

4.4 Carnot Engine and Carnot Cycle

DEFINITION

A **Carnot engine** is a **reversible heat engine** that works between **two temperatures**: a **source** at T_1 and a **sink** at T_2 .

Ideal heat engine suggested by

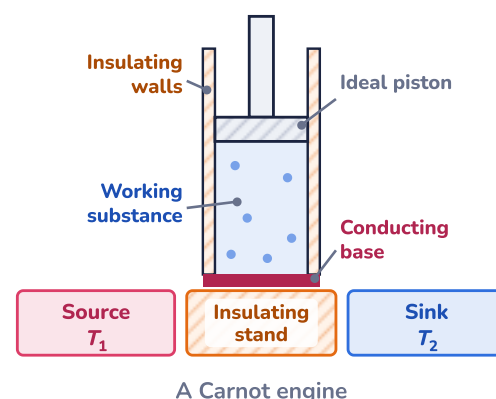
Sadi Carnot in 1824

NOTE

A Theoretical Engine

It is a **theoretical engine**. It has **none of the defects** of a real engine.

It **cannot be built** in practice. But it serves as a **standard**. The performance of any real engine is judged against it.



• MAIN PARTS OF A CARNOT ENGINE

i Source

A **hot reservoir** at temperature T_1 , with conducting walls. Its **thermal capacity is infinite**. So we can draw any amount of heat from it, and its temperature stays the same.

ii Sink

A **cold reservoir** at temperature T_2 . Its **thermal capacity is also infinite**. So it can take in any amount of heat with no change in its temperature.

iii Cylinder

It has a **conducting base** and **insulating walls**. It holds the working substance. An **insulating, frictionless piston** is fitted in it, as shown in the figure.

iv Working Substance

An **ideal gas** is used as the working substance in the cylinder.

v Insulating Stand

The base of the cylinder can be placed on this stand. It **isolates the gas completely** from the surroundings.

• CARNOT CYCLE

DEFINITION

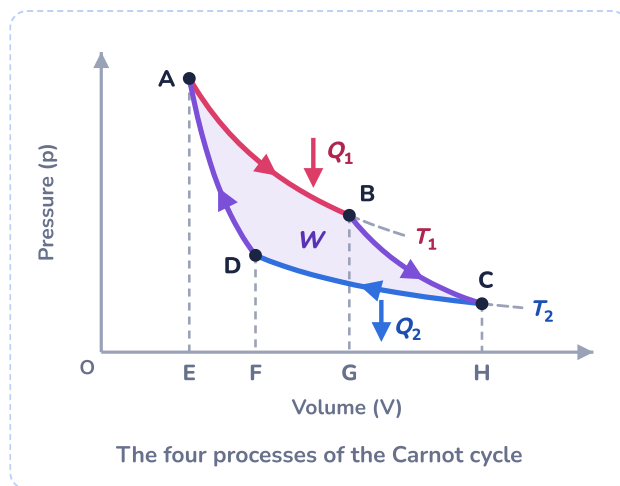
The cycle that the **working substance** of a Carnot engine goes through is called the **Carnot cycle**. It has **four strokes**.

The four states of the gas are:

- ◆ $A (p_1, V_1, T_1)$ and $B (p_2, V_2, T_1)$
- ◆ $C (p_3, V_3, T_2)$ and $D (p_4, V_4, T_2)$

E, F, G and H are the points on the V -axis just below A, D, B and C . The arrows show the direction of each stroke.

In this cycle, Q_1, Q_2 and W_1 to W_4 are written as positive amounts. The words **by/on** and **absorbed/released** give the direction.



1 First Stroke — Isothermal Expansion (Curve AB)

One mole of an **ideal gas** is the working substance. The cylinder is placed on the **source**. The gas **expands slowly** at the constant temperature T_1 . The work done by the gas equals the **heat absorbed**.

$$W_1 = Q_1 = \int_{V_1}^{V_2} p dV = RT_1 \log_e \left(\frac{V_2}{V_1} \right)$$

On the indicator diagram

$$W_1 = \text{area } ABGEA$$

2 Second Stroke — Adiabatic Expansion (Curve BC)

The cylinder is now placed on the **insulating stand**. The gas **expands adiabatically** until its temperature falls from T_1 to T_2 .

$$W_2 = \int_{V_2}^{V_3} p dV = \frac{R}{(\gamma - 1)} (T_1 - T_2)$$

On the indicator diagram

$$W_2 = \text{area } BCHGB$$

3 Third Stroke — Isothermal Compression (Curve CD)

The cylinder is placed on the **sink**. The gas is **compressed** at the constant temperature T_2 . The work done on the gas equals the **heat released** by it.

$$W_3 = Q_2 = - \int_{V_3}^{V_4} p dV = -RT_2 \log_e \frac{V_4}{V_3} = RT_2 \log_e \frac{V_3}{V_4}$$

On the indicator diagram

$$W_3 = \text{area } CDFHC$$

4 Fourth Stroke — Adiabatic Compression (Curve DA)

The cylinder is placed on the **insulating stand** again. The **compression continues** until the gas returns to its **initial state**.

$$W_4 = - \int_{V_4}^{V_1} p dV = - \frac{R}{\gamma - 1} (T_2 - T_1) = \frac{R}{\gamma - 1} (T_1 - T_2)$$

On the indicator diagram

$$W_4 = \text{area } ADFEA$$

4.5 Efficiency of a Carnot Engine

DEFINITION

The **efficiency** of an engine is the **ratio of the work done** by it to the **heat supplied** to it.

$$\eta = \frac{\text{Work done}}{\text{Heat input}} = \frac{W_{\text{net}}}{Q_1}$$

DERIVATION

In the four strokes, W_1 and W_2 are **done by the gas**. W_3 and W_4 are **done on the gas**.

1 **Net work done** in one complete cycle:

$$W = W_1 + W_2 + (-W_3) + (-W_4) = W_1 - W_3 = \text{area } ABCDA \quad [\text{as } W_2 = W_4]$$

2 So:

$$\therefore \eta = \frac{W}{Q_1} = \frac{W_1 - W_3}{W_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1}$$

3 Put the values of Q_1 and Q_2 from the strokes:

$$\eta = 1 - \frac{RT_2 \log_e(V_3/V_4)}{RT_1 \log_e(V_2/V_1)}$$

4 Points B and C lie on the **same adiabat**:

$$\therefore T_1 V_2^{\gamma-1} = T_2 V_3^{\gamma-1} \quad \text{or} \quad \frac{T_1}{T_2} = \left(\frac{V_3}{V_2} \right)^{\gamma-1} \quad \dots (i)$$

5 Points D and A also lie on the **same adiabat**:

$$\therefore T_1 V_1^{\gamma-1} = T_2 V_4^{\gamma-1} \quad \text{or} \quad \frac{T_1}{T_2} = \left(\frac{V_4}{V_1} \right)^{\gamma-1} \quad \dots (ii)$$

6 From Eqs. (i) and (ii):

$$\frac{V_3}{V_2} = \frac{V_4}{V_1} \quad \text{or} \quad \frac{V_3}{V_4} = \frac{V_2}{V_1} \Rightarrow \log_e \left(\frac{V_3}{V_4} \right) = \log_e \left(\frac{V_2}{V_1} \right)$$

7 So the two log terms in step 3 cancel, and only T_2/T_1 is left.

EFFICIENCY OF A CARNOT ENGINE

$$\eta = 1 - \frac{T_2}{T_1}$$

where, T_1 = temperature of the source, T_2 = temperature of the sink

• KEY POINTS ABOUT EFFICIENCY

- 1 The efficiency of a Carnot engine **depends only on the temperatures** of the source and the sink.
- 2 It **does not depend on the nature** of the working substance.
- 3 It would be **100%** only if the sink were at **0 K**. A sink at 0 K **cannot be reached** in practice. So 100% efficiency is **not possible**.

4.6 Carnot's Theorem

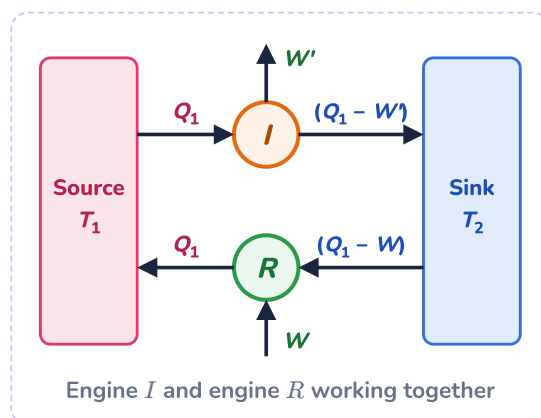
Carnot's theorem has two parts:

- I No heat engine can be **more efficient than a Carnot engine** working between the same two temperatures. These are T_1 of the hot reservoir (**source**) and T_2 of the cold reservoir (**sink**).
- II The efficiency of a Carnot engine is **independent of the nature** of the working substance.

• PROOF OF PART (I)

Take a **reversible Carnot engine** R and an **irreversible heat engine** I . Both work between the **same source** at T_1 and the **same sink** at T_2 .

The two engines are **coupled**. Engine I runs as a **heat engine**. Engine R runs backwards as a **refrigerator**.



DERIVATION

SETUP – IN ONE COMPLETE CYCLE

- Engine I takes heat Q_1 from the source. It gives work W' and releases the rest, $(Q_1 - W')$, to the sink.
- Engine R returns the same heat Q_1 to the source when work W is done on it. So it takes heat $(Q_1 - W)$ from the sink.

1 **Assume** that engine R is less efficient than engine I , that is, $\eta_R < \eta_I$.

2 Then, for the same Q_1 :

$$W < W' \quad \text{and} \quad (Q_1 - W) > (Q_1 - W')$$

3 So the coupled I – R system, as a whole, takes the heat

$$(Q_1 - W) - (Q_1 - W') = (W' - W)$$

from the sink. It gives the **same amount of work** $(W' - W)$ in one cycle. The source has **no net change**.

4 This is **against the second law** of thermodynamics (Kelvin–Planck statement). So the assumption $\eta_I > \eta_R$ is **wrong**.

KEY No engine can be more efficient than a Carnot engine. This proves part (i) of Carnot's theorem.

4.7 Coefficient of Performance

For a **Carnot refrigerator** (see the refrigerator diagram in topic 4.1):

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2} \Rightarrow \frac{Q_1 - Q_2}{Q_2} = \frac{T_1 - T_2}{T_2} \quad \text{or} \quad \frac{Q_2}{Q_1 - Q_2} = \frac{T_2}{T_1 - T_2}$$

COEFFICIENT OF PERFORMANCE

$$\beta = \frac{T_2}{T_1 - T_2}$$

where, T_1 = temperature of the surroundings, T_2 = temperature of the cold body, $Q_1 - Q_2 = W$ = work done on the refrigerator

NOTE

Clearly, $\beta = 0$ **when** $T_2 = 0$. So the coefficient of performance is **zero** if the cold body is at **absolute zero**.