

Topic 6.1 Assumptions of the Kinetic Theory of Gases

Thermodynamics

Thermodynamics is the branch of physics that deals with the relationships and conversions between heat and other forms of energy. It encompasses the principles governing the behaviour of systems at macroscopic scales, such as temperature, pressure and volume.

Significance

Almost all the raw energy available for our use is liberated in the form of heat, so thermodynamics plays a key role in technology.

LQ 1 starts here — What is Kinetic Molecular Theory? Write its assumptions.

Kinetic Theory of Gases

It is a fundamental theory which explains the behaviour of gases on the basis of the motion of their constituent particles. It links macroscopic properties such as pressure, temperature and volume to that motion.

Assumptions

Gas Particles are in Constant, Random Motion

Gas molecules are in perpetual, random motion. They move in straight lines until they collide with either another molecule or the walls of the container.

Negligible Volume of Gas Particles

The volume of the individual gas molecules is negligible as compared to the total volume of the gas, so the particles are considered point masses.

No Intermolecular Forces

There are no attractive or repulsive forces between the gas molecules. The particles exert no force on each other except during collisions.

Elastic Collisions

The collisions between gas molecules, and with the walls of the container, are perfectly elastic. There is no net loss of kinetic energy during collisions.

Large Number of Particles

A gas contains a large number of particles. This large number allows statistical methods to be used to describe the properties of the gas.

Average Kinetic Energy is Proportional to Temperature

The average kinetic energy of the gas particles is directly proportional to the absolute temperature. As the temperature increases, the speed of the gas particles also increases.

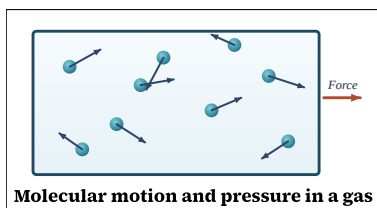
Pressure due to Particle Collisions

The pressure exerted by a gas on the walls of its container is due to the collisions of the gas particles with the walls. The force exerted during collisions generates the pressure.

Time of Collisions is Negligible

The time interval of a collision between gas particles is extremely short as compared to the time between collisions.

Diagram



LQ 1 ends here

LQ 2 starts here — What are the limitations of kinetic molecular theory? Explain the conditions where a real gas behaves as an ideal gas. Also prove that $PV = nRT$.

Limitations of the Kinetic Molecular Theory

The assumptions hold true for ideal gases only. Real gases show deviations because of intermolecular forces and finite molecular volume, especially at high pressure and low temperature.

Equation of State for an Ideal Gas

A gas that obeys the kinetic theory of gases is termed an ideal gas. Its equation of state is

$$PV = nRT$$

Here P is the pressure, V the volume, n the number of moles and T the absolute temperature of the gas.

Universal Gas Constant $R = 8.3145 \text{ J mol}^{-1}\text{K}^{-1}$

Meaning

The product of pressure and volume is directly proportional to the absolute temperature for an ideal gas.

Real Gas Behaving Like an Ideal Gas

The number of moles is the mass of the gas divided by its molar mass.

$$n = \frac{m}{M}$$

Putting this value in the equation of state

$$PV = \frac{m}{M}RT$$

$$PM = \frac{m}{V}RT$$

The density of the gas is its mass per unit volume, so the ratio m/V is the density ρ of the gas.

$$PM = \rho RT$$

Rearranging it for the density of the gas

$$\rho = \frac{PM}{RT}$$

$$\rho = \frac{M}{R} \times \frac{P}{T}$$

The molar mass of a gas and the general gas constant are both fixed quantities.

$$\frac{M}{R} = \text{constant}$$

So the density varies only with the ratio of the pressure to the absolute temperature.

$$\rho \propto \frac{P}{T}$$

Conclusion

The density is low at low pressure and high temperature, so the molecules stay far apart and the intermolecular forces become negligible. A real gas therefore behaves like an ideal gas at low pressure and high temperature.

Ideal Gas Equation in Terms of Boltzmann Constant

A mole is the number of atoms or molecules per unit Avogadro's number.

$$N_A = 6.02 \times 10^{23}$$

$$n = \frac{N}{N_A}$$

Here N is the number of atoms or molecules.

Substituting this in the equation of state

$$PV = \frac{N}{N_A}RT$$

$$PV = N \times \frac{R}{N_A} \times T$$

Boltzmann Constant

The gas constant for a single molecule is termed Boltzmann constant.

$$k_B = \frac{R}{N_A} = 1.38 \times 10^{-23} \text{ J K}^{-1}$$

Putting the Boltzmann constant for the ratio of the gas constant to Avogadro's number

Result

$$PV = Nk_B T$$

LQ 2 ends here

LQ 3 starts here — Discuss gas laws.

Gas Laws

Pressure, volume and temperature are the state functions which describe the quantity of a gas. When one of them changes the second changes with it while the third is kept constant, and the laws which relate them mutually for an ideal gas are termed as gas laws.

Boyle's Law

Pioneer Robert Boyle (1662)

Statement

For a fixed mass of an ideal gas, the pressure exerted by a gas varies inversely with the volume occupied by the gas at constant temperature.

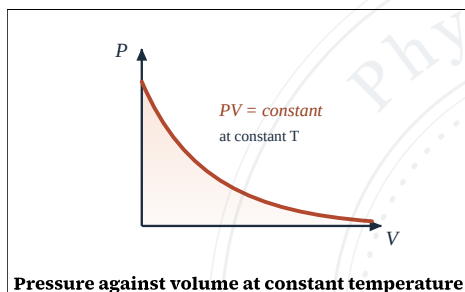
Mathematically

$$P \propto \frac{1}{V}$$

$$PV = \text{constant}$$

$$P_1 V_1 = P_2 V_2$$

Graph



Charles' Law

Pioneer Jacques Charles (1870)

Statement

The volume of a given mass of a gas at constant pressure is directly proportional to the absolute temperature.

Mathematically

$$V \propto T$$

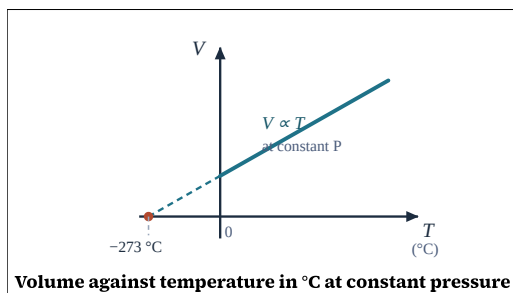
$$\frac{V}{T} = \text{constant}$$

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

Absolute Zero

The graph is a straight line which, extended backward, cuts the temperature axis at -273°C , that is at 0 K.

Graph



Joseph Gay-Lussac's Law

Statement

For a fixed mass of an ideal gas, the pressure exerted by a gas varies directly with the absolute temperature of the gas at constant volume.

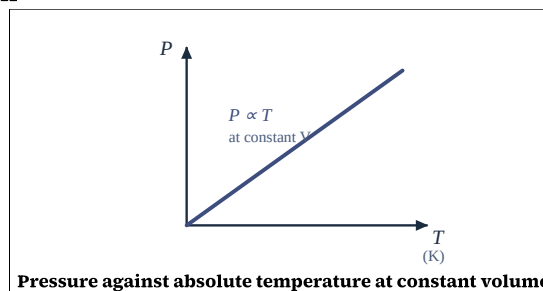
Mathematically

$$P \propto T$$

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

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

Graph



LQ 3 ends here

Thermal Equilibrium

When two bodies are at the same temperature, the thermal energy of each body is equal. As a result there is no driving force for heat transfer between them, and they remain in thermal equilibrium.

Example

When a metal spoon is put into a hot cup of coffee, the coffee is hotter at first and heat flows from the coffee to the spoon. Eventually both reach the same temperature, there is no net heat flow, and they are said to be in thermal equilibrium.

Book Examples

Example 6.1.1 One mole of an ideal gas is at a temperature of 300 K. If the Boltzmann constant is $1.38 \times 10^{-23} \text{ J K}^{-1}$, calculate the volume of the gas at a pressure of 1 atm. [1 atm = 101325 Pa]

Given Data

$$n = 1 \text{ mol}$$

$$T = 300 \text{ K}$$

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

$$N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$$

$$P = 1 \text{ atm} = 101325 \text{ Pa}$$

To Find

Volume of the gas $V = ?$

Formula

$$PV = nRT$$

$$R = N_A k_B$$

$$V = \frac{n N_A k_B T}{P}$$

Solution

Putting the values in the formula

$$V = \frac{1 \times 6.02 \times 10^{23} \times 1.38 \times 10^{-23} \times 300}{101325} = 0.0245 \text{ m}^3$$

Result $V = 0.0245 \text{ m}^3$

Short Questions

SQ 6.1.1 Why does thermodynamics play a key role in technology?

Role in Technology

Almost all the raw energy available for our use is liberated in the form of heat.

Result

Thermodynamics deals with the conversion of that heat into other forms of energy, so it governs the working of every device that runs on fuel.

SQ 6.1.2 Show that the density of an ideal gas is directly proportional to its pressure and inversely proportional to its absolute temperature.

Density of an Ideal Gas

The number of moles is the mass of the gas divided by its molar mass.

$$n = \frac{m}{M}$$

Putting this in the equation of state gives

$$PV = \frac{m}{M}RT$$

$$PM = \frac{m}{V}RT$$

The ratio m/V is the density ρ of the gas, therefore

$$PM = \rho RT$$

$$\rho = \frac{M}{R} \times \frac{P}{T}$$

The molar mass of the gas and the general gas constant are both fixed quantities.

$$\frac{M}{R} = \text{constant}$$

Result $\rho \propto \frac{P}{T}$

SQ 6.1.3 Why can statistical methods be used to describe the properties of a gas?

Statistical Method

A gas contains a large number of particles moving at random.

Result

The path of a single molecule cannot be followed, but the average behaviour of so many particles is predictable, so statistical methods describe pressure, volume and temperature.

SQ 6.1.4 How are the three gas laws obtained from the ideal gas equation?

Gas Laws from the Ideal Gas Equation

$$PV = nRT$$

Holding one of the three state variables constant leaves a law between the other two.

- Boyle's law: keeping T constant makes PV constant.
- Charles' law: keeping P constant makes V/T constant.
- Gay-Lussac's law: keeping V constant makes P/T constant.

SQ 6.1.5 Why must the mass of the gas be fixed in each of the gas laws?

Fixed Mass of Gas

Each gas law relates two state variables while the third is held constant, and this is possible only if the number of moles n is unchanged.

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

Result

Adding or removing gas alters n , so the product PV/T no longer stays constant.

SQ 6.1.6 A fixed mass of gas in a rigid cylinder is heated from 300 K to 600 K. What happens to its pressure?

Pressure at Constant Volume

The volume is fixed, so Gay-Lussac's law applies.

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

$$P_2 = P_1 \times \frac{600}{300} = 2P_1$$

Result

Doubling the absolute temperature doubles the pressure.

SQ 6.1.7 Show that the universal gas constant is the product of Avogadro's number and Boltzmann constant.

Universal Gas Constant

Boltzmann constant is the gas constant for a single molecule.

$$k_B = \frac{R}{N_A}$$

$$R = N_A k_B$$

Check

The product $6.02 \times 10^{23} \times 1.38 \times 10^{-23}$ comes to about 8.31, which is the value of the universal gas constant.

SQ 6.1.8 A metal spoon is put into a cup of hot coffee. Explain how the two reach thermal equilibrium.

Reaching Thermal Equilibrium

The coffee is hotter than the spoon, so heat flows from the coffee to the spoon.

Finally

Both reach the same temperature, the thermal energy of each is then equal and there is no net heat flow, so they are in thermal equilibrium.

MCQ 6.1.1 Almost all the raw energy available for our use is liberated in the form of:

- | | |
|-------------------|---------------|
| A light | B sound |
| C electric charge | D heat |

Solution: Almost all the raw energy we can use is released as heat, which is why thermodynamics plays a key role in technology.

MCQ 6.1.2 If the absolute temperature of a gas is doubled, the average kinetic energy of its molecules becomes:

- | | |
|--------------|-----------------|
| A half | B double |
| C four times | D unchanged |

Solution: The average kinetic energy is directly proportional to the absolute temperature, so doubling T doubles it.

MCQ 6.1.3 Which one of the following is NOT an assumption of the kinetic theory of gases?

- | | |
|---|---|
| A the collisions are perfectly elastic | B the volume of the molecules is negligible |
| C the motion of the molecules is random | D the molecules attract one another strongly |

Solution: The theory assumes no attractive or repulsive forces between the molecules except during a collision.

MCQ 6.1.4 At a constant temperature, the density of an ideal gas is directly proportional to its:

- | | |
|------------------------|-------------------|
| A pressure | B volume |
| C absolute temperature | D molar mass only |

Solution: From $PM = \rho RT$, at constant T the density ρ is directly proportional to the pressure P .

MCQ 6.1.5 An ideal gas at 27 °C is compressed to half its volume at constant temperature. Its pressure becomes:

- | | |
|-----------------|--------------|
| A half | B four times |
| C double | D unchanged |

Solution: At constant temperature $P_1V_1 = P_2V_2$, so halving the volume doubles the pressure.

MCQ 6.1.6 The number of molecules in 0.50 mole of a gas is about:

- | | |
|---|--------------------------|
| A 3.01×10^{23} | B 6.02×10^{23} |
| C 1.20×10^{24} | D 1.38×10^{-23} |

Solution: The number of molecules is $N = nN_A = 0.50 \times 6.02 \times 10^{23} = 3.01 \times 10^{23}$.

MCQ 6.1.7 In the equation $PV = Nk_B T$, the symbol N stands for the:

- | | |
|--|--------------------------------|
| A number of moles of the gas | B Avogadro's number |
| C number of molecules of the gas | D molar mass of the gas |

Solution: N is the number of atoms or molecules, obtained from $n = N/N_A$.

MCQ 6.1.8 For a fixed mass of gas at constant temperature, the graph of P against $1/V$ is:

- | | |
|----------------------------|--|
| A a hyperbola | B a parabola |
| C a horizontal line | D a straight line through the origin |

Solution: Boyle's law gives $P \propto 1/V$, so plotting P against $1/V$ gives a straight line through the origin.

MCQ 6.1.9 A fixed mass of gas at 27°C and 1 atm is heated in a rigid vessel to 327°C . Its pressure becomes:

- | | |
|---------------------------|---|
| A 1.5 atm | B 2 atm |
| C 4 atm | D 12 atm |

Solution: The volume is fixed, so P/T is constant. The temperatures are 300 K and 600 K , so the pressure doubles to 2 atm .

MCQ 6.1.10 When a metal spoon is placed in hot coffee, heat flows until:

- | | |
|--|-------------------------------------|
| A the spoon melts | B the coffee freezes |
| C both are at the same temperature | D the spoon changes its mass |

Solution: Heat flows from the coffee to the spoon until both reach the same temperature and are in thermal equilibrium.

Topic 6.2 Internal Energy

LO 4 starts here — What is internal energy? Explain briefly. Also explain heat and work done in thermodynamics.

Definition

The sum of all forms of molecular energies, kinetic and potential, of a substance is termed as its internal energy.

Ideal Gas as the Working Substance

In the study of thermodynamics an ideal gas is usually taken as the working substance. The molecules of an ideal gas are mere mass points which exert no forces on one another, so the internal energy of an ideal gas system is generally the translational kinetic energy of its molecules.

Relation with Temperature

The temperature of a system is defined as the average kinetic energy of its molecules. Hence for an ideal gas system the internal energy is directly proportional to its temperature.

Average Kinetic Energy

According to the kinetic theory of gases the average kinetic energy of the gas molecules is

$$\langle KE \rangle = \frac{3}{2} k_B T$$

$$\left\langle \frac{1}{2} m v^2 \right\rangle = \frac{3}{2} k_B T$$

Here k_B is Boltzmann constant.

Rise in Temperature

The rise in temperature of an object reflects an increase in the internal kinetic energy of its particles. It occurs due to the absorption of heat energy, which raises the average kinetic energy of the particles.

Diatomic Molecules

A diatomic gas molecule has both translational and rotational kinetic energy. It also has vibrational energy associated with the spring-like bond between its atoms.

Processes That Change Internal Energy

Heating

Heat added to the system raises the average kinetic energy of its particles, and thereby its temperature.

Adiabatic Compression or Expansion

The volume of the gas changes with no heat exchanged with the surroundings.

Phase Changes

Heat energy changes the state of matter without changing the temperature.

Function of State

Internal energy is a function of state. It does not depend on the path followed but only on the initial and final states of the system.

Analogy

Internal energy is similar to gravitational potential energy. Like potential energy, it is the change in internal energy and not its absolute value which is important.

Short Questions

SQ 6.2.1 Why is the internal energy of a real gas not the kinetic energy of its molecules alone?

Internal Energy of a Real Gas

Internal energy is the sum of all forms of molecular energies, kinetic and potential.

$$U = K.E. + P.E.$$

Real Gas

The molecules of a real gas exert forces on one another, so they possess potential energy as well. It is only for an ideal gas that this part is zero.

SQ 6.2.2 Name the processes by which the internal energy of a system can be changed.

Processes That Change Internal Energy

- Heating, which raises the average kinetic energy of the particles and thereby the temperature.
- Adiabatic compression or expansion, in which the volume changes with no heat exchanged with the surroundings.
- Phase changes, in which heat changes the state of matter without changing the temperature.

SQ 6.2.3 How is internal energy analogous to gravitational potential energy?

Analogy with Potential Energy

Neither has a natural zero from which it must be measured.

Result

As with gravitational potential energy, it is the change in internal energy and not its absolute value which is important.

SQ 6.2.4 A block of metal is heated. What happens to the average kinetic energy of its particles, and why?

Average Kinetic Energy on Heating

The average kinetic energy of the particles increases.

Reason

Temperature is a measure of the average kinetic energy of the particles, so the heat absorbed by the block raises the two together.

$$\overline{K.E.} = \frac{3}{2} k_B T$$

SQ 6.2.5 Find the average kinetic energy of a gas molecule at 600 K .

Average Kinetic Energy

$$\langle KE \rangle = \frac{3}{2} k_B T$$

$$\langle KE \rangle = \frac{3}{2} \times 1.38 \times 10^{-23} \times 600$$

Result

$$\langle KE \rangle = 1.24 \times 10^{-20}\text{ J}$$

MCQ 6.2.1 The average kinetic energy of a gas molecule at 600 K is about:

- | | |
|----------------------------|----------------------------|
| A 6.21×10^{-21} J | B 8.28×10^{-21} J |
| C 1.24×10^{-20} J | D 2.48×10^{-20} J |

Solution:

$$\langle KE \rangle = \frac{3}{2} k_B T = 1.5 \times 1.38 \times 10^{-23} \times 600 = 1.24 \times 10^{-20} \text{ J.}$$

MCQ 6.2.2 The internal energy of a real gas differs from that of an ideal gas because its molecules also possess:

- | | |
|--------------------|-------------------|
| A potential energy | B electric charge |
| C weight | D colour |

Solution: Internal energy is the sum of the kinetic and potential molecular energies; for an ideal gas the potential part is zero, but for a real gas it is not.

MCQ 6.2.3 Which one of the following does NOT change the internal energy of an ideal gas?

- | | |
|---------------------------|--------------------------------|
| A heating it | B compressing it adiabatically |
| C an isothermal expansion | D a change of state |

Solution: The internal energy of an ideal gas depends on its temperature alone, and an isothermal change leaves the temperature unaltered.

MCQ 6.2.4 Internal energy is analogous to:

- | | |
|-------------------|----------------------------------|
| A linear momentum | B gravitational potential energy |
| C electric charge | D power |

Solution: Like gravitational potential energy, it is the change in internal energy and not its absolute value which matters.

MCQ 6.2.5 If the absolute temperature of an ideal gas is halved, its internal energy becomes:

- | | |
|-------------|--------------|
| A double | B four times |
| C unchanged | D half |

Solution: For an ideal gas the internal energy is directly proportional to the absolute temperature, so halving T halves U .

MCQ 6.2.6 A diatomic molecule possesses vibrational energy because of the:

- | | |
|---------------------------------------|--------------------------------------|
| A charge on its nucleus | B spring-like bond between its atoms |
| C collisions with the container walls | D rotation of the container |

Solution: The bond joining the two atoms behaves like a spring, so the molecule can vibrate as well as translate and rotate.

Topic 6.3 Heat and Work

Introduction

Both heat and work correspond to the transfer of energy by some means.

Origin of the Sign Convention

The idea was first applied to the steam engine, where it was natural to transfer heat in and get work out. It therefore made sense to define both heat in and work out as positive quantities.

Sign Convention

Work done by the system on its environment is considered positive, while work done on the system by the environment is taken as negative.

Heat Entering a System

If an amount of heat Q enters the system, it could appear as an increase in internal energy, or as a quantity of work performed by the system on the surroundings, or both.

Work Done by an Expanding Gas

Consider a gas enclosed in a cylinder with a movable, frictionless piston of cross-sectional area A . In equilibrium the system occupies volume V and exerts a pressure P on the walls and the piston.

Force on the Piston $F = PA$

Derivation

The gas is assumed to expand through ΔV very slowly, so that it remains in equilibrium. As the piston moves up through a small distance Δy , the work done by the gas is

$$W = F\Delta y = PA\Delta y$$

The product of the area of the piston and the distance it moves is the change in volume of the gas.

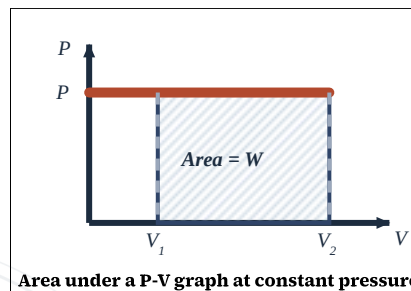
$$A\Delta y = \Delta V$$

Putting this in the expression for the work done

$$W = P\Delta V$$

Area Under the P-V Graph

The work done can also be calculated from the area of the curve under the P-V graph.



$$\text{Area} = \text{height} \times \text{base}$$

$$= P \times \Delta V$$

$$W = P\Delta V$$

Condition

The expansion must be slow so that the gas stays in equilibrium and P has a definite value at each stage.

Laws of Thermodynamics

Knowing the change in internal energy and the mechanical work done, the general principles which deal with heat energy and its transformation into mechanical energy can be described. These principles are known as the laws of thermodynamics.

LQ 4 ends here

Short Questions

SQ 6.3.1 Show that the product of pressure and change in volume carries the unit of work.

Product of Pressure and Volume Change

Pressure is measured in N m^{-2} and volume in m^3

$$\text{N m}^{-2} \times \text{m}^3 = \text{N m} = \text{J}$$

Result

The joule is the unit of work, so the quantity $P\Delta V$ is indeed work.

SQ 6.3.2 Why is no work done by a gas which is heated at constant volume?

Work at Constant Volume

$$W = P\Delta V$$

The volume of the gas does not change, so the change in volume is zero and the work done is zero with it.

Result

All the heat supplied then appears as an increase in the internal energy of the gas.

SQ 6.3.3 A gas expands at a constant pressure of 1.5×10^5 Pa through 0.02 m^3 . Find the work done by it.

Work Done by the Gas

$$W = P\Delta V$$

$$W = 1.5 \times 10^5 \times 0.02$$

Result $W = 3 \times 10^3 \text{ J}$

SQ 6.3.4 Why is it natural to take heat entering a system and work leaving it as positive?

Origin of the Sign Convention

The idea was first applied to the steam engine.

Reason

There it was natural to transfer heat in and to get work out, so it made sense to define both heat in and work out as positive quantities.

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

SQ 6.3.5 Why is the piston taken as frictionless in the derivation of the work done by a gas?

Frictionless Piston

Friction between the piston and the cylinder would dissipate a part of the energy as heat.

Result

With a frictionless piston the whole of the work done by the gas is delivered to the surroundings, so that work is exactly $P\Delta V$ as required.

MCQ 6.3.1 A gas expanding at a constant pressure of $1.5 \times 10^5 \text{ Pa}$ through 0.02 m^3 does work equal to:

- | | |
|-----------------------------|-------------------------------|
| A $3 \times 10^2 \text{ J}$ | B $3 \times 10^3 \text{ J}$ |
| C $3 \times 10^4 \text{ J}$ | D $7.5 \times 10^6 \text{ J}$ |

Solution: $W = P\Delta V = 1.5 \times 10^5 \times 0.02 = 3 \times 10^3 \text{ J}$.

MCQ 6.3.2 The quantity N m^{-2} multiplied by m^3 has the same unit as:

- | | |
|--------------|--------------|
| A the watt | B the newton |
| C the pascal | D the joule |

Solution: $\text{N m}^{-2} \times \text{m}^3 = \text{N m} = \text{J}$, which is the unit of work.

MCQ 6.3.3 When a gas is heated in a vessel of fixed volume, the work done by the gas is:

- | | |
|------------------------------|-------------|
| A equal to the heat supplied | B zero |
| C negative | D a maximum |

Solution: $W = P\Delta V$ and $\Delta V = 0$, so no work is done and all the heat raises the internal energy.

MCQ 6.3.4 The piston used in deriving $W = P\Delta V$ is taken as frictionless so that:

- | | |
|--|-------------------------------|
| A the gas is cooled | B the pressure rises steadily |
| C no part of the work is lost against friction | D the volume stays fixed |

Solution: With a frictionless piston the whole of the work done by the gas is delivered to the surroundings.

MCQ 6.3.5 On a P-V diagram, the work done by a gas expanding at constant pressure is the area of a:

- | | |
|-------------|------------|
| A rectangle | B triangle |
| C circle | D parabola |

Solution: The height of the strip is the constant pressure P and its base is ΔV , so the area under the graph is a rectangle of area $P\Delta V$.

MCQ 6.3.6 The general principles which deal with heat energy and its transformation into mechanical energy are the:

- | | |
|--------------------------|--------------------------|
| A laws of reflection | B laws of electrostatics |
| C laws of thermodynamics | D laws of motion |

Solution: Knowing the change in internal energy and the mechanical work done leads to the laws of thermodynamics.

Topic 6.4 First Law of Thermodynamics

LQ 5 starts here — Explain the first law of thermodynamics in detail. Give an example in support of your explanation. Give its two applications.

LQ 6 starts here — What is the first law of thermodynamics? Explain isothermal and adiabatic processes.

Introduction

When heat is added to a system there is an increase in its internal energy due to a rise in temperature, an increase in pressure or a change of state. If at the same time the substance does work on its environment by expansion, the heat required is the heat necessary to change the internal energy from U_1 to U_2 plus the work W done on the environment.

Mathematical Form

$$Q = (U_2 - U_1) + W$$

$$Q = \Delta U + W$$

The change in internal energy is therefore

$$\Delta U = U_2 - U_1 = Q - W$$

Statement

In any thermodynamic process, when heat Q is added to a system, this energy appears as an increase in the internal energy ΔU stored in the system plus the work W done by the system on its surroundings.

Sign Convention

Heat added to the system and work done by the system are taken as positive. Heat removed from the system and work done on the system are taken as negative.

Conservation Principle

The underlying principle of the first law is the conservation of energy. Energy can change from one form to another, such as from chemical potential energy to thermal energy, but the total energy in an isolated system remains constant over time.

Wider Applicability

Beyond mechanical systems the first law applies universally to all forms of energy and all types of processes, including chemical reactions, electrical systems and nuclear reactions. Energy can neither be created nor destroyed.

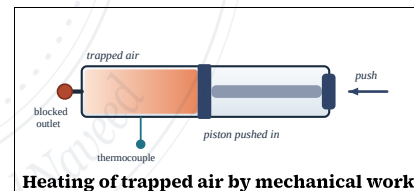
Example of a Bicycle Pump

When the handle of a bicycle pump with a blocked outlet is pumped rapidly, the pump becomes hot due to the mechanical work done on the gas. The push force does work on the air, thereby increasing its internal energy, which is shown by the rise in temperature of the air.

Thermocouple

A thermocouple connected through the blocked outlet allows the air temperature to be monitored, as a thermocouple thermometer can detect a minute variation of temperature.

Diagram



Human Metabolism

Human beings and other animals do work when they walk, run or move, and energy is also needed for growth. The energy transforming processes that occur within an organism are named as metabolism.

Applying the First Law

$$\Delta U = Q - W$$

Work done results in a decrease in the internal energy of the body. The body temperature, in other words its internal energy, is maintained by the food we eat.

LQ 5 ends here

Isothermal Process

It is a process which is carried out at constant temperature, so the condition for applying Boyle's law on the gas is fulfilled. The product of pressure and volume remains constant during the process.

$$P_1 V_1 = P_2 V_2$$

First Law for an Isothermal Change

The potential energy associated with the molecules of an ideal gas is zero, so its internal energy depends only on temperature, which here remains constant. Hence

$$\Delta U = 0$$

$$Q = W$$

Heat Supplied

If the gas expands and does external work W , an equal amount of heat Q has to be supplied to produce an isothermal change.

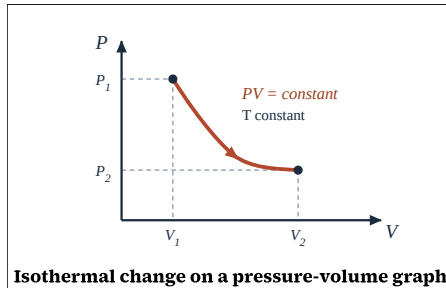
Condition

Transfer of heat from one place to another requires time, so to keep the temperature constant the expansion or compression must take place slowly.

Isotherm

The curve representing an isothermal process is called an isotherm.

Graph



Adiabatic Process

It is a process in which no heat enters or leaves the system. As no heat is exchanged, the first law gives

$$\Delta Q = 0$$

$$W = -\Delta U$$

Temperature Change

If the gas expands and does external work, it is done at the expense of the internal energy of its molecules, so the temperature of the gas falls. Conversely, an adiabatic compression raises the temperature because of the work done on the gas.

Condition

An adiabatic change occurs when the gas is expanded or compressed rapidly, particularly when it is contained in an insulated cylinder.

Examples of Adiabatic Change

- The rapid escape of air from a burst tyre.
- The rapid expansion and compression of air through which a sound wave is passing.
- Cloud formation in the atmosphere.

Mathematical Form

The temperature of the gas does not remain constant, so an adiabatic change obeys the relation

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

Ratio of Specific Heats

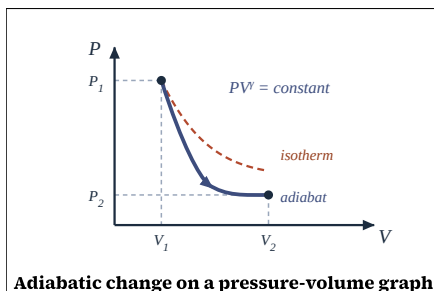
Here γ is the ratio of the molar specific heat of the gas at constant pressure to the molar specific heat at constant volume.

$$\gamma = \frac{C_p}{C_v}$$

Adiabat

The curve representing an adiabatic process is called an adiabat.

Graph



Comparison

For an isothermal change the index of V is 1, while for an adiabatic change it is $\gamma > 1$. Pressure therefore falls

more rapidly with volume in an adiabatic change, so the adiabat is steeper than the isotherm.

LO 6 ends here

Book Examples

Example 6.4.1 A gas is enclosed in a container fitted with a piston of cross-sectional area 0.10 m^2 . The pressure of the gas is maintained at 8000 N m^{-2} . When heat is slowly transferred, the piston is pushed up through a distance of 4.0 cm . If 42 J of heat is transferred to the system during the expansion, what is the change in internal energy of the system?

Given Data

$$A = 0.10 \text{ m}^2$$

$$P = 8000 \text{ N m}^{-2}$$

$$\Delta y = 4.0 \text{ cm} = 0.04 \text{ m}$$

$$Q = 42 \text{ J}$$

To Find

Change in internal energy $\Delta U = ?$

Formula

$$W = P\Delta y$$

$$\Delta U = Q - W$$

Solution

The work done by the gas on the piston is

$$W = 8000 \times 0.10 \times 0.04 = 32 \text{ J}$$

Putting this in the first law of thermodynamics

$$\Delta U = 42 \text{ J} - 32 \text{ J} = 10 \text{ J}$$

Result

$$\Delta U = 10 \text{ J}$$

Short Questions

SQ 6.4.1 Why does a bicycle pump with a blocked outlet become hot when its handle is pumped rapidly?

Heating of a Bicycle Pump

The push force does mechanical work on the air trapped inside the pump.

$$\Delta U = Q - W$$

Result

The work done on the air increases its internal energy, which is shown by the rise in temperature of the pump.

SQ 6.4.2 Why is a thermocouple used to follow the temperature of the air inside the pump?

Use of a Thermocouple

A thermocouple thermometer can detect a minute variation of temperature.

Arrangement

It is connected through the blocked outlet of the pump, so the temperature of the air itself is monitored as the handle is worked.

SQ 6.4.3 Apply the first law of thermodynamics to the human body.

Metabolism

The energy transforming processes which occur within an organism are called metabolism.

$$\Delta U = Q - W$$

Result

Work done in walking or running decreases the internal energy of the body, and the body temperature is maintained by the food we eat.

SQ 6.4.4 A gas absorbs 800 J of heat and its internal energy rises by 500 J. How much work does it do?	
Work Done by the Gas	
$Q = \Delta U + W$	
$W = 800 \text{ J} - 500 \text{ J}$	
Result $W = 300 \text{ J}$	
SQ 6.4.5 A gas gives out 100 J of heat while 250 J of work is done on it. Find the change in its internal energy.	
Sign Convention	
Heat removed and work done on the gas are both negative.	
$Q = -100 \text{ J}$	
$W = -250 \text{ J}$	
$\Delta U = Q - W = -100 + 250$	
Result $\Delta U = +150 \text{ J}$	
SQ 6.4.6 Give three examples of adiabatic change.	
Examples of Adiabatic Change	
- The rapid escape of air from a burst tyre. - The rapid expansion and compression of the air through which a sound wave is passing. - Cloud formation in the atmosphere.	
SQ 6.4.7 Why does the air escaping from a burst tyre cool down?	
Cooling of the Escaping Air	
The escape is so rapid that no heat is exchanged with the surroundings, so the expansion is <u>adiabatic</u> .	
$\Delta Q = 0$	
$W = -\Delta U$	
Result	
The air does external work at the expense of the internal energy of its molecules, so its temperature falls.	
SQ 6.4.8 A gas is compressed adiabatically. What happens to its internal energy and to its temperature?	
Adiabatic Compression	
$\Delta Q = 0$	
$W = -\Delta U$	
Work is done on the gas, so W is negative and ΔU is positive.	
Result	
The internal energy increases, so the temperature of the gas <u>rises</u> .	
MCQ 6.4.1 A gas absorbs 800 J of heat and its internal energy rises by 500 J. The work done by the gas is:	
A 300 J	B 1300 J
C 500 J	D 800 J
Solution: From $Q = \Delta U + W$, the work done is $W = 800 - 500 = 300 \text{ J}$.	
MCQ 6.4.2 When 100 J of heat is removed from a gas while 250 J of work is done on it, its internal energy:	
A decreases by 150 J	B increases by 350 J
C increases by 150 J	D stays the same
Solution: Here $Q = -100 \text{ J}$ and $W = -250 \text{ J}$, so $\Delta U = Q - W = -100 + 250 = +150 \text{ J}$.	
MCQ 6.4.3 A bicycle pump with a blocked outlet becomes hot when worked rapidly because:	
A work is done on the air inside it	B heat flows into it from the road
C the air inside it expands	D the tyre rubs against it
Solution: The push force does work on the trapped air, raising its internal energy and therefore its temperature.	

MCQ 6.4.4 A thermocouple is used in the bicycle pump experiment because it can detect:	
A a change of pressure	B a change of volume
C the humidity of the air	D a minute variation of temperature
Solution: A thermocouple thermometer responds to a very small change of temperature, so the warming of the trapped air can be followed.	
MCQ 6.4.5 The energy transforming processes which occur within an organism are called:	
A respiration	B metabolism
C diffusion	D osmosis
Solution: The processes by which an organism transforms energy are named metabolism.	
MCQ 6.4.6 Air escaping rapidly from a burst tyre cools because the expansion is:	
A isothermal	B reversible
C at constant volume	D adiabatic
Solution: The escape is too rapid for heat to be exchanged, so the air does work at the expense of its internal energy and its temperature falls.	
MCQ 6.4.7 For a gas, γ is greater than one because:	
A C_v is greater than C_p	B C_p is greater than C_v
C C_p equals C_v	D the gas is always diatomic
Solution: $\gamma = C_p/C_v$, and the molar specific heat at constant pressure is the larger of the two.	
MCQ 6.4.8 Starting from the same point on a P-V diagram, the curve which falls more steeply is the:	
A adiabat	B isotherm
C line of constant pressure	D line of constant volume
Solution: The index of V is 1 for an isotherm and $\gamma > 1$ for an adiabat, so pressure falls faster along the adiabat.	
MCQ 6.4.9 An ideal gas at $3 \times 10^5 \text{ Pa}$ occupying 2 m^3 expands isothermally to 6 m^3 . Its final pressure is:	
A $9 \times 10^5 \text{ Pa}$	B $3 \times 10^5 \text{ Pa}$
C $1 \times 10^5 \text{ Pa}$	D $2 \times 10^5 \text{ Pa}$
Solution: An isothermal change obeys $P_1 V_1 = P_2 V_2$, so $P_2 = (3 \times 10^5 \times 2)/6 = 1 \times 10^5 \text{ Pa}$.	
MCQ 6.4.10 In an adiabatic expansion the external work is done at the expense of the:	
A internal energy of the molecules	B pressure of the gas
C mass of the gas	D volume of the container
Solution: No heat enters the system, so $W = -\Delta U$ and the work comes out of the internal energy, which is why the gas cools.	

Topic 6.5 Reversible and Irreversible Processes

Reversible Process

A reversible process is one which can be retraced in exactly reverse order, without producing any change in the surroundings.

Explanation

In the reverse process the working substance passes through the same stages as in the direct process, but the thermal and mechanical effects at each stage are exactly reversed. If heat is absorbed in the direct process it is given out in the reverse process, and if work is done by the substance in the direct process, work is done on the substance in the reverse process. Hence the working substance is restored to its original condition.

Cycle

A succession of events which brings the system back to its initial condition is called a cycle.

Reversible Cycle

A reversible cycle is the one in which all the changes are reversible.

Practically Reversible Processes

No actual change is completely reversible, but some processes are practically reversible.

- The liquefaction and evaporation of a substance, performed slowly.
- The slow compression of a gas in a cylinder, as the compression can be changed to expansion by slowly decreasing the pressure on the piston.

Irreversible Process

If a process cannot be retraced in the backward direction by reversing the controlling factors, it is an irreversible process.

Irreversible Changes

All changes which occur suddenly, or which involve friction or dissipation of energy through conduction, convection or radiation, are irreversible.

Example

An example of a highly irreversible process is an explosion.

Short Questions

SQ 6.5.1 Define a cycle and a reversible cycle.

Cycle

A succession of events which brings the system back to its initial condition is called a cycle.

Reversible Cycle

A reversible cycle is the one in which all the changes are reversible.

SQ 6.5.2 Give two processes which are practically reversible.

Practically Reversible Processes

- The liquefaction and evaporation of a substance, performed slowly.
- The slow compression of a gas in a cylinder, which can be turned into expansion by slowly decreasing the pressure on the piston.

SQ 6.5.3 Why is no actual process completely reversible?

No Completely Reversible Process

Every real change involves friction, or the dissipation of energy through conduction, convection or radiation.

Result

The surroundings are permanently altered, so the change cannot be retraced exactly and only slow changes are practically reversible.

SQ 6.5.4 Why is an explosion a highly irreversible process?

Explosion as an Irreversible Process

It occurs suddenly and scatters energy through the surroundings by conduction, convection and radiation.

Result

The controlling factors cannot be reversed to bring the products back to their original state, so the change cannot be retraced.

MCQ 6.5.1 A reversible cycle is one in which:

A	heat is only absorbed	B	work is only done on the gas
C	the temperature stays constant	D	all the changes are reversible

Solution: A cycle brings the system back to its initial condition, and it is reversible when every change in it is reversible.

MCQ 6.5.2 The dissipation of energy by conduction, convection or radiation makes a process:

A	reversible	B	irreversible
C	isothermal	D	adiabatic

Solution: All changes involving friction or the dissipation of energy are irreversible.

MCQ 6.5.3 For a change to be practically reversible it must be carried out:

A	suddenly	B	with friction
C	explosively	D	slowly

Solution: Slow liquefaction, slow evaporation and slow compression are the changes the book calls practically reversible.

MCQ 6.5.4 If work is done by the substance in the direct process, then in the reverse process the work is:

A	done on the substance	B	doubled
C	zero	D	turned into heat

Solution: In a reversible process every thermal and mechanical effect is exactly reversed, so work done by the substance becomes work done on it.

MCQ 6.5.5 Which one of the following is NOT a cause of irreversibility?

A	friction	B	a sudden change
C	an infinitely slow, frictionless expansion	D	conduction of heat

Solution: A slow, frictionless change is exactly the kind that can be retraced, so it is the one that does not make a process irreversible.

Topic 6.6 Heat Engine

Definition

A heat engine converts some thermal energy to mechanical work. Usually the heat comes from the burning of a fuel.

Earliest Heat Engine

The earliest heat engine was the steam engine. It was developed on the fact that when water is boiled in a vessel covered with a lid, the steam inside tries to push the lid off, showing the ability to do work.

Working Principle

The working principle of a heat engine is based on the conversion of heat energy into mechanical work through a cyclic process.

Explanation

It involves the cyclic transfer of heat energy from a high temperature reservoir to a low temperature reservoir, with the objective of converting as much heat as possible into mechanical work.

Importance

The process is governed by the principles of thermodynamics and is essential in the various applications where mechanical energy is required from heat sources.

Short Questions

SQ 6.6.1 How does a vessel of boiling water covered with a lid show that steam can do work?

Steam Doing Work

When water is boiled in a covered vessel, the steam inside tries to push the lid off.

Result

Pushing the lid is work done against a force, so the steam shows its ability to do work. The steam engine was developed on this fact.

SQ 6.6.2 Why must a heat engine work through a cyclic process?

Need for a Cyclic Process

The working substance has to be returned to its initial state before it can absorb heat and produce work again.

$$\Delta U = 0$$

$$W = \Delta Q$$

Result

Only a cycle lets the conversion be repeated, so an engine delivers work continuously rather than once.

SQ 6.6.3 What is the object of the heat transfer that takes place in a heat engine?**Object of the Heat Transfer**

Heat is transferred in a cycle from a high temperature reservoir to a low temperature reservoir.

Object

The object is to convert as much of that heat as possible into mechanical work.

SQ 6.6.4 Why is the heat engine essential in so many applications?**Importance of the Heat Engine**

Most of the raw energy we use is released as heat, while machines need mechanical energy.

Result

The heat engine is the device which makes that conversion, so it is essential wherever mechanical energy has to be obtained from a heat source.

MCQ 6.6.1 Steam in a covered vessel of boiling water pushes the lid off, which shows its ability to:

- | | |
|------------------|-------------|
| A cool down | B freeze |
| C do work | D lose mass |

Solution: Pushing the lid is work done against a force, and the steam engine was developed on this observation.

MCQ 6.6.2 A heat engine returns its working substance to the initial state so that it can:

- | | |
|---|------------------------|
| A repeat the conversion continuously | B cool the source down |
| C stop working | D gain mass |

Solution: Only a cyclic process allows the engine to go on converting heat into work rather than doing so once.

MCQ 6.6.3 The object of the cycle of a heat engine is to convert into work as much as possible of the:

- | | |
|---|---|
| A work done on the engine | B heat given to the low temperature reservoir |
| C heat drawn from the high temperature reservoir | D mass of the fuel |

Solution: The cycle transfers heat from the hot reservoir to the cold one with the object of converting as much of it as possible into mechanical work.

MCQ 6.6.4 A heat engine is essential wherever mechanical energy has to be obtained from:

- | | |
|--------------------|------------------------|
| A an electric cell | B a heat source |
| C a magnet | D a stretched spring |

Solution: The heat engine is the device which converts thermal energy into mechanical work.

MCQ 6.6.5 Which one of the following is NOT true of a heat engine?

- | | |
|-------------------------------|---|
| A it works through a cycle | B it takes heat from a hot reservoir |
| C it produces mechanical work | D it converts all the heat it takes in into work |

Solution: Only a part of the heat taken in becomes work; the rest is expelled to the low temperature reservoir.

Topic 6.7 Second Law of Thermodynamics**Need for the Second Law**

The first law of thermodynamics tells us that heat energy can be converted into an equivalent amount of work, but it is silent about the conditions under which this conversion takes place. The second law is concerned with the circumstances in which heat can be converted into work, and with the direction of flow of heat.

Actual Operation of an Engine

The engine or the system absorbs a quantity of heat Q_1 from the heat source at temperature T_1 . It does work W and expels heat Q_2 to the low temperature reservoir at temperature T_2 of the sink.

Net Work Done

As the working substance goes through a cyclic process, in which it eventually returns to its initial state, the change in internal energy is zero. Hence from the first law the net work done is equal to the net heat absorbed.

$$W = Q_1 - Q_2$$

Practical Engines

The petrol engine of a motor car extracts heat from the burning fuel, converts a part of this energy into work and expels the rest to the atmosphere. It has been observed that petrol engines convert roughly 25% and diesel engines 35 to 40% of the available heat energy into work.

Lord Kelvin's Statement

It is impossible to devise a process which may convert heat, extracted from a single reservoir, entirely into work without leaving any change in the working system.

Single Reservoir

A single heat reservoir, no matter how much energy it contains, cannot be made to perform any work.

Oceans and Atmosphere

This is true for the oceans and our atmosphere, which contain a large amount of heat energy that cannot be converted into useful mechanical work. The reason is that there is no reservoir at a lower temperature than either of them.

Consequence

Two bodies at different temperatures are essential for the conversion of heat into work. For the working of a heat engine there must be a source of heat at a high temperature and a sink at a low temperature to which heat may be expelled.

Short Questions**SQ 6.7.1 Why is the first law of thermodynamics not enough to describe a heat engine?****Limitation of the First Law**

It tells us that heat can be converted into an equivalent amount of work, but it is silent about the conditions under which the conversion takes place.

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

Second Law

The circumstances of the conversion, and the direction of the flow of heat, are settled by the second law.

SQ 6.7.2 A heat engine absorbs 900 J of heat from its source and rejects 600 J to its sink. Find the work done in one cycle.**Work Done in One Cycle**

The working substance returns to its initial state, so there is no change in its internal energy and the net work equals the net heat absorbed.

$$W = Q_1 - Q_2$$

Calculation $W = 900 \text{ J} - 600 \text{ J} = 300 \text{ J}$

SQ 6.7.3 What becomes of the heat which a heat engine does not convert into work?**Heat Not Converted into Work**

It is expelled to the low temperature reservoir, the sink.

$$Q_2 = Q_1 - W$$

Example

The petrol engine of a car extracts heat from the burning fuel, converts a part of it into work and expels the rest to the atmosphere.

SQ 6.7.4 Why does a petrol engine convert only about a quarter of the heat of its fuel into work?**Efficiency of a Petrol Engine**

A part of the heat must always be expelled to a colder reservoir, and friction and heat losses waste more of it.

$$\eta = \frac{W}{Q_1}$$

Result

Only about 25% of the available heat energy appears as work, while a diesel engine manages 35 to 40%.

SQ 6.7.5 Why are two bodies at different temperatures essential for the conversion of heat into work?**Need for Two Temperatures**

Heat extracted from a single reservoir cannot be converted entirely into work, however much energy that reservoir holds.

$$T_1 = T_2$$

$$\eta = 0$$

Result

An engine needs a source at a high temperature to draw heat from and a sink at a low temperature to expel heat to.

MCQ 6.7.1 A heat engine absorbs 900 J and rejects 600 J in each cycle. The work done per cycle is:

- | | |
|----------|----------------|
| A 1500 J | B 300 J |
| C 600 J | D 900 J |

Solution: The internal energy is unchanged over a cycle, so $W = Q_1 - Q_2 = 900 - 600 = 300 \text{ J}$.

MCQ 6.7.2 The first law of thermodynamics is silent about the:

- | | |
|-----------------------------|--|
| A conservation of energy | B work done by an expanding gas |
| C change in internal energy | D direction in which heat flows |

Solution: The first law says heat can be converted into work but not under what conditions or in which direction; that is the business of the second law.

MCQ 6.7.3 The heat which a petrol engine does not convert into work is:

- | | |
|----------------------|-------------------------------------|
| A destroyed | B expelled to the atmosphere |
| C stored in the fuel | D converted into mass |

Solution: The engine extracts heat from the burning fuel, converts a part of it into work and expels the rest to the atmosphere.

MCQ 6.7.4 The fraction of the available heat which a diesel engine turns into work is:

- | | |
|---|------------------------------------|
| A less than that of a petrol engine | B equal to that of a petrol engine |
| C greater than that of a petrol engine | D always 100% |

Solution: Petrol engines convert roughly 25% and diesel engines 35 to 40% of the available heat energy into work.

MCQ 6.7.5 A heat engine placed where everything is at the same temperature would do work equal to:

- | | |
|---------------|-----------------------|
| A zero | B Q_1 |
| C $Q_1 - Q_2$ | D an unlimited amount |

Solution: A single reservoir cannot be made to perform work; a source and a colder sink are both needed.

MCQ 6.7.6 The second law of thermodynamics forbids a heat engine from:

- | | |
|---|---------------------------|
| A doing any work at all | B working through a cycle |
| C converting all the heat it absorbs into work | D using two reservoirs |

Solution: By Lord Kelvin's statement, heat extracted from a reservoir cannot be converted entirely into work without any other change.

Topic 6.8 Carnot Engine and Carnot's Theorem

LQ 8 starts here — What is a Carnot engine? Describe the Carnot cycle. State Carnot theorem and derive an expression for the efficiency of a Carnot engine.

Introduction

Sadi Carnot in 1824 described an ideal engine using only isothermal and adiabatic processes. He showed that a heat engine operating in an ideal reversible cycle between two heat reservoirs at different temperatures would be the most efficient engine.

Working Substance

A Carnot cycle using an ideal gas as the working substance consists of the following four steps.

Isothermal Expansion (AB)

The gas is allowed to expand isothermally at temperature T_1 , absorbing heat Q_1 from the hot reservoir.

Adiabatic Expansion (BC)

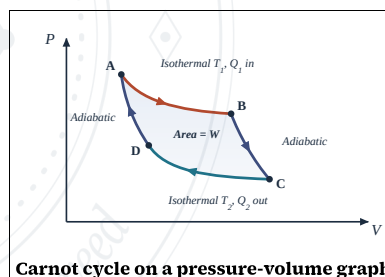
The gas is then allowed to expand adiabatically until its temperature drops to the lower value T_2 .

Isothermal Compression (CD)

The gas at this stage is compressed isothermally at temperature T_2 , rejecting heat Q_2 to the cold reservoir.

Adiabatic Compression (DA)

Finally the gas is compressed adiabatically to restore its initial state at the starting temperature T_1 .

P-V Graph**Reversibility**

Thermal and mechanical equilibrium is maintained all the time, so that each process is perfectly reversible.

Net Work Done

As the working substance returns to the initial state, there is no change in its internal energy.

$$\Delta U = 0$$

The net heat absorbed in one cycle is

$$Q = Q_1 - Q_2$$

From the first law of thermodynamics

$$Q = \Delta U + W$$

$$W = Q_1 - Q_2$$

The net work done during one cycle also equals the area enclosed by the path ABCDA of the P-V diagram.

Efficiency

The efficiency of a heat engine is defined as the ratio of the output to the input.

$$\eta = \frac{\text{Output (Work)}}{\text{Input (Energy)}} = \frac{W}{Q_1}$$

Putting the value of the net work done

$$\eta = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1}$$

In Terms of Temperature

The energy transfer in an isothermal expansion or compression turns out to be proportional to the kelvin temperature, so Q_1 and Q_2 are proportional to T_1 and T_2 respectively.

$$\frac{Q_2}{Q_1} = \frac{T_2}{T_1}$$

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

Percentage Efficiency $\% \eta = \frac{T_1 - T_2}{T_1} \times 100$

Depending Factors

The efficiency of a Carnot engine depends on the temperatures of the hot and cold reservoirs. It is independent of the nature of the working substance, and the larger the temperature difference of the two reservoirs, the greater is the efficiency.

Maximum Efficiency

The efficiency can never be one or 100% unless the cold reservoir is at absolute zero temperature.

$$T_2 = 0 \text{ K}$$

Such reservoirs are not available, so the maximum efficiency is always less than one. Nevertheless the Carnot cycle establishes an upper limit on the efficiency of all heat engines.

Carnot's Theorem

No heat engine can be more efficient than a Carnot engine operating between the same two temperatures.

Extended Statement

All Carnot engines operating between the same two temperatures have the same efficiency, irrespective of the nature of the working substance.

Practical Cases

In most practical cases the cold reservoir is near room temperature, so the efficiency can only be increased by raising the temperature of the hot reservoir. All real heat engines are less efficient than a Carnot engine due to friction and other heat losses, as no practical engine is perfectly reversible.

LQ 8 ends here

Book Examples

Example 6.8.1 The turbines in a steam power plant take steam from a boiler at 427°C and exhaust it into a low temperature reservoir at 77°C . What is the maximum possible efficiency?

Given Data

$$T_1 = 427^\circ\text{C} = 427 + 273 = 700 \text{ K}$$

$$T_2 = 77^\circ\text{C} = 77 + 273 = 350 \text{ K}$$

To Find

Maximum possible efficiency $\% \eta = ?$

Formula

The maximum efficiency is that of a Carnot engine working between the same two temperatures.

$$\% \eta = \frac{T_1 - T_2}{T_1} \times 100$$

Solution

$$\begin{aligned} \% \eta &= \frac{700 \text{ K} - 350 \text{ K}}{700 \text{ K}} \times 100 = 0.5 \times 100 \\ &= 50\% \end{aligned}$$

Result $\% \eta = 0.5 \times 100 = 50\%$

Short Questions

SQ 6.8.1 Show that the efficiency of a heat engine can be written as $\eta = 1 - \frac{Q_2}{Q_1}$.

Efficiency of a Heat Engine

$$\eta = \frac{W}{Q_1}$$

The net work done in one cycle is

$$W = Q_1 - Q_2$$

$$\eta = \frac{Q_1 - Q_2}{Q_1}$$

Result $\eta = 1 - \frac{Q_2}{Q_1}$

SQ 6.8.2 Why is the ratio $\frac{Q_2}{Q_1}$ equal to the ratio $\frac{T_2}{T_1}$ for a Carnot engine?

Heat Ratio and Temperature Ratio

The heat transferred in an isothermal expansion or compression turns out to be proportional to the kelvin temperature at which it is transferred.

Result

So $Q_1 \propto T_1$ and $Q_2 \propto T_2$, which gives

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

SQ 6.8.3 Why are the two adiabatic steps needed in the Carnot cycle?

Need for the Adiabatic Steps

The gas has to be carried between the temperature of the source and that of the sink without any heat being exchanged, so that no heat is wasted outside the two isothermal steps.

Result

The adiabatic steps make the cycle perfectly reversible.

SQ 6.8.4 A Carnot engine works between 500 K and 300 K . Find its percentage efficiency.

Percentage Efficiency

$$\% \eta = \frac{T_1 - T_2}{T_1} \times 100$$

$$\% \eta = \frac{500 - 300}{500} \times 100$$

Result $\% \eta = 40\%$

SQ 6.8.5 A heat engine absorbs 800 J of heat and rejects 600 J in each cycle. Find its efficiency.

Efficiency of the Engine $\eta = 1 - \frac{Q_2}{Q_1}$

$$\eta = 1 - \frac{600}{800}$$

Result $\eta = 0.25 = 25\%$

SQ 6.8.6 How is the efficiency of a practical heat engine increased?

Increasing the Efficiency

In most practical cases the cold reservoir is already near room temperature and cannot be cooled further.

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

Result

The efficiency can therefore be raised only by raising the temperature of the hot reservoir, since the greater the temperature difference the greater the efficiency.

SQ 6.8.7 What would the efficiency of a Carnot engine be if its sink were at absolute zero, and why is such an engine impossible?

Efficiency with the Sink at Absolute Zero

Putting a sink temperature of absolute zero into the formula gives

$$\eta = 1 - \frac{0}{T_1} = 1$$

The efficiency would then be 100%.

Reason

Reservoirs at absolute zero are not available, so the efficiency of every real engine stays below one.

MCQ 6.8.1 The efficiency of a Carnot engine working between 500 K and 300 K is:	
A 40%	B 60%
C 25%	D 66%
Solution: $\eta = (T_1 - T_2)/T_1 = (500 - 300)/500 = 0.4$, that is 40%.	
MCQ 6.8.2 A heat engine absorbs 800 J and rejects 600 J in each cycle. Its efficiency is:	
A 75%	B 33%
C 25%	D 20%
Solution: $\eta = 1 - Q_2/Q_1 = 1 - 600/800 = 0.25$, that is 25%.	
MCQ 6.8.3 The two adiabatic steps of the Carnot cycle change the temperature of the gas without:	
A any heat being exchanged	B any work being done
C any change of volume	D any change of pressure
Solution: No heat enters or leaves during an adiabatic step, so the gas is carried between the two reservoir temperatures without wasting heat.	
MCQ 6.8.4 A Carnot engine working between 400 K and 300 K takes in 1200 J of heat. The work it does is:	
A 900 J	B 400 J
C 1200 J	D 300 J
Solution: $\eta = (400 - 300)/400 = 0.25$, so $W = \eta Q_1 = 0.25 \times 1200 = 300$ J.	
MCQ 6.8.5 In practice the efficiency of a heat engine is raised by:	
A lowering the temperature of the hot reservoir	B raising the temperature of the hot reservoir
C raising the temperature of the sink	D using a heavier working substance
Solution: The cold reservoir is usually near room temperature and cannot be cooled further, so only the source temperature can be raised.	
MCQ 6.8.6 Two Carnot engines work between the same two temperatures, one using helium and the other nitrogen. Their efficiencies are:	
A in the ratio of the molar masses	B different, the lighter gas winning
C both 100%	D equal
Solution: All Carnot engines operating between the same two temperatures have the same efficiency, whatever the working substance.	
MCQ 6.8.7 During the isothermal compression of the Carnot cycle, the gas:	
A absorbs heat from the hot reservoir	B rejects heat to the cold reservoir
C exchanges no heat at all	D does work on the surroundings
Solution: In the third step the gas is compressed isothermally at T_2 and rejects heat Q_2 to the cold reservoir.	
MCQ 6.8.8 In one complete Carnot cycle, the heat converted into work is:	
A $Q_1 - Q_2$	B $Q_1 + Q_2$
C $Q_1 Q_2$	D $Q_2 - Q_1$
Solution: The internal energy is unchanged over the cycle, so the net work equals the net heat absorbed, $Q_1 - Q_2$.	

Topic 6.9 Refrigerator

LQ 7 starts here — What is a refrigerator? Explain its working. Derive an expression for its coefficient of performance.

Definition

A refrigerator is a device which maintains the temperature of a body below that of its surroundings.

Comparison with a Heat Engine

It operates in a cyclic process but in reverse to that of a heat engine. A refrigerator absorbs heat from a cold

reservoir and gives it off to a hot reservoir, so the work is done on the system, while in a heat engine work is done by the system.

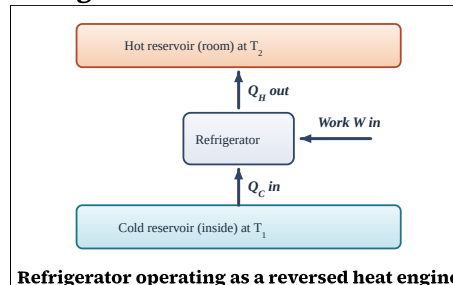
Principle

A refrigerator works on the basis of the Clausius statement of the second law of thermodynamics, that is, as a heat engine operating in reverse.

Working

Heat Q_C is drawn from the Low Temperature Reservoir at T_1 by the compressor and is thrown into the High Temperature Reservoir at T_2 with the help of external work done.

Schematic Diagram



Heat Rejected

The heat rejected to the High Temperature Reservoir is

$$Q_C + W = Q_H$$

$$W = Q_H - Q_C$$

Main Purpose

The main purpose of a refrigerator is to extract as much heat Q_C as possible from the low temperature reservoir with the expenditure of as little work W as possible.

Coefficient of Performance

The ratio of the heat removed from the Low Temperature Reservoir to the work done is called the coefficient of performance of a refrigerator.

$$E = \frac{Q_C}{W} = \frac{Q_C}{Q_H - Q_C}$$

Better Refrigerator

A better refrigerator removes a greater amount of heat from inside the refrigerator for the expenditure of a smaller mechanical or electrical energy.

In Terms of Temperature

For a Carnot refrigerator the heat exchanged with a reservoir is proportional to its absolute temperature.

$$\frac{Q_C}{Q_H} = \frac{T_1}{T_2}$$

Putting the temperatures in place of the quantities of heat

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

LQ 7 ends here

Book Examples

Example 6.9.1 A refrigerator has a coefficient of performance 8. If the temperature in the freezer is -23°C , then what is the temperature at which it rejects the heat?

Given Data

$$E = 8$$

$$T_1 = -23^\circ\text{C} = -23 + 273 = 250\text{ K}$$

To Find

Temperature of the High Temperature Reservoir $T_2 = ?$

Formula

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

Solution

Substituting the values

$$8 = \frac{250 \text{ K}}{T_2 - 250 \text{ K}}$$

$$T_2 - 250 \text{ K} = \frac{250 \text{ K}}{8} = 31.25 \text{ K}$$

$$T_2 = 250 \text{ K} + 31.25 \text{ K} = 281.25 \text{ K}$$

Result $T_2 = 281.25 \text{ K} = 8.25^\circ\text{C}$ **Short Questions****SQ 6.9.1** Show that a refrigerator rejects more heat to the room than it removes from inside itself.**Heat Rejected to the Room**Heat Q_C is drawn from the Low Temperature Reservoir and external work W is done on the system.

$$Q_H = Q_C + W$$

ResultThe heat given to the room is greater than the heat removed, by exactly the work done on the refrigerator.**SQ 6.9.2** A refrigerator removes 900 J of heat from its freezer with a work input of 300 J. Find its coefficient of performance and the heat rejected.**COP**

$$E = \frac{Q_C}{W} = \frac{900}{300} = 3$$

$$Q_H = Q_C + W = 900 + 300$$

Result $Q_H = 1200 \text{ J}$ **SQ 6.9.3** Why does the coefficient of performance of a refrigerator carry no unit?**COP as a Ratio**

$$E = \frac{Q_C}{W}$$

ReasonBoth the heat removed and the work done are energies measured in joule, so the ratio is a pure number.**SQ 6.9.4** A freezer is kept at 250 K in a kitchen at 300 K. Find the greatest possible coefficient of performance.**Greatest COP**

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

$$E = \frac{250}{300 - 250}$$

Result $E = 5$ **SQ 6.9.5** Why does the coefficient of performance of a refrigerator fall as the kitchen gets hotter?**Effect of a Hotter Kitchen**

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

A hotter kitchen raises T_2 while the freezer temperature T_1 is unchanged, so the difference in the denominator grows.**Result**More work is needed for the same heat removed, so E falls.**MCQ 6.9.1** A freezer at 250 K stands in a kitchen at 300 K. Its greatest possible coefficient of performance is:

- | | |
|-------|-------|
| A 6 | B 0.2 |
| C 1.2 | D 5 |

Solution: $E = T_1/(T_2 - T_1) = 250/(300 - 250) = 5$.**MCQ 6.9.2** The coefficient of performance of a refrigerator is measured in:

- | | |
|---------|--------------------------|
| A joule | B no unit, being a ratio |
| C watt | D kelvin |

Solution: It is the ratio of the heat removed to the work done, both energies, so it is a pure number.**MCQ 6.9.3** The heat a refrigerator rejects to the room is:

- | | |
|--------------------------------|---|
| A equal to the heat it removes | B less than the heat it removes |
| C zero | D greater than the heat it removes from inside |

Solution: $Q_H = Q_C + W$, so the heat given to the room exceeds the heat removed by the work done on the refrigerator.**MCQ 6.9.4** As the room around a refrigerator becomes hotter, its coefficient of performance:

- | | |
|------------------|----------------|
| A decreases | B increases |
| C stays the same | D becomes zero |

Solution: In $E = T_1/(T_2 - T_1)$ a larger T_2 makes the denominator larger, so E falls.**MCQ 6.9.5** In a refrigerator, the heat is drawn from the low temperature reservoir by the:

- | | |
|---------------------|-----------------|
| A freezer door | B hot reservoir |
| C compressor | D thermometer |

Solution: The compressor draws heat Q_C from the Low Temperature Reservoir and, with the help of external work, throws it into the High Temperature Reservoir.**MCQ 6.9.6** A refrigerator does not break the second law of thermodynamics because heat is moved from cold to hot at the cost of:

- | | |
|-----------------------------------|-----------------------------|
| A external work done on it | B nothing at all |
| C the mass of the working gas | D the volume of the freezer |

Solution: The second law forbids heat flowing from cold to hot of its own accord; in a refrigerator work is done on the system to drive it.**Topic 6.10 Entropy****LQ 9** starts here — Define and explain the term "entropy".**Introduction**The concept of entropy was introduced into the study of thermodynamics by Rudolph Clausius in 1856 to give a quantitative basis for the second law.**State Variable**

It provides another variable to describe the state of a system, to go along with pressure, volume, temperature and internal energy.

DefinitionIf a system undergoes a reversible process during which it absorbs a quantity of heat ΔQ at absolute temperature T , then the increase in the state variable called entropy S of the system is given by the following relation.**Mathematical Form**

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

SI Unit J K^{-1} **Change in Entropy**Like potential energy or internal energy, it is the change in entropy of the system which is important and not its absolute value.**Sign Convention**

The change in entropy is positive when heat is added to the system and negative when heat is removed from it.

Heat Flow Between Two ReservoirsSuppose an amount of heat Q flows from a reservoir at temperature T_1 through a conducting rod to a reservoir at temperature T_2 , the first being the hotter of the two.**Derivation**The reservoir at T_1 loses heat, so its entropy decreases by the amount Q/T_1 , while the reservoir at T_2 gains heat, so its entropy increases by the amount Q/T_2 instead.

$$\Delta S = \frac{Q}{T_2} - \frac{Q}{T_1}$$

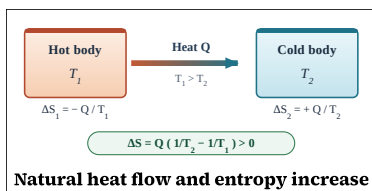
$$\Delta S = Q \frac{T_1 - T_2}{T_1 T_2}$$

Result

As $T_1 > T_2$, therefore Q/T_2 is greater than Q/T_1 and the net change in entropy is positive.

$$\Delta S > 0$$

Diagram



Entropy Statement of the Second Law

In all natural processes where heat flows from one system to another there is always a net increase in entropy. If a system undergoes a natural process, it will go in the direction that causes the entropy of the system plus the environment to increase.

Entropy and Disorder

A natural process tends to proceed towards a state of greater disorder, so there is a relation between entropy and molecular disorder.

Examples

- An irreversible heat flow from a hot to a cold substance increases disorder, because the molecules are initially sorted out into hotter and cooler regions and this order is lost when the system comes to thermal equilibrium.
- The addition of heat to a system increases its disorder, because of the increase in average molecular speeds and therefore in the randomness of molecular motion.
- The free expansion of a gas increases its disorder, because the molecules have greater randomness of position after expansion than before.

Reversible and Irreversible Processes

Only those processes are probable for which the entropy of the system increases or remains constant. The process for which entropy remains constant is a reversible process, whereas for all irreversible processes the entropy of the system increases.

Degradation of Energy

Every time entropy increases, the opportunity to convert some heat into work is lost. There is an increase in entropy when hot and cold water are mixed, and the warm water cannot then be separated into a hot layer and a cold layer.

Explanation

There has been no loss of energy, but some of the energy is no longer available for conversion into work. Increase in entropy therefore means degradation of energy from a higher level, where more work can be extracted, to a lower level at which less or no useful work can be done, the energy eventually ending up as thermal energy.

Entropy of the Universe

Even if the temperature of some system decreases, thereby decreasing its entropy, it is at the expense of a net increase in entropy for some other system. When all the systems are taken together as the universe, the entropy of the universe always increases.

IQ 9 ends here

Book Examples

Example 6.10.1 Calculate the entropy change when 1.0 kg of ice at 0 °C melts into water at 0 °C. The latent heat of fusion of ice is $3.36 \times 10^5 \text{ J kg}^{-1}$.

Given Data

$$m = 1.0 \text{ kg}$$

$$L_f = 3.36 \times 10^5 \text{ J kg}^{-1}$$

$$T = 0^\circ\text{C} = 273 \text{ K}$$

To Find

Change in entropy $\Delta S = ?$

Formula

The heat absorbed at the melting point is $\Delta Q = mL_f$, so

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

Solution

$$\Delta S = \frac{1.0 \times 3.36 \times 10^5}{273}$$

$$= 1.23 \times 10^3 \text{ J K}^{-1}$$

Result $\Delta S = 1.23 \times 10^3 \text{ J K}^{-1}$

Meaning

The entropy increases as the ice turns into water, because the molecules of the liquid are in greater disorder than those held in the solid.

Short Questions

SQ 6.10.1 Why is entropy called a state variable?

Entropy as a State Variable

Entropy describes the condition of a system in the same way as pressure, volume, temperature and internal energy do.

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

Result

It was introduced by Clausius to give a quantitative basis to the second law, and it depends only on the state a system is in.

SQ 6.10.2 Why is only the change in entropy important and not its absolute value?

Change in Entropy

Entropy has no natural zero from which it must be counted, just as potential energy and internal energy have none.

Result

Only the change in entropy of a system is of any use, and that is what the defining relation gives.

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

SQ 6.10.3 Find the change in entropy of a large reservoir at 300 K when 4200 J of heat is added to it.

Change in Entropy $\Delta S = \frac{\Delta Q}{T}$

$$\Delta S = \frac{4200}{300}$$

Result $\Delta S = 14 \text{ J K}^{-1}$

SQ 6.10.4 Heat of 600 J flows from a reservoir at 400 K to one at 300 K. Find the net change in entropy.

Net Change in Entropy

$$\Delta S = \frac{Q}{T_2} - \frac{Q}{T_1}$$

$$\Delta S = \frac{600}{300} - \frac{600}{400} = 2 - 1.5$$

Result $\Delta S = +0.5 \text{ J K}^{-1}$

SQ 6.10.5 Why does the mixing of hot and cold water represent a degradation of energy?	
Increase in Entropy Mixing increases the entropy, and the warm water cannot be separated again into a hot layer and a cold layer. $\Delta S > 0$	
Result No energy has been lost, but some of it can no longer be converted into work, which is what <u>degradation of energy</u> means.	
SQ 6.10.6 A refrigerator lowers the entropy of the food inside it. Does this violate the second law of thermodynamics?	
No, it does not violate the second law of thermodynamics.	
Reason The entropy of the food falls only at the expense of a larger increase in the entropy of the room and of the work supplied.	
Result Taken together, the entropy of the system plus its environment still <u>increases</u> . $\Delta S_{sys} + \Delta S_{surr} > 0$	
SQ 6.10.7 Give two natural processes in which the disorder, and hence the entropy, of a system increases.	
Natural Processes - Heat flowing from a hot to a cold body, because the molecules were sorted into hotter and cooler regions and that order is lost at equilibrium. - The free expansion of a gas, because the molecules have greater randomness of position afterwards.	
MCQ 6.10.1 When 4200 J of heat is added to a large reservoir at 300 K, its entropy increases by:	
A 14 J K ⁻¹	B 1.4 J K ⁻¹
C 140 J K ⁻¹	D 0.07 J K ⁻¹
Solution: $\Delta S = \Delta Q/T = 4200/300 = 14 \text{ J K}^{-1}$.	
MCQ 6.10.2 When 600 J of heat flows from a reservoir at 400 K to one at 300 K, the net change in entropy is:	
A -0.5 J K ⁻¹	B zero
C +0.5 J K ⁻¹	D +3.5 J K ⁻¹
Solution: $\Delta S = 600/300 - 600/400 = 2 - 1.5 = +0.5 \text{ J K}^{-1}$, a net increase.	
MCQ 6.10.3 Entropy describes the state of a system in the same way as:	
A internal energy	B work done
C heat supplied	D power
Solution: Entropy is a state variable, to go along with pressure, volume, temperature and internal energy.	
MCQ 6.10.4 While a refrigerator is running, the entropy of the food inside it:	
A increases	B stays constant
C falls to zero	D decreases, while that of the room increases more
Solution: A decrease of entropy in one system is always at the expense of a larger increase somewhere else, so the total still rises.	
MCQ 6.10.5 Hot and cold water once mixed cannot be separated again into a hot layer and a cold layer, because the mixing is:	
A reversible	B irreversible
C adiabatic	D isothermal
Solution: The entropy has increased, and only processes in which entropy increases or stays constant are possible, so the mixing cannot run backwards.	

MCQ 6.10.6 For a natural process, the entropy of the system plus its environment can never:	
A increase	B stay constant
C be calculated	D decrease
Solution: A natural process always goes in the direction which causes the entropy of the system plus the environment to increase.	
MCQ 6.10.7 For a given quantity of heat absorbed, the increase in entropy is greatest when the temperature is:	
A high	B low
C exactly 273 K	D exactly 373 K
Solution: $\Delta S = \Delta Q/T$, so for a fixed ΔQ the change in entropy is largest at the lowest temperature.	
MCQ 6.10.8 Entropy increases when ice melts into water because the molecules become:	
A more disordered	B more ordered
C heavier	D colder
Solution: The increase in entropy measures the increase in the disorder of the molecules as they pass from the solid to the liquid state.	

Chapter Exercise

SQ 6.1 What is meant by thermal equilibrium? Explain briefly.

Thermal Equilibrium

Two bodies at the same temperature have equal thermal energy, so no heat flows between them.

Example

A spoon in hot coffee takes heat until both reach one temperature. Then there is no net heat flow.

SQ 6.2 What is meant by internal energy? How is it related to temperature of an ideal gas?

Internal Energy

The sum of all molecular energies, kinetic and potential, of a substance.

Ideal Gas

Its molecules exert no force on one another, so only translational K.E. is left.

$$\langle K.E. \rangle = \frac{3}{2} k_B T$$

So it depends only on absolute temperature.

SQ 6.3 State 2nd law of thermodynamics in two different forms.

Kelvin's Statement

It is impossible to devise a process which may convert heat, extracted from a single reservoir, entirely into work without leaving any change in the working system.

Entropy Statement

If a system undergoes a natural process, it will go in the direction that causes the entropy of the system plus the environment to increase.

SQ 6.4 Is it possible to construct a heat engine of 100% efficiency? Explain.

No, it is not possible to construct a heat engine of 100% efficiency.

Reason

The efficiency of a Carnot engine, the most efficient of all, is

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

This becomes one only when the cold reservoir is at absolute zero.

$$T_2 = 0 \text{ K}$$

Conclusion

Such reservoirs are not available, so 100% efficiency is impossible.

SQ 6.5 Differentiate between reversible and irreversible processes.

Reversible Process	Irreversible Process
It can be <u>retraced in exactly reverse order</u> .	It <u>cannot be retraced</u> backwards.
No change is left in the surroundings.	A net change is left behind.
All effects are exactly reversed at each stage.	Friction or dissipation of energy occurs.
Slow evaporation of a liquid.	An explosion.

SQ 6.6 Why adiabat is steeper than isotherm? Explain.

Isothermal Process

Temperature is constant, so

$$PV = \text{constant}$$

Adiabatic Process

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

Since $\gamma > 1$, pressure falls more rapidly with volume, and the gas also cools as it expands.

SQ 6.7 A refrigerator transforms heat from cold to hot body. Does this violate the second law of thermodynamics? Justify your answer.

No, a refrigerator does not violate the second law of thermodynamics.

Energy Balance

It throws heat from the cold body to the hot body by using external work on its compressor.

$$Q_C + W = Q_H$$

Reason

The second law forbids such a flow only when it happens by itself, without external work.

SQ 6.8 Explain briefly heat death of universe in terms of entropy.

Increase in Entropy

In all natural processes the entropy of the universe increases and energy is degraded.

Heat Death

At maximum entropy energy is spread uniformly and no temperature difference is left, so no useful work can be done.

SQ 6.9 Is it possible for a cyclic reversible heat engine to absorb heat at constant temperature and transforms it completely into work without rejecting some heat at low temperature? Explain.

No, it is not possible.

Reason

Such an engine would reject no heat and be 100% efficient, which violates Kelvin's statement that heat from a single reservoir cannot be turned entirely into work.

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

Conclusion

Even a reversible engine must reject heat to the sink.

SQ 6.10 How does behaviour of real gases differ from ideal gas at high pressure and low temperature? Identify the reasons behind these differences based on kinetic theory of gases.

Deviation of Real Gases

A real gas does not obey the ideal gas equation at high pressure and low temperature.

At high pressure the molecules are close, so their finite volume is not negligible.

At low temperature the molecular K.E. falls, so intermolecular forces act.

Ideal Behaviour

A real gas behaves ideally at low pressure and high temperature.

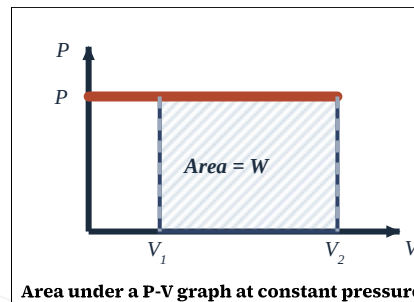
SQ 6.11 Show that area under P-V graph is equal to work done.

Work as P-V graph area

A gas at a pressure P expands through a small change of volume, and the work it does is the product of the two.

$$W = P\Delta V$$

The rectangle of height P and width ΔV standing under the P-V graph has an area equal to the work done by the gas.



$$\text{Area} = \text{height} \times \text{base}$$

$$= P \times \Delta V$$

$$W = P\Delta V$$

SQ 6.12 How is work done (i) by a gas (ii) on a gas?

Work Done by a Gas

On expansion the gas does work on its surroundings.

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

Here $V_2 > V_1$, so this work is positive.

Work Done on a Gas

On compression the surroundings do work on the gas.

Now $V_2 < V_1$, so this work is negative.

CRQ 6.1 Explain how thermodynamics relates to the concept of energy conservation.

First Law

Heat added to a system appears as an increase in internal energy plus the work done by the system.

$$Q = \Delta U + W$$

Energy Conservation

It is the law of conservation of energy applied to heat. Energy only changes form and is never created or destroyed.

CRQ 6.2 Explain how thermodynamics applies to biological systems, such as human body.

Metabolism

Energy transforming processes in an organism are called metabolism. Food energy is changed into internal energy, work and heat.

First Law

$$\Delta U = Q - W$$

Work done in walking and growth decreases internal energy.

Body temperature is maintained by the food we eat.

CRQ 6.3 A gas is expanding adiabatically. Explain what happens to temperature and pressure of the gas.

Both temperature and pressure decrease.

Adiabatic Condition

No heat enters or leaves the gas, so

$$W = -\Delta U$$

The gas works at the expense of its internal energy, so its temperature falls.

Pressure Volume rises and temperature drops, so pressure also decreases. $PV^\gamma = \text{constant}$	
CRQ 6.4 A coffee cup is left on a table, and overtime coffee cup cools down. Explain thermodynamics processes occurring during this process.	
Heat Transfer The hot coffee loses heat by conduction, convection, radiation and evaporation. Its internal energy and temperature fall, while the surroundings gain heat. Cooling stops at <u>room temperature</u> . Entropy The heat flow is irreversible, so total entropy increases.	
CRQ 6.5 How can we explain different weather patterns through thermodynamical processes like wind, rain, etc.	
Wind Uneven heating by the Sun makes air warm and rise, and cooler air rushes in. This movement of air is <u>wind</u> . Rain Rising air expands <u>adiabatically</u> and cools. Vapour condenses into clouds and large drops fall as rain.	
MCQ 6.1 In an isothermal change, the internal energy:	
A decreases	B increases
C remains the same	D becomes zero
Solution: The internal energy of an ideal gas depends only on temperature, which is constant here, so it remains the same.	
MCQ 6.2 The first law of thermodynamics is based upon the law of conservation of:	
A mass	B energy
C momentum	D charge
Solution: The first law is the law of conservation of energy applied to heat.	
MCQ 6.3 A device which converts thermal energy into mechanical energy is called:	
A heat engine	B Carnot engine
C refrigerator	D turbine
Solution: A heat engine is the device which converts some thermal energy into mechanical work.	
MCQ 6.4 When two objects having the same temperature are made in thermal contact, then they are at:	
A thermal equilibrium	B chemical equilibrium
C mechanical equilibrium	D physical equilibrium
Solution: At the same temperature there is no net heat flow between them, so they are in thermal equilibrium.	
MCQ 6.5 When a system is expanded by adding heat energy, then the work done will be:	
A positive and on the system	B negative and on the system
C positive and by the system	D negative and by the system
Solution: On expansion the gas pushes its surroundings, so the work is done by the system and is taken as positive.	
MCQ 6.6 The entropy of a system in a reversible process:	
A decreases	B increases
C is infinite	D is zero
Solution: Entropy remains constant in a reversible process, so its change is zero.	
MCQ 6.7 What happens to the internal energy of an object when its temperature increases?	
A decreases	B remains constant

C increases	D fluctuates
Solution: A rise in temperature reflects an increase in the internal kinetic energy of the particles, so the internal energy increases.	
MCQ 6.8 The value of Boltzmann constant is:	
A $1.38 \times 10^{-22} \text{ J K}^{-1}$	B $1.38 \times 10^{23} \text{ J K}^{-1}$
C $1.38 \times 10^{-23} \text{ J K}^{-1}$	D $1.38 \times 10^{-23} \text{ J}^{-1} \text{ K}^{-1}$
Solution: $k_B = R/N_A = 1.38 \times 10^{-23} \text{ J K}^{-1}$, that is joule per kelvin.	
MCQ 6.9 In an adiabatic process, there is no:	
A change in temperature	B exchange of heat
C change in internal energy	D work done
Solution: An adiabatic process is one in which no heat enters or leaves the system, so $\Delta Q = 0$.	
MCQ 6.10 Thermodynamics mostly deals with the:	
A measurement of quantity of heat	B transfer of quantity of heat
C changes of state	D conversion of heat into other forms of energy
Solution: Thermodynamics deals with the relationships and conversions between heat and other forms of energy.	
Numerical 6.1 A gas occupies 6.0 L of volume at a pressure of 12 atm. What will be the volume of the gas if the pressure is increased by 2.0 atm, assuming that the temperature remains constant? (Ans: 5.14 L)	
Given Data $V_1 = 6.0 \text{ L}$ $P_1 = 12 \text{ atm}$ $P_2 = 12 + 2.0 = 14 \text{ atm}$	
To Find Final volume $V_2 = ?$	
Formula The temperature is constant, so Boyle's law applies. $P_1 V_1 = P_2 V_2$ $V_2 = \frac{P_1 V_1}{P_2}$	
Solution $V_2 = \frac{12 \text{ atm} \times 6.0 \text{ L}}{14 \text{ atm}}$ $= 5.14 \text{ L}$	
Result $V_2 = 5.14 \text{ L}$	
Numerical 6.2 In a vacuum chamber connected to a cryogenic pump, a pressure as low as 1.00 nPa is attained. Calculate the number of molecules in a 1.00 m ³ vessel at this pressure and a temperature of 300 K. (Ans: 2.41×10^{11} molecules)	
Given Data $P = 1.00 \text{ nPa} = 1.00 \times 10^{-9} \text{ Pa}$ $V = 1.00 \text{ m}^3$ $T = 300 \text{ K}$ $k_B = 1.38 \times 10^{-23} \text{ J K}^{-1}$	
To Find Number of molecules $N = ?$	
Formula $PV = Nk_B T$ $N = \frac{PV}{k_B T}$	
Solution $N = \frac{1.00 \times 10^{-9} \times 1.00}{1.38 \times 10^{-23} \times 300}$ $= 2.41 \times 10^{11}$	
Result $N = 2.41 \times 10^{11} \text{ molecules}$	

Numerical 6.3 A gas undergoes a thermodynamic process in which it absorbs 500 J of heat energy and performs 300 J of work on its surroundings. Calculate the change in internal energy of the gas. (Ans: 200 J)

Given Data $Q = +500 \text{ J}$

$$W = +300 \text{ J}$$

Sign Convention

Heat absorbed by the gas and work done by the gas are both taken as positive.

To Find

Change in internal energy $\Delta U = ?$

Formula $\Delta U = Q - W$

Solution

$$\Delta U = 500 \text{ J} - 300 \text{ J} = 200 \text{ J}$$

Result $\Delta U = 200 \text{ J}$

Numerical 6.4 A Carnot engine is operating between a high temperature reservoir at 600 K and a low temperature reservoir at 300 K. Calculate (i) the maximum possible efficiency (ii) the amount of work output if the engine absorbs 500 J of heat from the high temperature reservoir. [Ans: (i) 50% (ii) 250 J]

Given Data

$$T_1 = 600 \text{ K}$$

$$T_2 = 300 \text{ K}$$

$$Q_1 = 500 \text{ J}$$

To Find

Efficiency $\% \eta = ?$ and work output $W = ?$

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

$$W = \eta Q_1$$

Solution

Putting the temperatures in the first relation

$$\eta = \frac{600 \text{ K} - 300 \text{ K}}{600 \text{ K}} = 0.5$$

The work output is this fraction of the heat drawn from the hot reservoir.

$$W = 0.5 \times 500 \text{ J} = 250 \text{ J}$$

Result $\% \eta = 50\%$

$$W = 250 \text{ J}$$

Numerical 6.5 A refrigerator extracts 1200 J of heat from its interior (the cold reservoir) and releases 1800 J of heat to the surrounding environment (the hot reservoir) during each cycle. Calculate (i) the work input required per cycle (ii) the coefficient of performance of the refrigerator. [Ans: (i) 600 J (ii) 2]

Given Data $Q_C = 1200 \text{ J}$

$$Q_H = 1800 \text{ J}$$

To Find

Work input $W = ?$ and coefficient of performance $E = ?$

Formula $W = Q_H - Q_C$

$$E = \frac{Q_C}{W}$$

Solution

The work supplied in each cycle is the difference of the two quantities of heat.

$$W = 1800 \text{ J} - 1200 \text{ J} = 600 \text{ J}$$

The coefficient of performance is the heat drawn from the cold body per joule of work.

$$E = \frac{1200 \text{ J}}{600 \text{ J}} = 2$$

Result $W = 600 \text{ J}$

$$E = 2$$

Numerical 6.6 Calculate the entropy change when 1.0 mole of ice at 0 °C melts to form liquid water at the same temperature. (Heat of fusion of ice per mole = $6.01 \times 10^3 \text{ J mol}^{-1}$) (Ans: 22.0 J K^{-1})

Given Data

$$n = 1.0 \text{ mol}$$

$$L_f = 6.01 \times 10^3 \text{ J mol}^{-1}$$

$$T = 0^\circ \text{C} = 273 \text{ K}$$

To Find

Change in entropy $\Delta S = ?$

Formula

Melting is carried out at a constant temperature, so

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

Solution

$$\Delta S = \frac{1.0 \times 6.01 \times 10^3}{273} = 22.0 \text{ J K}^{-1}$$

Result $\Delta S = 22.0 \text{ J K}^{-1}$

Numerical 6.7 A gas occupies 400 mL at 20 °C. What volume will it occupy at 80 °C, assuming constant pressure? (Ans: 482 mL)

Given Data

$$V_1 = 400 \text{ mL}$$

$$T_1 = 20^\circ \text{C} = 293 \text{ K}$$

$$T_2 = 80^\circ \text{C} = 353 \text{ K}$$

To Find Final volume $V_2 = ?$

Formula

The pressure is constant, so Charles' law applies.

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

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

Solution

$$V_2 = \frac{400 \text{ mL} \times 353 \text{ K}}{293 \text{ K}} = 482 \text{ mL}$$

Result $V_2 = 482 \text{ mL}$

Numerical 6.8 A gas has a pressure of 2 atm at 300 K. What pressure will it have at 450 K, assuming constant volume? (Ans: 3 atm)

Given Data

$$P_1 = 2 \text{ atm}$$

$$T_1 = 300 \text{ K}$$

$$T_2 = 450 \text{ K}$$

To Find Final pressure $P_2 = ?$

Formula

The volume is constant, so Gay-Lussac's law applies.

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

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

Solution

$$P_2 = \frac{2 \text{ atm} \times 450 \text{ K}}{300 \text{ K}} = 3 \text{ atm}$$

Result $P_2 = 3 \text{ atm}$

Self Test

Seventeen questions across the whole chapter. Work through them without the notes, then check the answers keyed at the foot of the page.

Q 1 The kinetic theory treats the molecules of a gas as point masses because their own volume is negligible compared with the volume of the:

- | | | | |
|---|-----------|---|-----------------------|
| A | container | B | molecules of a liquid |
| C | walls | D | piston |

Q 2 The pressure a gas exerts on the walls of its container is produced by:

- | | | | |
|---|--------------------------------------|---|--|
| A | the weight of the gas | B | the collisions of its molecules with the walls |
| C | the attraction between its molecules | D | the volume of its molecules |

Q 3 At the same temperature, the average kinetic energies of a hydrogen molecule and of an oxygen molecule are:

- | | | | |
|---|------------------------------|---|--------------------|
| A | in the ratio of their masses | B | greater for oxygen |
| C | greater for hydrogen | D | equal |

Q 4 The value of the universal gas constant R is:

- | | | | |
|---|--|---|---|
| A | $1.38 \times 10^{-23} \text{ J K}^{-1}$ | B | $6.02 \times 10^{23} \text{ mol}^{-1}$ |
| C | $8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$ | D | $273 \text{ J mol}^{-1} \text{ K}^{-1}$ |

Q 5 The volume of a fixed mass of gas at constant pressure is doubled when its absolute temperature is:

- | | | | |
|---|-----------------|---|-----------|
| A | halved | B | doubled |
| C | raised by 273 K | D | unchanged |

Q 6 A gas is described as ideal when it obeys the equation $PV = nRT$:

- | | | | |
|---|-----------------------------------|---|-------------------------|
| A | only at high pressure | B | only at low temperature |
| C | at all pressures and temperatures | D | only in a rigid vessel |

Q 7 The internal energy of an ideal gas depends only on its:

- | | | | |
|---|----------|---|-------------|
| A | pressure | B | volume |
| C | density | D | temperature |

Q 8 The work done by a gas is taken as positive when the gas:

- | | | | |
|---|---------------|---|------------------------------|
| A | is compressed | B | expands |
| C | is cooled | D | is heated at constant volume |

Q 9 When a gas is compressed adiabatically, its temperature:

- | | | | |
|---|----------------|---|------------------------|
| A | rises | B | falls |
| C | stays constant | D | falls to absolute zero |

Q 10 In an isothermal expansion of an ideal gas, the heat supplied is equal to:

- | | | | |
|---|-----------------------------|---|--------------------|
| A | the rise in internal energy | B | zero |
| C | the work done by the gas | D | half the work done |

Q 11 Which one of the following is NOT a state function?

- | | | | |
|---|-----------------|---|----------|
| A | internal energy | B | pressure |
| C | heat | D | volume |

Q 12 A Carnot engine takes in 600 J of heat and rejects 240 J in each cycle. Its efficiency is:

- | | | | |
|---|-----|---|-----|
| A | 40% | B | 24% |
| C | 60% | D | 76% |

Q 13 The efficiency of a Carnot engine depends only on:

- | | | | |
|---|-----------------------|---|--|
| A | the working substance | B | the temperatures of the two reservoirs |
| C | the mass of the gas | D | the size of the cylinder |

Q 14 The coefficient of performance of a refrigerator:

- | | | | |
|---|-------------------------|---|----------------------|
| A | can be greater than one | B | can never exceed one |
| C | is measured in joule | D | is always zero |

Q 15 Over one complete cycle of a heat engine, the change in the internal energy of the working substance is:

- | | | | |
|---|----------------------------|---|------------------------|
| A | equal to the heat absorbed | B | equal to the work done |
| C | zero | D | always negative |

Q 16 Entropy is measured in the same unit as:

- | | | | |
|---|-------------|---|---------------|
| A | heat | B | work |
| C | temperature | D | heat capacity |

Q 17 A process is impossible if it would make the total entropy of a system and its surroundings:

- | | | | |
|---|----------|---|-----------------|
| A | increase | B | stay constant |
| C | decrease | D | become positive |

Answers 1 (a) 2 (b) 3 (d) 4 (c) 5 (b) 6 (c) 7 (d) 8 (b) 9 (a) 10 (c) 11 (c) 12 (c) 13 (b) 14 (a) 15 (c) 16 (d) 17 (c)