Unit 06 Heat and Thermodynamics

STUDENT'S LEARNING OUTCOMES (SLO's)

After studying this unit, the students will be able to:

- Describe the basic assumptions of the kinetic theory of gasses. [Including understanding the temperature, pressure and density conditions under which an ideal gas is a good approximation of a real gas.]
- State that regions of equal temperature are in thermal equilibrium
- Relate a rise in temperature of an object to an increase in its internal energy
- Apply the equation of state for an ideal gas[expressed as PV = nRT, where n = amount of substance (number of moles) and as PV =N kBT, where N =number of molecules]
- State that the Boltzmann constant k is given by kB = R / NA
- Use W = PDV for the work done when the volume of a gas changes at constant pressure.
- Describe the difference between the work done by a gas and the work done on a gas.
- Define and use the first law of thermodynamics [DU = Q - W expressed in terms of the increase in internal energy, the heating of the system (energy transferred to the system by heating) and the work done on the system]
- Explain qualitatively, in terms of particles, the relationship between the pressure, temperature and volume of a gas [Specifically the below case:
  (a) pressure and temperature at constant volume
  (b) volume and temperature at constant pressure
  (c) pressure and volume at a constant temperature
- Use the equation, including a graphical representation of the relationship between pressure and volume for a gas at constant temperature.
- Justify how the first law of thermodynamics expresses the conservation of energy.
- Relate a rise in temperature of a body to an increase in its internal energy.
- State the working principle of a heat engine.
- Describe the concept of reversible and irreversible processes.
- State and explain the second law of thermodynamics.
- State the working principle of Carnot's engine
- Describe that refrigerator is a heat engine operating in reverse as that of an ideal heat engine.
- Explain that an increase in temperature, increases the disorder of the system.
- Explain that increase in entropy means degradation of energy.
- Explain that energy is degraded during all natural processes.
- Identifying that system tends to become less orderly over time.
- Explain that Entropy, S is a thermodynamic quantity that relates to the degree of disorder of the particles in a system.
- State that the Carnot cycle sets a limit for the efficiency of a heat engine at the temperatures of its heat reservoir given by;
  Efficiency = $1 - \frac{T_{cold\ reservoir}}{T_{hot\ reservoir}}$

6.1 ASSUMPTIONS OF THE KINETIC THEORY OF GASES

Q1. What is thermodynamics? Describe its role.

Ans. Thermodynamics

Definition

It is the branch of Physics that deals with the relationship between heat, work, temperature and energy is called thermodynamics.

Role of Thermodynamics

1. Energy conversion

Thermodynamics is essential in understanding how energy is converted from one form to another (e.g., heat to mechanical energy in engines).

2. **Heat transfer**
   It describes how heat flows between objects and systems, which is crucial in designing heating and cooling systems.
3. **Laws of nature**
   It defines the fundamental laws (the four laws of thermodynamics) that govern all physical and chemical processes.
4. **Engineering applications**
   It is used in designing engines, refrigerators, air-conditioners, power plants, and even in spacecrafts.
5. **Biological and chemical processes**
   Thermodynamics also plays a role in understanding metabolic processes in biology and reaction spontaneity in chemistry.

Q 2. What is the kinetic theory of gases? Describe its assumptions.

Ans. The Kinetic Theory of Gases

The kinetic theory of gases is a scientific theory that explains the behaviour of gases at the microscopic level using the idea that gas particles are in constant, random motion. It connects the microscopic properties of gases; like pressure, temperature, and volume.

Assumptions of Kinetic Theory of Gases

The kinetic theory of gases is a fundamental theory in physics and chemistry that explains the behaviour of gases based on the motion of their constituent particles. This theory provides a macroscopic understanding of gas properties such as pressure, temperature, and volume.

Here are the key assumptions of the kinetic theory of gases:

1. **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.
2. **Negligible Volume of Gas Particles**
   The volume of the individual gas molecules is negligible as compared to the total volume of the gas. This means that the particles are considered point masses with no significant volume.
3. **No Intermolecular Forces**
   There are no attractive or repulsive forces between the gas molecules. The particles do not exert any force on each other except during collisions.
4. **Elastic Collisions**
   The collisions between gas molecules, and with the walls of the container are perfectly elastic. This means that there is no net loss of kinetic energy during collisions. The total kinetic energy is conserved.
5. **Large Number of Particles**
   A gas contains a large number of particles. This large number allows for the use of statistical methods to describe the properties of the gas.
6. **Average Kinetic Energy is Proportional to Temperature**
   The average kinetic energy of gas particles is directly proportional to the absolute temperature of the gas. This implies that as the temperature increases, the speed of the gas particles also increases.
7. **Pressure due to Particle Collisions**
   The pressure exerted by a gas on the walls of its container is due to the collisions of gas particles with the walls. The force exerted by the particles during collisions generates pressure.
8. **Time of Collisions is Negligible**
   The time interval of a collision between gas particles is extremely short compared to the time between collisions. This assumption simplifies the analysis of particle dynamics.

Q 3. What are the limitations of kinetic molecular theory of gases?

Ans. Limitations of Kinetic Molecular Theory of Gases

The assumption of KMT hold true for ideal gases, but real gases exhibit deviations due to intermolecular forces and finite molecular volume, especially at high pressure and low temperature.

KMT has several limitations:

1. **Assumes ideal gas behaviour**
KMT assumes that gas particles have no volume and intermolecular forces, which is not true for real gases, especially at high pressures and low temperature.
2. **Cannot accurately predict real gas behaviour**
Real gases deviate from ideal behaviour due to attractions or repulsions between molecules and because gas particles do occupy space.
3. **Fails at high pressures**
At high pressures, gas particles are closer together, so their volume and intermolecular forces cannot be ignored, making KMT less accurate.
4. **Inaccurate at low temperature**
At low temperatures, intermolecular attractions become significant, and gases may condense, which is not predicted by KMT.
5. **Does not apply to liquids or solids**
KMT is designed for gases only. It does not explain the behaviour of liquids and solids, where particle interactions and ordered structure dominate.
6. **Assume elastic collisions**
All collisions are assumed to be perfectly elastic (no energy loss), which is not always true in reality.

Q 4. What is the equation of state for an ideal gas?

Ans. Equation of State for an Ideal Gas

A gas that obeys kinetic theory of gases is termed as an ideal gas. Ideal gas equation is given by

$$PV = nRT \quad \text{...... (i)}$$

Here P represents pressure, V is volume, n is number of moles of the gas, R is universal gas constant ($R = 8.3145\ \text{J mol}^{-1}\ \text{K}^{-1}$) and T is the absolute temperature.

Equation (i) implies that product of pressure and volume is directly proportional to the absolute temperature for an ideal gas.

Q 5. Derive a relation for ideal gas equation in the form of $PV = Nk_BT$, from general gas equation.

Ans. Real Gases to Behave Like an Ideal Gas

According to kinetic theory of gases, a gas has no intermolecular interaction and molecules are far apart from each other. For a real gas to behave like an ideal gas, some conditions must be satisfied. Potential energy (P.E) of the gas molecules is negligible and this have only kinetic energy (K.E).

In equation PV = nRT, n represents number of moles which can be given by

$$n = \frac{\text{Mass of gas}}{\text{Molar mass of gas}} = \frac{m}{M}$$

So, the equation PV = nRT becomes:

$$PV = \frac{m}{M}RT \quad \text{or} \quad PM = \left(\frac{m}{V}\right)RT$$

As density; $\rho = \frac{m}{V}$ So $\rho = \frac{PM}{RT}$ or $\rho \propto \frac{P}{T}$, where $\frac{M}{R}$ is constant.

The density of a gas will be low at low pressure and high temperature due to which molecules of the gas will be at large distance from each other and the intermolecular forces will be negligible. So, the real gas behaves like an ideal gas at low pressure and high temperature.

Ideal Gas Equation in Terms of Boltzmann Constant

From ideal gas equation:

$$PV = nRT \quad \text{...... (i)}$$

Here 'n' represents number of moles of the ideal gas.

Mole

A mole is defined as the number of atoms or molecules per unit Avogadro's number ($N_A = 6.02 \times 10^{23}$).

Mathematically,

$$n = \frac{N}{N_A} \quad \text{...... (ii)}$$

where 'n' is number of atoms or molecules.

Substituting Eq. (ii) in Eq. (i), we have

$$PV = \frac{N}{N_A} RT \quad \text{...... (iii)}$$

> **For Your Information**
> Real gases approach ideal behaviour under:
> (i) low pressure
> (ii) high temperature

The term $\frac{R}{N_A}$ is termed as Boltzmann constant k_B.

Mathematically;

$$k_B = \frac{R}{N_A} \quad \text{...... (iv)}$$

Substituting the value of R and N_A, we have

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

Substituting Eq. (iv) in Eq (iii),

$$PV = N k_B T \quad \text{...... (v)}$$

Equation (v) gives ideal gas equation in terms of Boltzmann constant k_B.

Example 6.1: One mole of an ideal gas is at a temperature of 300 K. If the Boltzmann constant is 1.38×10^{-23} J K^{-1}, calculate the volume of the gas at a pressure of 1 atom. [1 atm = 101325 Pa]

Solution:

Given that;

$T = 300$ K

$k_B = 1.38 \times 10^{-23}$ JK^{-1}

$P = 1$ atm

1 atm = 101325 Pa

To Find:

$V = ?$

Calculations:

We know that;

$$PV = nRT$$

$$R = N_A \times k_B \quad \text{where } k_B = \frac{R}{N_A}$$

Thus $$V = \frac{nN_A k_B T}{P}$$

Putting the values

$$V = \frac{1\ \text{mol} \times 6.02 \times 10^{23}\ \text{mol}^{-1} \times 1.38 \times 10^{-23}\ \text{J K}^{-1} \times 300\ \text{K}}{101325\ \text{Pa}}$$

$V \approx 0.0245$ m^3 **Ans.**

Thus, volume of gas would be 0.0245 m^3.

Q 6. State and explain gas laws.

Ans. Gas Laws

There are some variables (state functions) which describe quantity of gas which includes pressure, volume, and temperature (P, V, and T) with change in one variable, the second variable changes while the third is kept constant. The laws that relate these variables mutually for an ideal gas are termed as gas laws.

Boyle's Law

Statement

It sated that for a fixed mass of an ideal gas, the pressure P exerted by a gas varies inversely with volume V occupied by the gas at constant temperature.

Mathematically;

$$P \propto \frac{1}{V} \text{ at constant } T$$

or $$P = \text{constant} \frac{1}{V}$$

or $$PV = \text{constant}$$

or $$P_1V_1 = P_2V_2$$

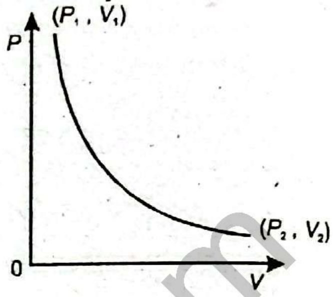


Fig. 1: Boyle's law

Charles' Law

Statement

It states that the volume of given mass of gas at constant pressure is directly proportional to the absolute temperature.

Mathematically;

$$V \propto T \text{ at constant pressure}$$

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

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

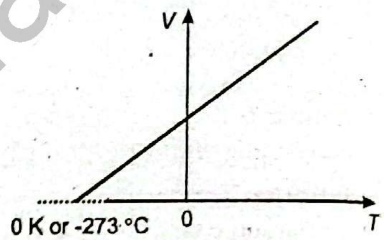


Fig. 2: Charles' law

Joseph lussac's Law

Statement

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

Mathematically;

$$P \propto T \text{ at constant volume}$$

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

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

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

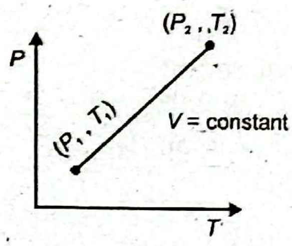


Fig. 3: Joseph lussac's law

Q 7. Define thermal equilibrium and give examples.

Ans. Thermal equilibrium

Definition

Thermal equilibrium is a state in which two or more objects that are in contact with each other no longer transfer heat between them. This happens when they all reach the same temperature.

Examples

1. **Hot coffee cooling to room temperature**
   A cup of hot coffee left on the table eventually cools down to the same temperature as the surrounding air. Once both are at the same temperature, thermal equilibrium is reached.
2. **Ice melting in water**
   When you drop ice cubes into a glass of water, the ice absorbs heat and melts. Eventually, both the ice (row water) and the original water reach the same temperature.

3. **Refrigerator items**
Food placed in a refrigerator will gradually cool down to match the internal temperature of the fridge. Once this happens, it is the thermal equilibrium with its environment.

4. **Metal rod heated at one end and insulated**
If a metal rod is heated at one end and then left alone, heat will flow until the entire rod reaches the same temperature, achieving thermal equilibrium.

mCQ's

1. **Ideal gas law is:**
(A) PV = NUK (B) P = NkT
(C) PV = nRT✓ (D) None of these

2. **Heat is a form of:**
(A) Power (B) Momentum
(C) Torque (D) Energy✓

3. **According to Charles' law:**
(A) $V \propto T$✓ (B) $V \propto n$
(C) $P \propto \frac{1}{n}$ (D) $P \propto \frac{1}{V}$

4. **Gas law; PV = constant is for:**
(A) Isothermal process✓ (B) Adiabatic process
(C) Isochoric process (D) Isobaric process

5. **In thermodynamics, the change in the internal energy depends upon:**
(A) The initial state only (B) Final state only
(C) Path taken between these 2 states
(D) The initial and final state✓

6. **Boltzmann constant k is equal to:**
(A) $\frac{N_A}{R}$ (B) $\frac{R}{N_A}$✓
(C) $\frac{R}{No}$ (D) $\frac{No}{R}$

7. **The value of Boltzmann constant is:**
(A) $6.02 \times 10^{23}\ JK^{-1}$ (B) $1.38 \times 10^{23}\ JK^{-1}$
(C) $1.38 \times 10^{-23}\ JK^{-1}$✓ (D) $6.02 \times 10^{-23}\ JK^{-1}$

8. **At constant temperature and pressure, if volume of given mass of a gas is doubled, then density of the gas becomes:**
(A) Double (B) $\frac{1}{4}$ of original
(C) $\frac{1}{2}$ of original✓ (D) Unchanged

9. **If temperature of a gas is constant, then $<\frac{1}{2}mv^2>$ of the molecule of gas will be:**
(A) Constant✓ (B) Zero
(C) Increased (D) Decreased

10. **At constant temperature, if pressure is halved then its volume is:**
(A) Constant (B) Halved
(C) Four times (D) Double✓

11. **According to kinetic theory of gases, the size of molecule than the separation between them is:**
(A) Much Smaller than✓ (B) Than Smaller
(C) Larger than (D) Much larger that

12. **The K.E of molecules of an ideal gas at absolute zero will be:**
(A) Zero✓ (B) Infinite
(C) Very high (D) Below zero

13. **For one mole of an ideal gas, the gas equation becomes:**
(A) PV = nRT (B) PV = 3RT
(C) $PV = \frac{3}{2}RT$ (D) PV = RT✓

14. **At constant temperature, the kinetic theory of gases leads to:**
(A) Boyle's law✓ (B) Charles' law
(C) Avogadro's law (D) Joseph Lussac's law

15. **The pressure exerted by a gas is inversely proportional to:**
(A) Temperature (B) Number of moles
(C) Volume✓ (D) Velocity

16. **The value of universal gas constant 'R' is:**
(A) $0.0821\ L\ atm\ mol^{-1}\ K^{-1}$ (B) $8.31\ J\ mol^{-1}\ K^{-1}$✓
(C) $1.38 \times 10^{-23}\ JK^{-1}$ (D) $273\ J\ mol^{-1}\ K^{-1}$

17. **Joseph Lussac's law relates:**
(A) Volume and pressure (B) Volume and temperature
(C) Pressure and volume
(D) Pressure and temperature✓

18. **Which law relates all three variables (pressure, volume and temperature) in one equation?**
(A) Boyle's law (B) Charles' law
(C) Avogadro's law (D) Combined gas law✓

19. **Which gas law explains why a balloon expands when heated?**
(A) Boyle's law (B) Charles' law✓
(C) Combined gas law (D) Joseph Lussac's law

20. **The dimensional formula of gas constant R is:**
(A) $[MLT^{-2}]$ (B) $[ML^2T^{-2}K^{-1}]$✓
(C) $[ML^2T^{-3}]$ (D) $[L^3T^{-1}K^{-1}]$

6.2 INTERNAL ENERGY

8. What is internal energy and temperature of a gas? Explain.

Ans. Internal Energy

Definition

The sum of all forms of molecular energies (kinetic and potential) of a substance is termed as its internal energy. In the study of thermodynamics, usually ideal gas is considered as a working substance. The molecules of an ideal gas exert no forces on one another. So, the internal energy of an ideal gas system is generally the translational K.E. of its molecules.

Since the temperature of a system is defined as the average K.E. of its molecules, thus for an ideal gas system, the internal energy is directly proportional to its temperature.

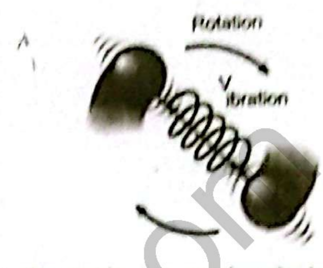
According to the kinetic theory of gases, the average kinetic energy of gas molecules is given by

$$\langle \frac{1}{2}mv^2 \rangle = \frac{3}{2}k_B T$$

where k_B is Boltzmann constant.

Therefore, the rise in temperature of an object reflects an increase in the internal kinetic energy of its particles. This increase in internal energy can occur due to the absorption of heat energy, which raises the average kinetic energy of the particles and thus increases the temperature of the object.

Do You Know



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

Tidbit

Different processes can lead to changes in internal energy and temperature, such as heating (adding heat), adiabatic compression or expansion (no heat exchange), or phase changes (where heat energy changes the state of matter without changing temperature).

9. Explain that in thermodynamics, internal energy is a function of state.

Ans. In thermodynamics, internal energy is considered as

State function, meaning it depends only on the current state of the system and not on the **path**, the system took to reach that state.

A state is defined by properties such as pressure, volume and temperature. If a system moves from one state to another, the change in internal energy ΔU depends completely on the initial and final states, not on how the process occurred.

Mathematically, it can be written as:

$$\Delta U = U_{final} - U_{initial}$$

This is in contrast to path functions like heat Q and work W, which do depend on the process taken between two states. Even though heat and work may vary depending on the path, their combined effect on internal energy remains fixed for a given change in state due to the first law of thermodynamics

$$\Delta U = Q - W$$

For Your Information

Internal energy is a function of state. Consequently, it does not depend on path but depends on initial and final states of the system. Thus, internal energy is similar to the gravitational P.E. So, like the potential energy, it is the change in internal energy and not its absolute value, which is important.

6.3 HEAT AND WORK

10. What is the relationship between heat and work? Calculate the work done when a gas is enclosed in a cylinder.

Ans. Work and Heat

Heat and work are two fundamental forms of energy transfer in thermodynamic. Their relationship is described by the relation.

$$\Delta U = Q - W$$

The work done by the system on its surrounding is considered positive while work done on the system by the surrounding is taken as negative. If an amount of heat Q enters the system, then there is an increase in internal energy or as a resulting quantity of work performed by the system on the surrounding or both.

Consider the gas enclosed in the cylinder with a moveable, frictionless piston of cross-sectional area A; Fig. 4(a). In equilibrium, the system occupies volume V and exerts a pressure P on the walls of the cylinder and its piston. The force F exerted by the gas on the piston is PA.

We assume that the gas expands through ΔV very slowly, so that it remains in equilibrium; Fig. 4(b). As the piston moves up through a small distance Δy, the work W done by the gas is:

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

Since $A\Delta y = \Delta V$ (Change in volume)

Hence $W = P\Delta V$

The work done can also be calculated by area of the curve under P-V graph; Fig. 5.

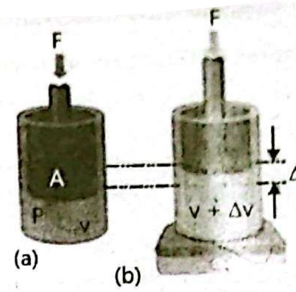


Fig. 4: A gas is sealed in a cylinder by a weightless, frictionless piston. The constant download downward applied force F equals PA, and when the piston is displaced, downward work is done on the gas.

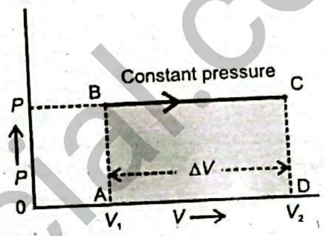


Fig. 5

6.4 FIRST LAW OF THERMODYNAMICS

11. State and explain first law of thermodynamics. Give an example in support of your answer.

Ans. First Law of Thermodynamics

Statement

Energy can neither be created nor destroyed, only transformed from one form to another. The total energy of an isolated system remains constant.

or

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.

Explanation

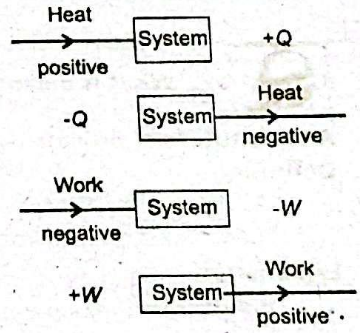
When heat is added to a system, there is an increase in the internal energy due to the rise in temperature, and an increase in pressure or change in the state. If at the same time, a substance is allowed to do work on its environment by expansion, the heat Q required will be the heat necessary to change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

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

or $Q = \Delta U + W$ ...... (i)

Thus, the change in internal energy $\Delta U = U_2 - U_1$ is defined as $Q - W$.

For Your Information



1. **Conservation Principle**: The underlying principle of the first law of thermodynamics is the conservation of energy. It asserts that while energy can change from one form to another (such as from chemical potential energy to thermal energy), the total energy in an isolated system remains constant over time.
2. **Wider Applicability**: Beyond mechanical systems, the first law of thermodynamics applies universally to all forms of energy and all types of processes, including chemical reactions, electrical systems, and nuclear reactions. It provides a foundational understanding that allows scientists and engineers to predict and understand energy transformations in various contexts.

Examples of First Law of Thermodynamics

1. A bicycle pump is a good example of first law of thermodynamics. When we pump on the handle rapidly, it becomes hot due to mechanical work done on the gas, raising thereby its internal energy. One such simple arrangement is shown in Fig. 6. It consists of a bicycle pump with a blocked outlet. A thermocouple connected through the blocked outlet allows the air temperature to be monitored. Thermocouple thermometer can detect a minute variation of the temperature. When the piston is rapidly pushed, thermometer shows a temperature rise due to increase of internal energy of the air. The push force does work on the air, thereby, increasing its internal energy, which is shown, by the increase in temperature of the air.

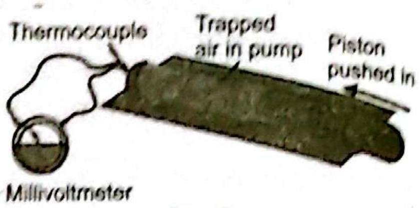


Fig. 6

2. Human metabolism also provides an example of energy conservation. Human beings and other animals do work when they walk, run, or move. Work requires energy. Energy is also needed for growth to make new cells and to replace old cells that have died. Energy transforming processes that occur within an organism are named as metabolism. We can apply the first law of thermodynamics ($\Delta U = Q - W$), to an organism of the human body. Work done will result in the decrease in internal energy of the body. Consequently, the body temperature or in other words internal energy is maintained by the food we eat.

Example 6.2: 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 heat is transferred to the system during the expansion, what is the change in internal energy of the system?

Solution:

Given that;

$$A = 0.10\ m^2$$
$$P = 8000\ Nm^{-2}$$
$$\Delta y = 4.0\ cm$$
$$Q = 42\ J$$

To Find:

$$\Delta U = ?$$

Calculations:

The work done by the gas is

$$W = P\Delta V = PA\Delta y = 8000\ N\ m^{-2} \times 0.01\ m^2 \times 4.0 \times 10^{-2}\ m$$
$$= 32\ N\ m = 32\ J$$

The change in internal energy is found from first law of thermodynamics

$$\Delta U = Q - W = 42\ J - 32\ J = 10\ J$$ **Ans.**

12. What is meant by isothermal process? Explain.

Ans. Isothermal Process

Definition

An isothermal process is a thermodynamic process in which the temperature of the system remains constant throughout the process.

Explanation

If P_1, V_1 are initial pressure and volume whereas P_2, V_2 are pressure and volume after the isothermal change takes place; Fig. 7, respectively, then

$$P_1V_1 = P_2V_2$$

In case of an ideal gas, the *P.E.* associated with its molecules is zero, hence, the internal energy of an ideal gas depends only on its temperature, which in this case remains constant, therefore, $\Delta U = 0$. Hence, the first law of thermodynamics reduces to

$$Q = W$$

Thus, if gas expands and does external work W, an amount of heat Q

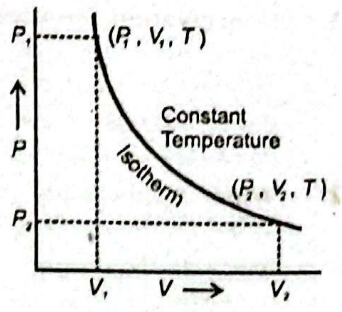


Fig. 7

has to be supplied to the gas in order to produce an isothermal change.

Since transfer of heat from one place to another requires time, hence, to keep the temperature of the gas constant, the expansion or compression must take place slowly. The curve representing an isothermal process is called an isotherm; Fig. 7.

13. What is an adiabatic process? Explain.

Ans. Adiabatic Process

Definition

An adiabatic process is the one in which no heat enters or leaves the system.

Explanation

As $\Delta Q = 0$ and the first law of thermodynamics gives: $W = -\Delta U$

Thus, if the gas expands and does external work, it is done at the expense of the internal energy of its molecules and, hence, the temperature of the gas falls. Conversely, an adiabatic compression causes the temperature of the gas to rise because of the work done on the gas.

Adiabatic change occurs when the gas expands or compressed rapidly, particularly when the gas is contained in an insulated cylinder. The examples of adiabatic process are:

(i) The rapid escape of air from a burst tyre.

(ii) The rapid expansion and compression of air through which a sound wave is passing.

(iii) Cloud formation in the atmosphere.

As the temperature of the gas does not remain constant, so it has been seen that;

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

where γ is the ratio of the molar specific heat of the gas at constant pressure to molar specific heat at constant volume. The curve representing an adiabatic process is called an adiabat; Fig. 8.

> **Brain Teaser**
>
> **Why does the internal energy of an ideal gas remain constant during isothermal expansion?**
>
> **Ans.** The internal energy of an ideal gas remains constant during an isothermal expansion because the temperature remains constant, and for an ideal gas, internal energy depends only on temperature.

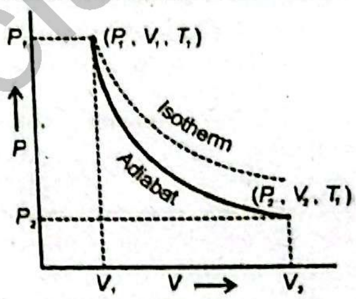


Fig. 8

MCQs

1. **Internal energy of an ideal gas depends only on:**
   (A) Pressure (B) Volume
   (C) Temperature ✓ (D) Both (A) and (B)
2. **The internal energy of a system is a measure of:**
   (A) K.E. only (B) P.E. only
   (C) Sum of K.E. and P.E. ✓ (D) Work done by system
3. **In thermodynamics, the internal energy is a:**
   (A) Path function (B) State function ✓
   (C) Random variable (D) All of these
4. **When heat is added to a system and no work is done, the change in internal energy equals:**
   (A) Zero (B) Work done
   (C) Heat added ✓ (D) Negative heat
5. **Which of the following is a path function?**
   (A) Work ✓ (B) Internal energy
   (C) Temperature (D) Enthalpy
6. **The work done by a gas during expansion can be calculated using:**
   (A) $W = P\Delta V$ ✓ (B) $W = V\Delta P$
   (C) $W = \Delta U$ (D) $W = O$
7. **The first law of thermodynamics is the statement of:**
   (A) Conservation of mass
   (B) Conservation of energy ✓
   (C) Conservation of momentum
   (D) Conservation of volume
8. **When a gas expands against an external pressure, the work done by the gas is:**
   (A) Positive ✓ (B) Negative
   (C) Zero
   (D) Dependent on temperature
9. **The first law of thermodynamics can be expressed as:**
   (A) $\Delta U = Q \times W$ (B) $\Delta U = W - Q$
   (C) $\Delta U = Q + W$ (D) $\Delta U = Q - W$ ✓
10. **During an isothermal process, the change in internal energy ΔU is:**
    (A) Positive (B) Negative
    (C) Zero ✓ (D) Depends on the pressure
11. **What remains constant in adiabatic process?**
    (A) Volume (B) Pressure
    (C) Entropy ✓ (D) Temperature
12. **Which one is true for the isothermal process?**
    (A) $Q = 0$ (B) $W = 0$
    (C) $Q = W$ ✓ (D) None of these

13. **Isothermal process is carried out at constant:**
(A) Volume (B) Pressure
(C) Entropy (D) Temperature✓

14. **In case of adiabatic process, 1st law of thermodynamics is:**
(A) $W = \Delta U$ (B) $W = Q$
(C) $W = -\Delta U$✓ (D) $W = -\Delta Q$

15. **According to 1st law of thermodynamic, the quantity which is conserved is:**
(A) Energy✓ (B) Force
(C) Momentum (D) Power

16. **The curve representing an adiabatic process is called:**
(A) An isotherm (B) Isobar
(C) Both of them (D) None of these✓

17. **A good example of first law of thermodynamics is:**
(A) Simple pendulum (B) Centripetal force
(C) Bicycle pump✓ (D) Doppler's effect

18. **Boyle's law is applicable to:**
(A) Isobaric process (B) Isochoric process
(C) Isothermal process✓ (D) Adiabatic process

19. **Which is called the internal energy of an ideal gas?**
(A) Potential energy
(B) Translational kinetic energy✓
(C) Vibrational kinetic energy
(D) All of these

20. **Which of the following is not an example of adiabatic process?**
(A) Rapid escape of air from burst tyre
(B) Conversion of water into ice in refrigerator✓
(C) Cloud formation in atmosphere
(D) Raid expansion of air

21. **Area under PV-diagram of Carnot Engine represents:**
(A) Heat input (B) Heat output
(C) Efficiency (D) Work done✓

22. **Cloud formation in atmosphere is an example of:**
(A) Isothermal process (B) Adiabatic process✓
(C) Isobaric process (D) Isochoric process

23. **The measure of hotness or coldness of a substance is:**
(A) Temperature✓ (B) Heat
(C) Internal energy (D) Energy

24. **The formula connecting the pressure and volume of a gas undergoing an adiabatic change is:**
(A) PV = constant (B) PV = constant
(C) PV^{-1} = constant (D) PV = constant✓

25. **At which of the following temperature, a body has maximum internal energy:**
(A) – 270° (B) 0 K
(C) 273 K✓ (D) – 273K

26. **In which case the work done is zero:**
(A) Constant pressure (B) Constant volume✓
(C) Constant temperature (D) Constant mass

27. **In thermodynamics system, internal energy decreases by 100 J and 100 J of the work done on the system, then heat lost will be:**
(A) Zero (B) 100 J
(C) 200 J✓ (D) – 200 J

28. **A diatomic gas molecules have:**
(A) Translation energy only (B) Rotational energy only
(C) Vibrational energy only (D) All of these✓

29. **The change in internal energy is defined as:**
(A) Q – W✓ (B) Q – T
(C) Q + P (D) Q – P

30. **For an ideal gas system, the internal energy is directly proportional to:**
(A) Pressure (B) Volume
(C) Mass (D) Temperature✓

31. **The work done in isochoric process is:**
(A) Constant (B) Variable
(C) Zero✓ (D) Depend on condition

32. **If P = Pressure; V = Volume of gas PΔV represents:**
(A) Work✓ (B) Density
(C) Power (D) Temperature

33. **An adiabatic change is the one in which:**
(a) No heat is added to or taken out of a system✓
(b) No change of temperature take place
(c) Boyle's law is applicable
(d) Pressure and volume remains constant

34. **What remains constant in an adiabatic process?**
(A) Volume (B) Pressure
(C) Entropy✓ (D) Temperature

35. **According to first law of thermodynamics, the quantity which is conserved is:**
(A) Force (B) Momentum
(C) Power (D) Energy✓

36. **In case of adiabatic process, 1st law of thermodynamics is written as:**
(A) $W = \Delta U$ (B) $W = Q$
(C) $W = Q - \Delta U$ (D) $W = -\Delta U$✓

37. **Human metabolism is the example of:**
(A) First law of thermodynamics✓
(B) Entropy
(C) Second law of thermodynamics
(D) Adiabatic process

38. **A system does 700 joules of work and at the same time its internal energy increases to 400 Joules, heat supplied by the source is:**
(A) 700 Joules (B) 400 Joules
(C) 1100 Joules✓ (D) 300 Joules

39. **The direction of flow of heat between two bodies in thermal contact is determined by**
(A) Internal energies✓ (B) Kinetic energies
(C) Potential energies (D) Atmospheric pressure

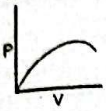
40. **The sum of all the energies of molecules is known as:**
(A) Elastic potential energy (B) Kinetic energy
(C) Internal energy✓ (D) Gravitational potential energy

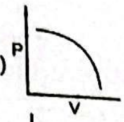
41. **The SI unit of product of pressure and volume is:**
(A) watt (B) joule✓
(C) pascal (D) Nm

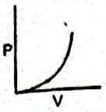
42. **If internal energy decreases by 300 J and 120 J of work is done on the system, then heat will be:**
(A) 420 J✓ (B) 320 J
(C) 400 J (D) 300 J

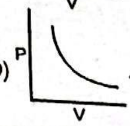
43. **A gas performs 10J of work while expanding adiabatically. The change in internal energy is:**
(A) 10 J (B) −10 J ✓
(C) 100 J (D) −100 J

44. **An isotherm is drawn as:**

(A) 

(B) 

(C) 

(D)  ✓

45. **Which one of the following parameters is kept constant in order to compare two specific heats of a thermodynamic system?**
(A) Work (B) Pressure
(C) Internal energy ✓ (D) Volume

46. **Non-entropy changes take place in:**
(A) Isothermal process (B) Isochoric process
(C) Isobaric process (D) Adiabatic process ✓

6.5 REVERSIBLE AND IRREVERSIBLE PROCESSES

Q 14. What are reversible and irreversible processes? Explain.

Ans. Reversible Process

Definition

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

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

Cycle

Definition

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

Reversible Cycle

Definition

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

Examples of Reversible Process

1. The processes of liquification and evaporation of a substance, performed slowly, are practically reversible.
2. The slow compression of a gas in a cylinder is reversible process as the compression can be changed to expansion by slowly decreasing the pressure on the piston to reverse the operation
3. Isothermal expansion of an ideal gas is a reversible process.
4. Melting of ice at in equilibrium is a reversible process.

Irreversible Process

Definition

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

Examples

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

(i) An example of highly irreversible process is an explosion.
(ii) Force expansion of a gas into vacuum is also an example of irreversible process.

Do You Know?

First practical steam-engine was designed by John Braithwaite and John Ericsson in England around1829.

6.6 HEAT ENGINE

Q 15. What is a heat engine? State its working principle.

Ans. Heat Engine

A heat engine is a device that converts thermal energy into mechanical work by exploiting the temperature difference between a hot source and a cold sink.

Working Principle

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

Here is how a heat engine typically operates. The working principle of a heat engine 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. This process is governed by principles of thermodynamics and is essential in various applications where mechanical energy is required from heat sources.

6.7 SECOND LAW OF THERMODYNAMICS

Q16. State and explain second law of thermodynamics.

Ans. Second Law of Thermodynamics

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.

Explanation

Let us analyze briefly the factual operation of an engine. The engine or the system absorbs a quantity of heat Q_1 from the heat source at temperature T_1; Fig. 9. It does work W and expels heat Q_2 to low temperature reservoir at temperature T_2.

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

$$W = Q_1 - Q_2$$

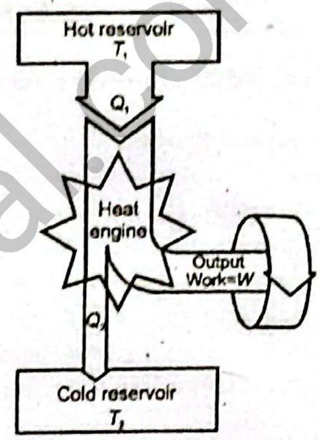


Fig. 9: Schematic representation of a heat engine. The engine absorbs heat Q_1 from the hot reservoir, expels heat Q_2 to the cold reservoir and does work W.

In practice, the petrol engine of a motor car extracts heat from the burning fuel and converts a part of this energy to mechanical energy or work and expels the rest to the atmosphere.

The second law of thermodynamics is a formal statement based on these observations. It can be stated in a number of different ways:

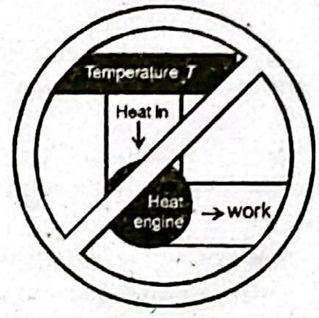
Lord Kelvin Statement

It is impossible to convert the heat from a single heat reservoir entirely into work without producing any other effect.

In simple way:

No heat engine can operate in a cycle and convert all the absorbed heat into work.

Tidbits



According to the Kelvin statement of the second law of thermodynamics, the process pictured here is impossible. Heat from a source at a single temperature cannot be converted entirely into work.

Clausius's Statement

It is impossible for heat to flow from a colder body to a hotter body without any external work being done on the system.

From the statement of second law of thermodynamics (Lord Kelvin), it is clear that a single heat reservoir, no matter how much energy it contains, cannot be made to perform any work. This is true for oceans and our atmosphere which contain a large amount of heat energy but cannot be converted into useful mechanical work.

As a consequence of second law of thermodynamics, two bodies at different temperatures are essential for the conversion of heat into work. Hence, for the working of heat engine there must be a source of heat at a high temperature and a sink at low temperature to which heat may be expelled.

6.8 CARNOT ENGINE AND CARNOT'S THEOREM

17. Describe Carnot engine and Carnot's theorem. Find an expression for efficiency of Carnot engine.

Ans. Carnot Engine

Sadi Carnot 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.

Carnot's Theorem

A Carnot cycle using an ideal gas as the working substance is shown on *PV* diagram. It consists of following four steps:

1. The gas is allowed to expand isothermally at temperature T_1 absorbing heat Q_1 from the hot reservoir. The process is represented by the curve AB.
2. The gas is then allowed to expand adiabatically until its temperature drops to T_2. The process is represented by the curve BC.
3. The gas at this stage is compressed isothermally at temperature T_2 rejecting heat Q_2 to the cold reservoir. The process is represented by the curve CD.
4. Finally, the gas is compressed adiabatically to restore its initial state at temperature T_1. The process is represented by the curve DA.

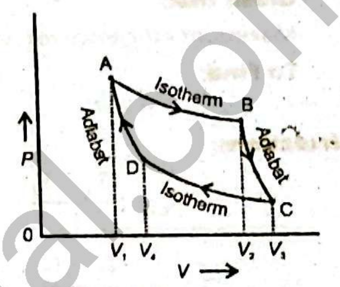


Fig. 10

Thermal and mechanical equilibrium is maintained all the time so that each process is perfectly reversible. As the working substance returns to the initial state, there is no change in its internal energy i.e., $\Delta U = 0$.

The net work done during one cycle equals to the area enclosed by the path ABCDA of the *PV* diagram. It can also be estimated from net heat ΔQ absorbed in one cycle.

$$Q = Q_1 - Q_2$$

From 1st law of thermodynamics:

$$Q = \Delta U + W$$

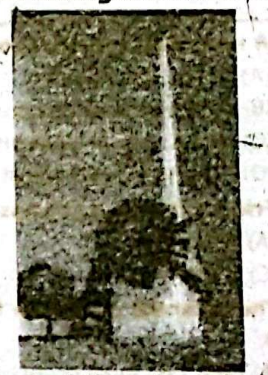
or $$W = Q_1 - Q_2 \qquad (\because \Delta U = 0)$$

The efficiency η of the heat engine is defined as:

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

Thus $$\eta = \frac{Q_1 - Q_2}{Q_1} \qquad \text{...... (i)}$$

Interesting Information



A waterfall analogy for the heat engine.

The energy transfer in an isothermal expansion or compression turns out to be proportional to Kelvin temperature. So Q_1 and Q_2 are proportional to Kelvin temperatures T_1 and T_2 respectively and hence,

$$\eta = \frac{T_1 - T_2}{T_1} = 1 - \frac{T_2}{T_1} \qquad \text{...... (ii)}$$

The efficiency is usually taken in percentage, in that case:

$$\text{Percentage efficiency} = \left(1 - \frac{T_2}{T_1}\right) \times 100 \qquad \text{...... (iii)}$$

Thus, the efficiency of Carnot engine depends on the temperature of hot and cold reservoirs. It is independent of the nature of working substance. The larger the temperature difference of two reservoirs, the greater is the efficiency. But it can never be one or 100% unless cold reservoir is at absolute zero temperature ($T_2 = 0$ K).

Such reservoirs are not available and hence the maximum efficiency is always less than one. No practical heat engine can be perfectly reversible and also energy dissipation is inevitable. **This fact is stated in Carnot's theorem:**

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

The Carnot's theorem can be extended to state that:

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

In most practical cases, the cold reservoir is near room temperature. So, the efficiency can only be increased by raising the temperature of hot reservoir. All real heat engines are less efficient than Carnot engine due to friction and other heat losses.

Example 6.3: The turbine in a steam power plant takes steam from a boiler at 427 °C and exhausts into a low temperature reservoir at 77 °C. What is the maximum possible efficiency?

Solution:

Given that;

Maximum efficiency for any engine operating between temperatures T_1 and T_2 is:

To Find:

$$\eta = ?$$

Calculations:

$$\%\eta = \frac{T_1 - T_2}{T_1} \times 100\% \qquad T_1 = 427 + 273 = 700\text{ K} \quad , \quad T_2 = 77 + 273 = 350\text{ K}$$

So $$\eta = \frac{T_1 - T_2}{T_1} = \frac{700\text{ K} - 350\text{ K}}{700\text{ K}} = \frac{350\text{ K}}{700\text{ K}} = \frac{1}{2} = 0.5$$

or $$\%\eta = 0.5 \times 100 = 50\% \text{ **Ans.**}$$

MCQs

1. **A reversible process is one which:**
(A) occurs very rapidly
(B) can be reversed by an infinitesimal change ✓
(C) occurs only in isothermal conditions
(D) Cannot be reversed at all

2. **Friction makes a process:**
(A) Reversible (B) Ideal
(C) Isothermal (D) Irreversible ✓

3. **The essential condition for a process to be reversible is:**
(A) Heat loss must occur
(B) Work done should be maximum
(C) It should occur infinitely slowly
(D) Both (B) and (C) ✓

4. **Reversible processes are:**
(A) Natural and spontaneous
(B) Practical and commonly observed
(C) Ideal and theoretical ✓
(D) Always adiabatic

5. **Which of the following is an example of an irreversible process?**
(A) Slow compression of a gas
(B) Melting of ice at 0°C under equilibrium
(C) Free expansion of a gas in vacuum ✓
(D) Static expansion of an ideal gas

6. **Which one of the following process is irreversible?**
(a) Slow compression of an elastic spring.
(b) Slow evaporation of a substance in an isolated vessel.
(c) Slow compression of a gas.
(d) A chemical explosion. ✓

7. **An ideal reversible heat engine has.**
(a) 100% efficiency (b) Highest efficiency ✓
(c) An efficiency which depends on the nature.
(d) None of these.

8. **The device which operates based on the second law of thermodynamics is:**
(A) Thermometer (B) Voltmeter
(C) Barometer (D) Heat engine ✓

9. **The second law of thermodynamics explains the direction of:**
(A) Electric current (B) Nuclear decay
(C) Chemical reactions (D) Heat transfer ✓

10. **For working of heat engine, there must be:**
(A) Source (B) Sink
(C) Either of these (D) Both (A) and (B) ✓

11. **The efficiency of Carnot engine depends upon:**
(A) Sink temperature (B) Source temperature
(C) Both source and sink temperature ✓
(D) The working substance

12. **The most important factor regarding the significance of the Carnot engine is that:**
(A) It is partially impossible
(B) Its efficiency is 100%
(C) Its efficiency is possible max ✓
(D) Its efficiency is minimum

13. **The efficiency of petrol engine is:**
(A) 25 – 30% ✓ (B) 45 – 50%
(C) 34 -67% (D) 49 – 60%

14. **Heat engine is device which converts:**
(A) Heat energy into chemical energy

(B) Heat energy into mechanical work ✓
(C) Heat energy into electrical energy
(D) Heat energy into potential energy

15. If the temperature of the sink is decreases, the efficiency of Carnot engine:
(A) Decreases
(B) Increase ✓
(C) Remains the same
(D) First increases then decreases

16. Efficiency of steam locomotive is:
(A) 10%
(B) 8% ✓
(C) 9%
(D) 7%

17. Number of spark plugs needed in the diesel engine are:
(A) 0 ✓
(B) 1
(C) 2
(D) 3

18. The Celsius scale starts from:
(A) 32 °C
(B) 273 °C
(C) 0°C ✓
(D) 100 °C

19. The actual efficiency of property tuned petrol engine is:
(A) 20 % to 30%
(B) 30 % to 35%
(C) 40% to 45%
(D) 25 % to 30% ✓

20. A device based upon the thermodynamic property of matter is called:
(A) Calorimeter
(B) Heat Engine
(C) Thermometer ✓
(D) Voltmeter

21. The Dimensions of entropy are:
(A) $[ML^2T^2]$
(B) $[ML^2T^{-1}k]$
(C) $[ML^2T^{-2}K^{-1}]$ ✓
(D) $[ML^2T^3]$

22. Triple point of water is:
(A) 273.16°F
(B) 273.16°C
(C) 273.16 K ✓
(D) 373.16 K

23. Unit of thermodynamics scale of temperature is:
(A) Centigrade
(B) Fahrenheit
(C) Kelvin ✓
(D) Celsius

24. The temperature scale which is independent of nature of substance is:
(A) Thermodynamic scale
(B) Centigrade scale
(C) Fahrenheit scale ✓
(D) Rankine scale

25. What would be the efficiency of a Carnot engine operating with boiling water as one reservoir and freezing mixture of ice and water as the other reservoir?
(A) 100%
(B) 27% ✓
(C) 67%
(D) 12%

26. The efficiency of diesel engine is about:
(A) 25% to 30%
(B) 35% to 40% ✓
(C) 40% to 50%
(D) 50 % to 60%

27. Force acting on the piston to move outward in:
(A) Compression stroke
(B) Power stroke ✓
(C) All strokes
(D) Exhaust stroke

28. A heat engine operates between the temperature 1000K and 400K. Its efficiency can be equal to:
(A) 50%
(B) 60% ✓
(C) 70%
(D) 100%

29. If the temperature of sink is absolute zero, then the efficiency of heat engine should be:
(A) 100% ✓
(B) 50%
(C) Zero
(D) Infinite

30. Efficiency of a heat engine working between temperature 27°C and 327°C will be:
(A) 50% ✓
(B) 90%
(C) 40%
(D) 61%

31. The Carnot cycle can be shown by a graph between:
(A) V – T graph
(B) P – T graph
(C) Q – T graph
(D) P – V graph ✓

32. Efficiency of diesel engine is:
(A) 25 % to 30%
(B) 30% to 35% ✓
(C) 35% to 40%
(D) 40% to 50%

33. The efficiency of diesel engine is about:
(A) 10% to 20%
(B) 15% to 25%
(C) 25% to 35% ✓
(D) 35% to 40%

34. If temperature of sink is decreased, the efficiency of Carnot engine:
(A) Decreases
(B) Increases ✓
(C) Remain same
(D) First increases then decreases

35. A Carnot engine has an efficiency of 50% when its sink temperature is 27°C. The temperature of source is:
(A) 300°C
(B) 327°C ✓
(C) 373°C
(D) 273°C

36. Solid ice, liquid water and water vapours consist in thermal equilibrium at a temperature:
(A) 273 K
(B) 273.16 K ✓
(C) 273°C
(D) 100°C

37. Carnot engine cycle consists of:
(A) Four steps ✓
(B) Three steps
(C) Single step
(D) Two steps

38. If $T_H = T_1 = 327°$ and $T_L = T_2 = 27°C$, then efficiency will be:
(A) 50% ✓
(B) 52%
(C) 100%
(D) Zero

39. If the temperature of sink is equal to absolute zero, the efficiency of heat engine should be:
(A) 100% ✓
(B) 50%
(C) Zero
(D) Infinity

40. In which stroke, the inlet valve is closed and the mixture is compressed adiabatically for the petrol engine.
(A) Intake
(B) Compression ✓
(C) Power
(D) Exhaust

41. Sadi Carnot described an ideal engine is:
(A) 1640
(B) 1740
(C) 1940
(D) 1840 ✓

42. In carnot engine, each process is:
(A) Reversible
(B) Perfectly reversible ✓
(C) Irreversible
(D) Perfectly irreversible

43. The efficiency of a Carnot engine is:
(A) Infinite
(B) Zero
(C) Greater than one
(D) Less than one ✓

18. What is a refrigerator? Describe its working. Find an expression for coefficient of performance of a refrigerator.

Ans. Refrigerator

Refrigerator is a device which maintains the temperature of a body below that of its surrounding. It operates in a cyclic process but in reverse as that of the heat engine.

Working Principle

A refrigerator absorbs heat from a cold reservoir and gives it off to a hot reservoir. This shows that in a refrigerator, the work is done on the system while in a heat engine work is done by the system.

A refrigerator works on the basis of Clausius statement of second law of thermodynamics, i.e., a heat engine is operating in reverse. Heat Q_C is drawn from Low Temperature Reservoir (LTR) T_1 by compressor and is thrown into High Temperature Reservoir (HTR) T_2 with the help of external work done. The heat rejected to HTR (Q_H) is given by

$$Q_C + W = Q_H$$

or $$W = Q_H - Q_C$$

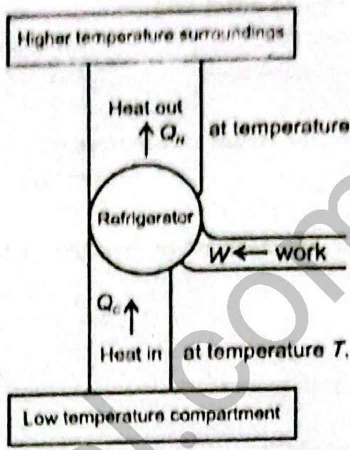


Fig. 11: A refrigerator transfers heat from a low-temperature compartment to higher-temperature surroundings with the help of external work. It is a heat engine operating in reverse order.

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

Coefficient of Performance of Refrigerator

The ratio of heat removed from LTR (Q_C) to the work done (W) is called coefficient of performance of a refrigerator.

A better refrigerator will remove a greater amount of heat from inside the refrigerator for the expenditure of a smaller mechanical work or electrical energy. The coefficient of performance of a refrigerator can be given by

$$E = \frac{Q_c}{W} = \frac{qC}{Q_H - Q_c}$$

The coefficient of performance in terms of temperature, where $Q \propto T$ is:

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

Example 6.4: A refrigerator has a coefficient of performance 8. If temperature in the freezer is −23°C, then what is the temperature at which it rejects the heat?

Solution:

Given that:

Coefficient of performance E = 8

Temperature of cold reservoir (freezer) $T_1 = -23°C = -23 + 273 = 250\ K$

To Find:

Temperature of hot reservoir (room) $T_2 = ?$

Calculations:

Coefficient of performance $= \frac{T_1}{T_2 - T_1}$

Substituting the values $8 = \frac{250\ K}{T_2 - 250\ K}$

or $8(T_2 - 250\ K) = 250\ K$

or	$T_2 - 250\text{ K} = \dfrac{250\text{ K}}{8}$
or	$T_2 = 31.25\text{ K} + 250\text{ K}$
	$= 281.25\text{ K} = 8.25^{o}\text{C}$ **Ans.**

6.10 ENTROPY

19. Define and explain the term entropy. State the second law of thermodynamics in terms of entropy. Does increase in entropy mean degradation of energy? Explain.

Ans. Entropy

Definition

Entropy is a measure of the disorder or randomness in a system.

Explanation

If a system undergoes a reversible process during which it absorbs a quantity of heat ΔQ at absolute temperature T, then entropy S of the system is given by

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

The change in entropy is positive when heat is added and negative when heat is removed from the system. Suppose an amount of heat Q flows from a reservoir at temperature T_1 through a conducting rod to a reservoir at temperature T_2 when $T_1 > T_2$. The change in entropy of the reservoir, at temperature T_1, which loses heat, decreases by Q / T_1 and of the reservoir at temperature T_2, which gains heat, increases by Q / T_2. As $T_1 > T_2$, so Q / T_2 will be greater than Q / T_1, i.e. $Q / T_2 > Q / T_1$.

Hence, net change in entropy $\left(\dfrac{Q}{T_2} - \dfrac{Q}{T_1}\right)$ is positive.

Second Law of Thermodynamics in Terms of Entropy

It follows that in all natural processes where heat flows from one system to another, there is always a net increase in entropy. This is another statement of 2nd law of thermodynamics. It states that;

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.

It is observed that a natural process tends to proceed towards a state of greater disorder. Thus, there is a relation between entropy and molecular disorder. For example, an irreversible heat flow from a hot to a cold substance of a system increases disorder because the molecules are initially sorted out in hotter and cooler regions. This order is lost when the system comes to thermal equilibrium. Addition of heat to a system increases its disorder because of increase in average molecular speeds and therefore, the randomness of molecular motion. Similarly, free expansion of gas increases its disorder because the molecules have greater randomness of position after expansion than before. Thus, in both examples, entropy is said to be increased.

We can conclude that only those processes are probable for which entropy of the system increases or remains constant. The process for which entropy remains constant is a reversible process; whereas for all irreversible processes, entropy of the system increases.

Increase in Entropy Means Degradation of Energy

Every time entropy increases, the opportunity to convert some heat into work is lost. For example, there is an increase in entropy when hot and cold waters are mixed. Finally, the warm water cannot be separated into a hot layer and a cold layer. There has been no loss of energy but some of the energy is no longer available for conversion into work. Therefore, increase in entropy 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 in a sense is degraded, going from more orderly form to less orderly form, eventually ending up as thermal energy.

In all real processes where heat transfer occurs, the energy available for doing useful work decreases, eventually, the entropy increases. Even if the temperature of some system decreases, thereby decreasing the entropy, it is at the expense of 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.

Yes, an increase in entropy generally means degradation of energy-particularly in terms of its usefulness for doing work.

Example 6.5: Calculate the entropy change when 1.0 kg ice at 0°C melts into water at 0°C. Latent heat of fusion of ice $L_f = 3.36 \times 10^5\ J\ kg^{-1}$.

Solution:

Given that;

$m = 1$ kg

$T = 0°C = 273$ K

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

To Find: $\Delta S = ?$

Calculations:

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

where $\Delta Q = mL_f$

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

Substituting the values

$$\Delta S = \frac{1.00\ kg \times 3.36 \times 10^5\ J\ kg^{-1}}{273\ K}$$

$\Delta S = 1.23 \times 10^3\ J\ K^{-1}$ **Ans.**

Thus, entropy increases as it changes to water. The increase in entropy in this case is a measure of increase in the disorder of water molecules that change from solid to liquid state.

Brain Teaser

Why does a deck of cards become more disordered when shuffled?

Ans. A deck of cards becomes more disordered when shuffled because shuffling increases entropy. Due to this disorder is more probable because there are so many more ways for a deck to be messy than to be neat. Shuffling randomly moves you into one of those many disordered states.

MCQ's

1. **The working principle of refrigerator is based on:**
   (A) First law of thermodynamics
   (B) Second law of thermodynamics ✓
   (C) Third law of thermodynamics
   (D) Zeroth law of thermodynamics
2. **In a refrigerator, heat flows from:**
   (A) Hot reservoir to cold reservoir
   (B) Cold reservoir to hot reservoir ✓
   (C) Both directions
   (D) None of these
3. **The performance of a refrigerator is measured in terms of:**
   (A) Efficiency (B) Specific heat
   (C) Thermal conductivity (D) Coefficient of performance (COP) ✓
4. **The coefficient of performance of a refrigerator is given by:**
   (A) $\frac{Q_H}{W}$ (B) $\frac{Q_C}{W}$ ✓
   (C) $\frac{W}{Q_H}$ (D) $\frac{Q_C}{Q_H}$
5. **Which of the following statement is true about an ideal refrigerator?**
   (A) It transfers heat without external work
   (B) COP can be infinite ✓
   (C) It follows the first law of thermodynamics only
   (D) It does not obey any thermodynamics laws
6. **What is the function of the refrigerant in a refrigerator?**
   (A) To provide cooling only by conduction
   (B) To act as a lubricant
   (C) To absorb and carry heat from the cold reservoir ✓
   (D) To supply electrical energy
7. **The coefficient of performance of a refrigerator can be:**
   (A) Less than 1 (B) Equal to 1
   (C) Greater than 1 (D) All of these ✓
8. **What is the primary function of the refrigerator?**
   (A) To produce cold
   (B) To destroy heat
   (C) To convert heat into work
   (D) To transfer heat from a lower temperature to a higher temperature ✓
9. **In a refrigerator, the working fluid is known as:**
   (A) Lubricant (B) Refrigerant ✓
   (C) Coolant (D) Catalyst
10. **In a refrigeration cycle, the heat is rejected to the surroundings in the:**
    (A) Evaporator (B) Compressor
    (C) Expansion value (D) Condenser ✓
11. **Entropy is a measure of:**
    (A) Disorder or randomness in a system ✓
    (B) Heat energy
    (C) Work done by a system

(D) Pressure in a system

12. **Entropy of the universe always:**
(A) Decreases
(B) Remains constant
(C) Increases for irreversible processes ✓
(D) Decreases for irreversible processes

13. **The unit of entropy in the SI system is:**
(A) joule (B) JK^{-1} ✓
(C) KJ^{-1} (D) WK^{-1}

14. **In an irreversible process, the total entropy change is:**
(A) Less than zero (B) Equal to zero
(C) Greater than zero ✓ (D) Unpredictable

15. **In a reversible process, entropy changes of the system and surrounding is:**
(A) Zero ✓ (B) Positive
(C) Negative (D) Infinite

16. **According to second law of thermodynamics, in any process:**
(A) The entropy of the system remains constant
(B) The entropy of the universe increases ✓
(C) The entropy of the universe decreases
(D) None of these

17. **What happens to the entropy of an ideal gas, when it is compressed reversibly?**
(A) Increases (B) Decreases ✓
(C) Remains the same (D) Becomes zero

18. **The change in entropy ΔS for a reversible process is given by**
(A) $\Delta S = \frac{Q}{W}$ (B) $\Delta S = Q \times T$
(C) $\Delta S = \frac{Q_{rev}}{T}$ ✓ (D) $\Delta S = \frac{QT}{Q_{rev}}$

19. **Which of the following processes involves an increase in entropy?**
(A) Freezing of water (B) Condensation of steam
(C) Evaporation of water ✓ (D) Compression of a gas

20. **Entropy change is a state function; meaning:**
(A) It depends only on the initial and final states ✓
(B) It depends only the path taken
(C) It depends only on temperature
(D) It is always zero

ADDITIONAL SHORT ANSWER QUESTIONS

SQ

1. What are the main assumptions of kinetic theory of gases?
Ans. Gas particles are in constant random motion, they have negligible volume, collisions are perfectly elastic, and there are no intermolecular forces.

Q.2 Does kinetic theory apply to real gases at all conditions?
Ans. No, it fails at high pressures and low temperatures where intermolecular forces and molecular volume become significant.

Q.3 Why do real gases deviate from ideal behaviour?
Ans. Due to intermolecular forces and finite molecular volume, especially under non-ideal conditions.

Q.4 What are the main components of internal energy.
Ans. The K.E. (due to motion of molecules) and P.E. (due to intermolecular forces).

Q.5 Is internal energy a state function?
Ans. Yes, internal energy depends only on the state of the system, not on the path taken.

Q.6 How does internal energy change in an adiabatic process?
Ans. In an adiabatic process, internal energy changes due to work done, since no heat is exchanged.

Q.7 What happens to head and work in an adiabatic process?
Ans. No, heat is exchanged ($\Delta Q = 0$), so the change in internal energy equals the work done; $\Delta U = -W$.

Q.8 Give two examples of adiabatic process.
Ans. The examples of adiabatic process are:
(i) Rapid escape of air from bust tyre.
(ii) Cloud formation in atmosphere.
(iii) The rapid expansion and compression of air through which a sound wave is passing.

Q.9 What is the similarity between internal energy and gravitational P.E?
Ans. In thermodynamics, both internal energy and gravitational P.E. are state functions, which do not depend on the path but depend on the initial and final states of the system.

Q.10 What would be the heat lost if internal energy decreases by 10 J and 20 J of work is done on the system simultaneously?
Ans. Data:

$\Delta U = -10\ J$

$W = -20\ J$

Formula: According to first law of thermodynamics.

$Q = \Delta U + W$

$Q = -10 + (-20)$

$\boxed{Q = -30\ J}$

So the heat lost is of 30 J.

Q.11 An engine absorbs heat of 10 J and rejects 5J heat, What is the heat being used by the engine?

Ans. Data:

$Q_1 = 10\ J$

$Q_2 = 5\ J$

Formula: The heat used by the engine.

$W = Q_1 - Q_2$

$W = 10 - 5$

$\boxed{W = 5\ J}$

Q.12 A heat engine works between 327° C and 27° C. Find its efficiency.

Ans. Data:

$T_1 = 327°\ C = 372 + 273 = 600\ K$

$T_2 = 27°\ C = 27 + 273 = 300\ K$

Formula:

$$\eta = \left(1 - \frac{T_2}{T_1}\right) \times 100\%$$

$$\Rightarrow \quad \eta = \left(1 - \frac{300}{600}\right) \times 100\%$$

$$\Rightarrow \quad \eta = (1 - 0.5) \times 100\%$$

$$\Rightarrow \quad \eta = 0.5 \times 100\%$$

$$\Rightarrow \quad \boxed{\eta = 50\%}$$

Q.13 Under what circumstances the efficiency of a Carnot engine will be 100%? Is it possible?

Ans. Efficiency of a Carnot engine depends on the temperature of hot & cold reservoir. It is independent of the nature of the working substance.

The larger the temperature difference of the two reservoirs, the greater is the efficiency. So the efficiency can be increased by raising the temperature of hot reservoir.

But it can never be one or 100% **unless cold reservoir is at absolute zero temperature ($T_2 = 0\ K$)**

The efficiency of the Carnot engine is given by

$$\eta = \left(1 - \frac{T_2}{T_1}\right) \times 100\%$$

So, put $T_2 = 0\ K$

$$\boxed{\eta = 100\ \%}$$

Q.14 What is the effect on efficiency of Carnot engine, if the temperature of the sink only be decreased?

Ans. An efficiency of Carnot's heat engine can be expressed as

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

So, by decreasing the value of T_2 (temperature of the sink), the smaller factor will subtract from T_1. So the efficiency of Carnot's engine will increase.

Q.15 Carnot cycle provides the basis to define a temperature scale that is independent of material properties. Explain.

Ans. A temperature scale is defined by using thermometric property of certain working substance. If the working substance is not pure then its thermometry property is changed and reading of temperature measuring instrument becomes unreliable.

Thermodynamic scale of temperature is independent of nature of working substance.

According to this scale, the ratio $\frac{Q_1}{Q_2}$ is equal to the ratio of temperature of source and sink.

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

Thermodynamics scale of temperature is defined by choosing 273.16K as the absolute temperature of triple point of water as one fixed point (upper fixed point) and absolute zero as the other (Lower fixed point).

Q.16 A system absorbs 200 J heat at an absolute temperature 200K. Calculate the change in entropy.

Ans. Data:

$\Delta Q = 200$ J

$T = 200$ K

Formula:

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

$$\Delta S = \frac{200}{200}$$

$$\boxed{\Delta S = 1\ JK^{-1}}$$

Q.17 Explain that the average velocity of the molecules in a gas zero but the average of the square of velocities is not zero?

Ans. The molecules of a gas are always in a random motion. The number of molecules moving in a certain direction are equal to the number of molecules moving in opposite direction with same velocity.

$$\frac{v + (-v)}{2} = 0$$

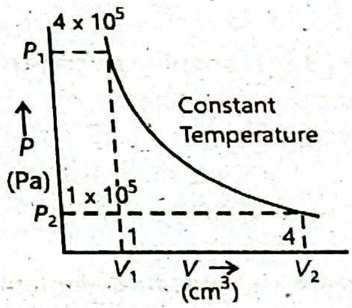
Thus their average velocity is zero. But the average of square of velocities is not zero because square of negative values become positive.

$$\frac{v^2 + (-v)^2}{2} = v^2$$

Q.18 Why does the pressure of a gas in a car tyre increase when it is driven through some distance?

Ans. When a car is driven through some distance then heat is produced due to force of friction between the road and the tyre. A part of this heat is transferred to the molecules of the gas in the tyre. And the K.E. of the molecules increases. The molecule moving with greater velocities collide with the walls of the tyre with greater velocities. Consequently, pressure of gas molecules increases.

Q.19 A system undergoes from state P_1V_1 to state P_2V_2. What will be the change in internal energy?



Ans. The change in internal energy of the system is zero.

Explanation:

The temperature of a system is the measure of its internal energy. As the temperature of the system is constant therefore, its internal energy is also constant. Hence there is no change in the internal energy of the system.

Q.20 Variation of volume by pressure is given in Fig. (a) gas is taken along the paths ABCDA, ABCA and A to A. What will be change in internal energy?

Ans. The change in internal energy of the system is zero in all cases.

Reason:

As all the processes are cyclic. So the system returns to its initial state after each cycle. Hence, the internal energy of the system does not change.

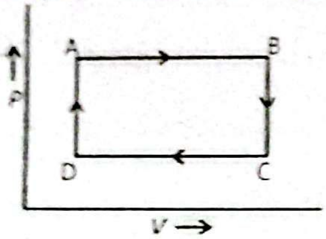


Fig. (a)

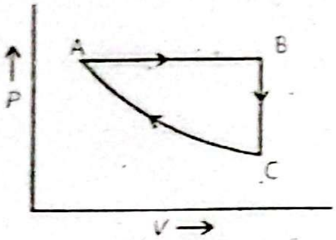


Fig. (b)

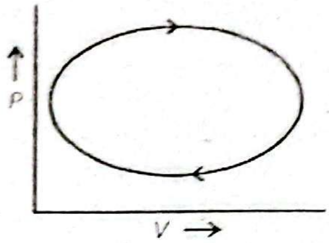


Fig. (c)

Q.21 Give an example of a process in which no heat is transferred to or from the system but the temperature of the system changes.

Ans. In adiabatic process no heat enters or leaves the system take place but temperature of the system change.

$$Q = \Delta U + W$$

For adiabatic process $Q = 0$

So $0 = \Delta U + W$

$-\Delta U = W$ (adiabatic expansion)

or $\Delta U = -W$ (adiabatic compression)

So by doing so whole mechanical energy is converted into internal energy.

Examples

(i) Rapid escape of air from a burst tyre.

(ii) Rapid expansion and compression of air through which sound wave is passing.

(iii) Cloud formation in the atmosphere.

Q.22 Is it possible to convert internal energy into mechanical energy? Explain with an example.

Ans. When an ideal gas is allowed to expand adiabatically, the piston of the cylinder moves outward. Work is done at the cost of internal energy. Internal energy of the system decreases. Thus internal energy is converted into work, which is mechanical energy. Thus it is possible to convert internal energy into mechanical energy.

According to first law of thermodynamic,

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

For an adiabatic process expansion,

$$\Delta Q = 0$$

$$0 = \Delta U + W$$

$$\Delta U + W = 0$$

$$W = -\Delta U$$

Work done = Decrease in internal energy.

Work is done at the cost of internal energy.

Q.23 Is it possible to construct a heat engine that will not expel heat into the atmosphere?

Ans. No, it is not possible.

Explanation:

If it is possible, then it will be violation of second law of thermodynamics, which states that it is not possible to construct a heat engine that will not expel heat into atmosphere without leaving any change on the working substance.

Q.24 A thermos flask containing milk is shaken rapidly. Does the temperature of milk rise?

Ans. Yes, the temperature of the milk rises.

Reason: So, when we rapidly shake the thermos flask we do some work on milk, this work done increases the K.E of molecules of milk. Hence, the temperature of milk rises.

Q.25 What happens to the temperature of the room, when an air-conditioner is left running on a table in the middle of the room?

Ans. The temperature of the room will not decreases even it increases slightly.

Reason: As air conditioner is running at the middle of room it absorbs as well as rejects heat in the same room at the same rate. So, temperature of the room remains unchanged. But due to working of compressor some heat is produced due to friction. So, temperature of the room will increases slightly.

Q.26 Can the mechanical energy be converted completely into heat energy? If so, give an example.

Ans. When a gas is compressed at a constant temperature, work done is completely converted into heat while internal energy of the gas remains constant.

According to first law of thermodynamics,

$$Q = \Delta U + W$$

In this case, $\Delta U = 0$

Work is done on the gas. So W is negative. Heat leaves the gas, so Q is negative.

$$-Q = 0 - W$$

$$-Q = -W$$

or $$W = Q$$

Thus mechanical energy can be completely converted into heat energy. To keep temperature of the gas constant, the compression should be carried slowly. This process is called isothermal compression.

Q.27 Does entropy of a system increases or decreases due to friction?

Ans. Yes, the entropy of the system increases due to friction.

Reason: Since $\Delta S = \dfrac{\Delta Q}{T}$

Due to friction, some mechanical energy is converted into heat (i.e., heat is added up into system) which increase the entropy of system.

Q.28 Give an example of a natural process that involves an increase in entropy?

Ans. We know that entropy is measured by following equation.

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

Example: The melting of ice involves the increase in entropy. Ice absorbs the heat from its surrounding and changes its state. (i.e., from solid into liquid). Thus entropy increases.

All natural processes in which friction is involved, the entropy of the system increases.

Q.29 What is the physical significance of first law of thermodynamics?

Ans. It is shows that heat and work are two forms of energy transfer and that internal energy changes depend on them.

Q.30 Is entropy change zero in a reversible process?

Ans. Yes, the total entropy change of the system and surroundings is zero in a reversible process.

Q.31 Is entropy change positive in an irreversible process?

Ans. Yes, the total entropy of the system and surroundings increases in an irreversible process.

Q.32 What is significance of second law of thermodynamics?

Ans. It sets a direction for energy transfer and explains why some processes are irreversible.

Q.33 How does the second law of thermodynamics apply to refrigerators?

Ans. A refrigerator moves heat from a cold to a hot body, but only by doing external work, in agreement with the second law of thermodynamics.

Q.34 Does the Carnot's theorem depend on the working substances?

Ans. No, Carnot's efficiency is independent of the working substances used in the engine.

Q.35 What is implication of Carnot's theorem for real engines?

Ans. All real engines are less efficient than a Carnot engine working between the same two temperatures.

Q.36 What factors affect the coefficient of performance of a refrigerator?

Ans. Temperature difference between the hot and cold reservoirs, insulation, and mechanical efficiency of the components.

Q.37 Can entropy ever be negative?

Ans. Entropy itself cannot be negative, but the change in entropy can be negative if a system loses heat.

Q.38 Does entropy increases or decreases in an irreversible process?

Ans. Entropy increases in an irreversible (natural) process.

Q.39 What is the total entropy change of the universe in a reversible process?

Ans. The total entropy change of the universe is zero in a perfectly reversible process.

SOLVED EXERCISE

MULTIPLE CHOICE QUESTIONS

Tick (✓) the correct answer.

6.1 In an isothermal change, internal energy:
(a) decreases (b) increases (c) remains the same✓ (d) becomes zero

6.2 First law of thermodynamics is based upon law of conservation of:
(a) mass (b) energy✓ (c) momentum (d) charge

6.3 A device which converts thermal energy into mechanical energy is called:
(a) heat engine (b) Carnot engine (c) refrigerator✓ (d) turbine

6.4 When two objects are made in thermal contact having same temperature, then they are at:
(a) thermal Equilibrium✓ (b) chemical Equilibrium
(c) mechanical Equilibrium (d) physical Equilibrium

6.5 When the 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

6.6 Entropy of a system in reversible process:
(a) decreases (b) increases (c) is Infinite (d) is zero✓

6.7 What happens to internal energy of an object when its temperature:
(a) decreases (b) remains constant (c) increases✓ (d) fluctuates

6.8 The value of Boltzmann constant is:
(a) 1.38×10^{-23} J K^{-1}✓ (b) 1.38×10^{23} J K^{-1} (c) 1.38×10^{26} J K^{-1} (d) 1.38×10^{-23} J-1 K^{-1}

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

6.10 Thermodynamics mostly deals with:
(a) measurement of quantity of heat (b) transfer of quantity of heat
(c) change of state (d) Conversion of heat to other forms of energy✓

SHORT ANSWER QUESTIONS

6.1 What is meant by thermal equilibrium? Explain briefly.

Ans. Thermal equilibrium is the state in which two or more objects or systems in contact with each other no longer exchange heat because they are at the same temperature.

In simple terms, when objects are different temperatures come into contact, heat flows from the hotter to the cooler object. This heat transfer continues until all objects reach the same temperature. At that point, they are in thermal equilibrium, and no further heat exchange occurs.

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

Ans. Internal energy is the total energy contained within a system due to the microscopic motion and interactions of its particles (atoms and molecules). It includes; kinetic energy of particles (due to their motion), and P.E (due to interactions between particles, though this is negligible in an ideal gas).

In the case of an ideal gas, internal energy depends only on the K.E. of the gas molecules because ideal gases are assumed to have no intermolecular forces (no P.E. between particles).

For an ideal gas, internal energy is directly proportional to its temperature, specially, for a monoatomic ideal gas

Internal energy $U = \frac{3}{2}nRT$

So, as the temperature increases, the internal energy increases, and vice versa.

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

Ans. 1. Kelvin-Planck Statement

"It is impossible to construct a device that operates on a cycle and produces no effect other than the absorption of heat from a reservoir and the performance of an equivalent amount of work."

In simpler terms, you cannot have a 100% efficient heat engine.

Clausius Statement

"It is impossible to construct a device that operates on a cycle and produces no effect other than the transfer of heat from a colder body to an hotter body without any external work."

In short, heat cannot flow from cold body to hot body without work being done.

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

Ans. No, it is not possible to construct a heat engine with 100% efficiency. This is explained by the second law of thermodynamics and fundamental physical principles.

Explanation

1. **Second Law of Thermodynamics**

A heat engine operates by extracting heat from a high-temperature reservoir, performing useful work, and releasing some of the heat to a low-temperature reservoir.

According to the second law of thermodynamics, it is impossible to convert all the heat from the high-temperature reservoir entirely into work without releasing some of it to a colder reservoir.

2. **Carnot Efficiency**

The maximum efficiency of any heat engine is given by Carnot's formula:

$$\eta = 1 - \frac{T_{cold}}{T_{hot}}.$$

To achieve 100% efficiency ($\eta = 1$), the cold reservoir temperature (T_{cold}) would have to be absolute zero (0 K), which is unattainable according to the third law of thermodynamics.

3. **Entropy Considerations**

The operation of a heat engine involves an increase in the entropy of the system and its surroundings. A 100% efficient engine would violate the principle of entropy increase, which states that in any real process, entropy must either increase or stay constant.

6.5 Differentiate between reversible and irreversible processes.

Ans. Reversible Process

"A process that can be reversed without leaving any change in the system and surroundings is said to be a reversible process."

Examples: Ideal gas expansion / compression at infinitesimal pressure difference, melting of ice at 0°C under equilibrium conditions.

- A reversible process happens infinitely slowly, maintaining equilibrium at every stage.
- Maximum work is obtained in a reversible process.
- No net change in the entropy of the system and surroundings in a reversible process.

Irreversible Process

"A process that cannot be reversed without leaving changes in the system and surroundings is called an irreversible process."

Examples: Sudden expansion of gas, combustion, natural processes like mixing of two gases.

- An irreversible process happens rapidly and is far from equilibrium.
- Less work is obtained as compared to a reversible process.
- In an irreversible process, entropy of the system and surroundings increases.

6.6 Why adiabat is steeper than isotherm? Explain.

Ans. An adiabatic curve is steeper than an isothermal curve because of the difference in how pressure and volume are related in these processes, which arises from the role of heat transfer and internal energy.

1. **Adiabatic Process**

In an adiabatic process, there is no heat exchange ($\Delta Q = 0$). The change in internal energy is entirely due to work done on or by the gas. The relationship between pressure (P) and volume (V) is given by

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

where $\gamma = \frac{C_p}{C_v}$ (the adiabatic index or ratio of specific heats), $\gamma > 1$ meaning pressure decreases more rapidly with an increase in volume compared to the isothermal case.

2. **Isothermal Process**

In an isothermal process, the temperature remains constant. The internal energy of the system does not change, and any work done is exactly balanced by heat exchange with the surroundings. The relationship between pressure and volume follows:

$$PV = \text{Constant}$$

This implies a slower decrease in pressure as the volume increases compared to the adiabatic case.

Why Adiabatic is Steeper?

(i) In an adiabatic process, since no heat is added to the system, the temperature decreases as the gas expands. This leads to a faster drop in pressure with volume because both the reduced temperature and increased volume contribute to the lower pressure.

(ii) In an isothermal process, the temperature is constant, so the pressure only decreases due to the volume increase, leading to a less steep curve.

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

Ans. No, a refrigerator does not violate the second law of thermodynamics. The second law states that heat cannot spontaneously flow from a colder body to a hotter body. However, a refrigerator operates by doing work, usually through a compressor, to transfer heat from the cold interior (the body you want to cool) to the warmer exterior (the environment).

This process involves the refrigerator absorbing heat from the cold space and then expelling it to the outside environment, usually through a condenser coil, by using electrical energy to drive the compressor. So, while the refrigerator moves heat from a cooler to a warmer place, this is accomplished by the input of external energy, not by spontaneous transfer. This external energy input is key, and it is in accordance with the second law of thermodynamics because the total entropy of the system (the refrigerator and its surroundings) still increases.

Thus, the second law of thermodynamics is not violated by a refrigerator.

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

Ans. The heat death of the universe is a theory that suggests the universe will eventually reach a state of maximum entropy, where all energy is evenly distributed. Entropy is a measure of disorder or randomness, and in thermodynamics, it tends to increase over time. As the universe evolves, stars burn out, matter decays, and energy spreads out, leading to a uniform temperature and lack of usable energy. This state of no thermodynamic work, where everything is in equilibrium and no more processes can occur, is known as the heat death.

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.

Ans. No, it is not possible for a cyclic reversible heat engine to absorb heat at a constant temperature and completely transform it into work without rejecting some heat at a lower temperature. This is a consequence of the second law of thermodynamics.

In a cyclic process, the heat engine operates between two heat reservoirs: a hot reservoir (where heat is absorbed) and a cold reservoir (where heat is rejected). The second law states that it is impossible to construct a heat engine that converts all the absorbed heat into work. Some amount of heat must always be rejected to the cold reservoir.

This concept is illustrated by the Carnot cycle, which is an idealized, reversible heat engine. Even in a Carnot engine, some heat is always rejected to the cold reservoir, and the efficiency of the engine is determined by the temperatures of the hot and cold reservoirs. The efficiency is given by

$$\eta = 1 - \frac{T_{hot}}{T_{cold}}$$

From this equation, we see that some energy is always lost as heat to the cold reservoir in order for the engine to do work. Thus, it is not possible to completely transform heat into work without rejecting some heat at a lower temperature.

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.

Ans. At high pressure and low temperature, real gases behave differently from ideal gases due to deviations from the ideal gas assumptions. Here is a breakdown of how these behaviors differ and the reasons behind them based on the kinetic theory of gases:

1. **Volume Occupied by Gas Molecules**

Ideal Gas: Assumes gas molecules have negligible volume.

Real Gas: Molecules have a finite volume. At high pressure, the volume of the gas becomes significant compared to the total volume, as the molecules are compressed into a smaller space.

Reason: In the kinetic theory of gases, the assumption is that the gas molecules are point particles with no volume. However, at high pressures, molecules are forced closer together, and their actual volume becomes noticeable, leading to deviations from ideal gas behavior.

2. **Intermolecular Forces**

Ideal Gas: Assumes no intermolecular forces between molecules (except during elastic collisions).

Real Gas: Molecules experience attractive (and sometimes repulsive) forces, especially at low temperatures where kinetic energy is lower, allowing these forces to have more impact.

Reason: The kinetic theory assumes that gas molecules are in constant random motion and only interact during collisions. At low temperatures, the kinetic energy decreases, and intermolecular forces (e.g., Van der Waals forces) become more significant, leading to deviations from ideal gas behavior.

3. **Pressure Deviations**

Ideal Gas: Follows the equation of state (PV = nRT) without deviation under any condition.

Real Gas: At high pressure and low temperature, real gases experience higher pressure than predicted by the ideal gas law due to the attractive forces between molecules (which reduce the frequency of collisions with the walls of the container).

Reason: As molecules are closer together under high pressure, intermolecular attractions reduce the force with which molecules hit the container walls, lowering the pressure compared to what is predicted by the ideal gas law. At low temperature, the kinetic energy is too low to overcome these attractive forces effectively.

4. **Temperature Effects**

Ideal Gas: The kinetic energy of the molecules is solely dependent on temperature, and the gas behaves ideally as long as the temperature is sufficiently high.

Real Gas: At low temperatures, real gases deviate more from ideal behavior because the intermolecular forces become more influential, and the kinetic energy is not sufficient to overcome these forces.

Reason: According to the kinetic theory, temperature is directly related to the average kinetic energy of molecules. As the temperature decreases, the molecules move slower, and the effect of attractive intermolecular forces becomes significant, causing real gases to behave non-ideally.

5. **Compressibility**

Ideal Gas: Ideal gases can be compressed infinitely without any changes in behaviour, as no interactions between molecules exist.

Real Gas: At high pressure and low temperature, real gases become less compressible due to the finite size of molecules and the intermolecular forces that resist further compression.

Reason: As the gas molecules are packed closer together under high pressure, repulsive forces between molecules begin to dominate, which leads to a decrease in compressibility. This is in contrast to the ideal gas, which assumes no such forces.

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

Ans. To show that the area under the Pressure-Volume (P-V) graph is equal to the work done, we need to relate the work done by a gas during a thermodynamic process to the P-V graph.

Work Done in Thermodynamics

The work done by or on a gas is given by the following equation:

$$W = P\Delta V$$

The equation above tells us that the work done during a process is equal to pressure P with respect to volume V, taken from the initial volume v_i to the final volume v_f.

Interpretation of the P-V Graph:

The P-V graph plots pressure P on the vertical axis and volume V on the horizontal axis. The area under the curve of the P-V graph represents the work done during the process.

- If the graph is a curve, the area under the curve can be calculated using the above formula.
- For simple processes, such as isobaric (constant pressure), isochoric (constant volume), or adiabatic processes, the area can often be determined geometrically.

For example:

- **Isobaric process:** If the pressure is constant ($P = P_o$), the work done is the area of the rectangle under the curve, which is $P_o \times (v_f - v_i)$.
- **Isochoric process:** The volume is constant, so no work is done, and the area under the curve is zero.
- **Adiabatic process:** The curve is non-linear, and the work is the integral of P(V) with respect to volume over the specific range.

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

Ans. (i) The work done by a gas is given by the formula:

$$W = P\Delta V$$

In thermodynamics, the work done by a gas can also be calculated for more specific processes (isobaric, isothermal, adiabatic, etc.).

Examples

1. For an Isobaric Process (constant pressure):

$$W = P\,(V_f - V_i)$$

where V_f is the final volume and V_i is the initial volume.

2. For an Isothermal Process (constant temperature):

The work done by an ideal gas during an isothermal expansion or compression can be calculated using the formula:

$$W = nRT$$

3. **For an Adiabatic Process (no heat exchange):**

For an ideal gas undergoing an adiabatic process, the work is calculated by:

$$W = \frac{P_iV_i - P_fV_f}{\gamma - 1}$$

where γ is the heat capacity ratio $\left(\frac{C_P}{C_V}\right)$.

(ii) When work is done on a gas, then its volume changes to the external pressure. The basic idea is compression (volume decreases) work is done on the gas. Then

$$\Delta W = -P\Delta V$$

If the gas is compressed, then $\Delta V < 0$, then work is positive, (work is done on the gas).

CONSTRUCTED RESPONSE QUESTIONS

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

Ans. Thermodynamics is fundamentally concerned with the study of energy and its transformations. The concept of energy conservation is directly related to the First law of thermodynamics, also known as the law of energy conservation. This law states that energy cannot be created or destroyed, only transformed from one form to another.

In a thermodynamic system, energy can change forms. For example, from kinetic energy to heat energy or from chemical energy to mechanical work. However, the total energy within an isolated system remains constant. This principle of conservation means that the energy entering a system (through heat, work, etc.) must be accounted for in terms of changes in the internal energy of the system or the energy leaving the system.

In essence, thermodynamics provides the framework that governs how energy behaves, transforms, and is conserved in all physical processes.

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

Ans. Thermodynamics plays a crucial role in understanding the energy transformations and processes in biological systems, such as the human body. The four laws of thermodynamics govern how energy is transferred, transformed, and used within organisms.

1. **First Law of Thermodynamics (Conservation of Energy):** This law states that energy cannot be created or destroyed, only transformed from one form to another. In the human body, the energy in food (chemical energy) is converted into various forms, such as heat, mechanical work (muscle contractions), and electrical energy (nerve signalling). The body takes in food to maintain its energy balance, with excess energy stored as fat or glycogen.
2. **Second Law of Thermodynamics (Entropy):** This law states that in any energy transformation, some energy becomes unusable, increasing the system's entropy (or disorder). In biological systems, this means that energy transfers are not perfectly efficient. For instance, when the body converts food into energy for muscle movement, some of that energy is lost as heat, increasing entropy in the system. The body works to maintain order (low entropy) by constantly taking in energy and expelling waste.
3. **Third Law of Thermodynamics (Absolute Zero Entropy):** This law states that as the temperature of a system approaches absolute zero, the entropy of the system approaches a minimum value. While absolute zero is not practically achievable in the human body, this law reflects the importance of temperature in metabolic processes. The body's enzymes and biochemical reactions are optimized to work within a narrow temperature range to maintain life-sustaining processes.
4. **Zeroth Law of Thermodynamics (Thermal Equilibrium):** This law states that if two systems are in thermal equilibrium with a third system, they are in thermal equilibrium with each other. In biological systems, maintaining body temperature within a certain range (e.g., through thermoregulation) is essential for proper cellular function, as metabolic processes are sensitive to temperature.

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

Ans. When a gas expands adiabatically, no heat is exchanged with the surroundings, and the process occurs without any heat input or loss. Here's what happens to the temperature and pressure during this expansion:

Temperature: As the gas expands, it does work on its surroundings. Since no heat is added (adiabatic process), the internal energy of the gas decreases. For an ideal gas, the temperature is directly related to the internal energy. Therefore, the temperature of the gas decreases during an adiabatic expansion.

Pressure: As the volume of the gas increases during expansion, the pressure also decreases. This is a result of the gas molecules having more space to move, leading to fewer collisions with the walls of the container. Therefore, the pressure of the gas decreases during the expansion.

6.4 A coffee cup is left on a table, and overtime coffee cup cools down. Explain thermodynamics processes occurring during this process.

Ans. The cooling of a coffee cup on a table involves several thermodynamic processes, primarily heat transfer through conduction, convection, and radiation. Here is how each process works:

Conduction: The coffee cup, which is initially hot, comes into contact with the table. Heat flows from the hot cup to the cooler surface of the table through direct molecular collisions, which is conduction. The heat moves from the coffee cup to the table and then spreads out, cooling the cup.

Convection: As the coffee cup cools, the temperature of the air around the cup also changes. The hot air around the cup heats up and becomes less dense, rising away from the cup. Cooler air moves in to take its place, creating a convection current. This process helps carry away heat from the surface of the coffee cup into the surrounding air, further cooling the cup.

Radiation: The coffee cup also emits infrared radiation as its temperature decreases. This radiation is the release of energy in the form of electromagnetic waves, which is emitted from all objects above absolute zero temperature. The cup loses energy in the form of radiation, further contributing to its cooling.

Thermal Equilibrium: Over time, the heat from the coffee cup is transferred to the surrounding environment (table, air, etc.), and the temperature of the cup gradually drops. Eventually, the coffee cup reaches thermal equilibrium with its surroundings, meaning there is no longer a temperature difference between the cup and the environment, and the cooling process stops.

This combination of processes ensures that the coffee cup loses heat and cools down until it reaches room temperature.

6.5 How can we explain different weather patterns through thermodynamically processes like wind, rain, etc.

Ans. Weather patterns are a result of complex thermodynamic processes that involve the transfer of energy, heat, and moisture within Earth's atmosphere. Here is a breakdown of how various weather phenomena like wind, rain, and others are explained through thermodynamics:

1. Wind

Wind is essentially the movement of air caused by differences in air pressure, which in turn are driven by temperature gradients. Here's the thermodynamic process:

Heating and Cooling: When sunlight heats the Earth's surface, the air above it warms up, becomes less dense, and rises (this is called convection). On the other hand, cooler air tends to sink.

Pressure Differences: As warm air rises, it creates areas of lower pressure at the surface. Cool air then rushes in to fill this gap, causing wind.

Coriolis Effect: The rotation of Earth causes moving air to be deflected, creating wind patterns like trade winds, westerlies, and polar easterlies.

2. Rain

Rain is the result of water vapor in the atmosphere condensing into liquid droplets that become heavy enough to fall to the Earth's surface. The thermodynamic processes involved are:

Evaporation: Water from oceans, lakes, and other bodies evaporates due to the heat from the sun. This process requires energy (latent heat), which is absorbed from the environment, cooling the surrounding air.

Rising Air and Cooling: As air rises, it cools. The cooling process causes the water vapor to condense into tiny droplets, forming clouds. The condensation releases latent heat, which warms the air and causes it to rise further, sustaining the cycle.

Cloud Formation: When the air cools to its dew point, the water vapor condenses into cloud droplets or ice crystals (depending on the temperature). As the droplets combine and grow, they can become heavy enough to fall as rain.

Precipitation: If the droplets are large enough, gravity overcomes the upward movement of air, and they fall to the ground as rain.

3. Thunderstorms

Thunderstorms are a result of the rapid upward movement of warm, moist air:

Instability: When warm, moist air near the surface rises quickly into colder regions of the atmosphere, it creates a condition of instability. The air continues to rise because it's warmer (and thus lighter) than the surrounding air.

Thunder and Lightning: As the rising air carries moisture upward, it can cause the formation of large thunderclouds. Within these clouds, the friction between water droplets and ice particles can lead to a buildup of static electricity. When this charge is released, it creates a lightning strike, which heats the surrounding air rapidly, causing the thunderous sound.

Convective Heating: The rising air from the surface keeps feeding the thunderstorm, allowing it to develop stronger winds, more lightning, and heavier rain.

4. Cyclones (Hurricanes, Typhoons)

Cyclones are large-scale systems driven by the energy from warm ocean waters and atmospheric conditions:

Heat and Moisture Transfer: Warm ocean water heats the air above, causing it to rise and create a low-pressure system. As the air rises, it cools and condenses, releasing latent heat that fuels the storm.

Coriolis Effect: The Earth's rotation causes the rising air to spin, leading to the characteristic rotation of cyclones.

Convergence and Divergence: Winds converge toward the low-pressure center, and as they rise, they diverge at higher altitudes, causing the storm to strengthen. The release of latent heat keeps the storm fueled, making it stronger.

COMPREHENSIVE QUESTIONS

6.1 What are the postulates of kinetic theory of gases? Derive a relation for ideal gas equation in the form $PV = Nk_B T$ from general gas equation.

Ans. See Q. 2, Q. 4 and Q. 5.

6.2 Statement and explain various gas laws.

Ans. See Q. 6.

6.3 Explain first law of thermodynamics in detail. Give an example in support of yoru explanation. Give its two applications.

Ans. See Q. 11.

6.4 What is a refrigerator? Explain its working. Derive an expression for its coefficient of performance.

Ans. See Q. 18.

6.5 What is Carnot engine? Describe Carnot cycle. State Carnot theorem and derive an expression for efficiency of Carnot engine.

Ans. See Q. 17.

6.6 Define and explain the term "Entropy".

Ans. See Q. 19.

NUMERICAL PROBLEMS

6.1 A gas occupies 6.0 L of volume at a pressure of 12 atm. What will be the volume of gas if the pressure is increased by 2.0 atm, assuming that temperature remains constant?

Solution:

Given data:

$P_1 = 12$ atm

$V_1 = 6$ L

$P_2 = 12 + 2 = 14$ atm

To Find:

$V_2 = ?$

Calculations: Using Boyle's law:

$$P_1V_1 = P_2V_2$$

or
$$V_2 = \frac{P_1V_1}{P_2}$$

Putting the values

$$V_2 = \frac{12 \times 6}{14} = \frac{72}{14}$$

$V_2 = 5.14$ L **Ans.**

The volume of the gas will be 5.14 L.

6.2 In a vacuum chamber which is connected to a cryogenic pump, pressure as low as 1.00 nPa is being attained. Calculate the number of molecules in 1.00 m³ vessel at this pressure and temperature of 300 K.

Solution:

Given data:

Pressure = P = 1.00 nPa = 1.00×10^{-9} Pa

Volume = V = 1.00 m^3

Temperature = T = 300 K

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

To Find:

Number of molecules = ?

Calculations: Using the ideal gas law:

$$PV = nRT$$

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

Putting the values

$$n = \frac{(1.00 \times 10^{-9}) \times 1.00}{8.314 \times 300}$$

$$n = \frac{1.00 \times 10^{-9}}{2494.2} \approx 4.01 \times 10^{-13} \text{ mol}$$

Now converting moles to number of molecules

Use Avogadro's number:

$N_A = 6.022 \times 10^{23}$ molecules / mol

Number of molecules = $n \times N_A$

$= 4.01 \times 10^{-13} \times (6.022 \times 10^{23})$

$= 2.41 \times 10^{11}$ molecules **Ans.**

6.3 A gas undergoes a thermodynamic process where it absorbs 500 J of heat energy and performs 300 J work on its surroundings. Calculate the change in internal energy of the gas.

Solution:

Given data:

Heat = Q = +500 J

Work = W = +300 J

To Find:

Change in internal energy = ΔU = ?

Calculations: According to first law of thermodynamics:

$$\Delta U = Q - W$$

Putting the values

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

$\Delta U = 200$ J **Ans.**

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.

Solution:

Given data:

$T_1 = 600\ K$

$T_2 = 300\ K$

$Q_1 = 500\ J$

To Find:

(i) Efficiency = η = ?

(ii) Work output = W = ?

Calculations: (i) Using the formula:

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

or

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

Putting the values

$$\eta = \frac{600\ K - 300\ K}{600} = \frac{1}{2} = 0.5 = 50\%\ \textbf{Ans.}$$

(ii) Work output:

Efficiency is also defined as:

$$\eta = \frac{W}{T_1} \quad \text{or} \quad W = \eta \times T_1$$

$$W = 0.5 \times 500\ J = 250\ J\ \textbf{Ans.}$$

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 (COP) of the refrigerator.

Solution:

Given data:

Heat extracted from the cold reservoir (interior) = $T_C = 1200\ J$

Heat released to the surroundings (hot reservoir) = $T_H = 1800\ J$

To Find:

(i) Work input per cycle = W = ?

(ii) Coefficient of performance (COP) = ?

Calculations:

(i) From first law of thermodynamics:

$$W = Q_H - Q_C$$

$$W = 1800\ J - 1200\ J = 600\ J\ \textbf{Ans.}$$

(ii) For a refrigerator:

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

$$COP = \frac{1200\ J}{600\ J} = 2\ \textbf{Ans.}$$

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 = 6.01×10^3 J)

Solution:

To calculate the entropy change (ΔS) for the melting of 1 mole of ice at 0°C (273 K).

We use the formula:

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

where $\Delta Q_f = 6.01\ kJ$ or $6.01 \times 10^3\ J$

It is heat of fusion of ice per mole.

Putting the values

$$\Delta S = \frac{6.01 \times 10^3\ J}{273\ K}$$

$$\Delta S = 22\ JK^{-1}\ \textbf{Ans.}$$

6.7 A gas occupies 400 mL at 20°C. What volume will it occupy at 80°C, assuming constant pressure?

Solution:

Given data:

$V_1 = 400\ mL$

$T_1 = 20°C = 293\ K$

$T_2 = 80°C = 353\ K$

To find:

V_2 = ?

Calculations: Using Charles' law

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

or

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

Putting the values

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

$$V_2 = 482\ mL\ \textbf{Ans.}$$

6.8 A gas has a pressure of 2 atm at 300 K. What pressure will it have at 450 K, assuming constant volume?

Solution:

Given data:

$P_1 = 2$ atm

$T_1 = 300$ K

$T_2 = 450$ K

To find:

$P_2 = ?$

Calculations: Using Gay-Lussac's law

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

or $$P_2 = P_1 \times \frac{T_2}{T_1} = 2 \times \frac{450}{300}$$

$$= 2 \times 1.5 = 3 \text{ atm} \quad \textbf{Ans.}$$

Thus, pressure will be 3 atm at 450 K.