12

Thermodynamics is the field of Physics relating heat and work tansfer and the associated changes in the properties (such as pressure, volume, temperature, etc) of a working substance. Thermodynamics is a macroscopic science. It involves few macroscopic variables of the system. Thermodynamics avoids the molecular description all together. The state of a gas in thermodynamics is specified by macroscopic variables such as pressure, volume, temperature, mass and composition of gas.

THERMODYNAMICS

## |TOPIC 1|
Heat and First Law of Thermodynamics

THERMODYNAMIC SYSTEM, SURROUNDINGS AND BOUNDARY

Thermodynamic system is an assembly of an extremely large number of particles (atoms or molecules) so that the assembly has a certain value of pressure, volume and temperature. The thermodynamic system may exist in the form of a solid, liquid or gas or a combination of two or more of these states.

Everything outside the system which has a direct effect on the system is called its **surroundings**. All space in universe outside the system is surroundings. e.g. Environment.

A system is separated from its surroundings by a **boundary**.

A system boundary is a real or imaginary two-dimensional closed surface that encloses the volume or region that a thermodynamic system occupies, through which energy exchange can or cannot be possible and work could be done on the system and by the system.
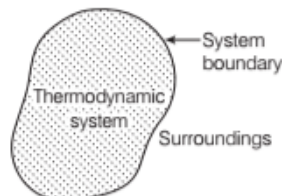
A thermodynamic system having boundary and surroundings

CHAPTER CHECKLIST

- Thermodynamic System, Surroundings and Boundary
- Thermodynamic Equilibrium
- Thermal Equilibrium
- Zeroth Law of thermodynamics
- Heat, Internal Energy and Work
- First Law of Thermodynamics as Energy Balance
- Heat Capacity
- Thermodynamic State Variables and Equation of State
- Thermodynamic Processes
- Second Law of Thermodynamics
- Reversible and Irreversible Process
- Carnot Engine

CLASSIFICATION OF THERMODYNAMIC SYSTEM

A thermodynamic system can be classified by the nature of the transfer of heat that are allowed to occur across its boundary.

A thermodynamic system may be open, closed and isolated.

(i) **Open System** It exchanges both energy and matter with the surroundings.

(ii) **Closed System** It exchanges only energy (not matter) with its surroundings.

(iii) **Isolated System** It exchanges neither energy nor matter with its surroundings.

THERMODYNAMIC EQUILIBRIUM

A thermodynamic system is said to be in thermodynamic equilibrium when macroscopic variables (like pressure, volume, temperature, mass, composition etc.) that characterise the system do not change with time.

e.g. Consider a gas inside a closed rigid container, completely insulated from its surroundings. Since, the pressure, volume, temperature, mass and composition of the gas do not change with time, therefore the gas is said to be in a state of thermodynamic equilibrium.

Whether or not a system is in a state of thermodynamic equilibrium, depends on the surroundings and the nature of the wall that separates the system from the surroundings. Consider two gases A and B occupying two different containers. Let the pressure and volume of the gases be (p_A, V_A) and (p_B, V_B), respectively.

Systems A and B
separated by adiabatic wall
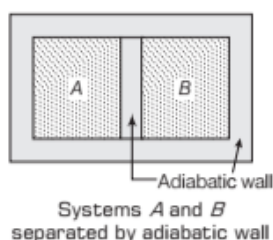
Suppose first that the two systems are put in proximity but are separated by an **adiabatic wall** (i.e. an insulating wall that does not allow flow of energy or heat from one to another). The system are insulated from the rest of the surroundings also by similar adiabatic walls.

The situation is shown schematically in figure. In **this case**, it is observed that any possible pair of values (p_A, V_A) will be in equilibrium with any possible pair of values (p_B, V_B).

THERMAL EQUILIBRIUM

Two systems are said to be in thermal equilibrium with each other if they are at the same temperature.

Again, consider the adiabatic wall separating the two gases A and B is replaced by **diathermic wall** (i.e. a wall that allows energy flow or heat from one to another). On account of flow of heat energy, the macroscopic variables of the two gases change spontaneously, either pressure or volume or both the pressure and volume of two gases may change.

Let the pressure and volume of two gases after change are (p_A', V_A') and (p_B', V_B') such that the new states of A and B are in equilibrium with each other. There is no more energy flow from one to another.

Two systems A and B in thermal equilibrium
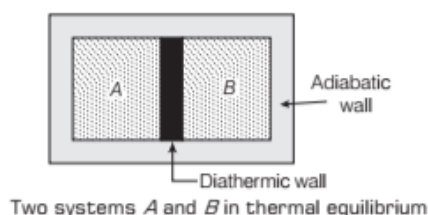
Hence, the temperature of two gases become equal and the gases are said to be in thermal equilibrium with each other. This condition is shown in figure below.

Thus, two systems are said to be in thermal equilibrium with each other if they are at the same temperature.

- If there is no unbalanced force and torque is acting on the system, then the system is said to be in mechanical equilibrium.

- If the system does not undergo any spontaneous change in its internal structure due to chemical reaction, diffusion etc., then the system is said to be in chemical equilibrium.

- Two systems are said to be in thermal equilibrium, if there is no net flow of heat between them when they are brought into thermal contact.
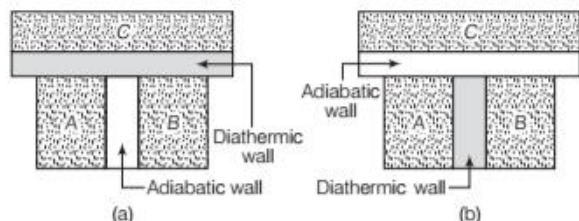
ZEROTH LAW OF THERMODYNAMICS

This law was formulated by **RH Fowler** in 1931. The zeroth law of thermodynamics states that

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

Let us consider two systems A and B separated by a fixed adiabatic wall. The two systems A and B are in contact with a third system C through diathermic wall. The macroscopic variables of A and B will vary until both A and B come in thermal equilibrium with the third system C.

This shows that two systems A and B are separately in thermal equilibrium with a third system C. This condition is shown in Fig. (a)

(a)   (b)

Let the adiabatic wall between A and B is replaced by a diathermic wall and an adiabatic wall insulates C from A and B. A and B are found in thermal equilibrium with each other. This condition is shown in Fig. (b), **both the experiments prove the zeroth law of thermodynamics.**

Concept of Temperature

Zeroth law of thermodynamics implies that temperature is a physical quantity which has the same value for all systems which are in thermal equilibrium with each other.

Hence, zeroth law says that if systems A and B are separately in thermal equilibrium with C, then

$$T_A = T_C \quad \text{and} \quad T_B = T_C \quad \Rightarrow \quad T_A = T_B$$

So, systems A and B will also be in thermal equilibrium with each other.

⌄ Some Definitions of Temperature

- Temperature is that thermodynamic variable which determines whether the two systems in contact will be in thermal equilibrium or not.
- Temperature of a body is that parameter which determine the degree of hotness or coldness of a body.
- Temperature of a body is that parameter which determine the direction of flow of heat when the body is brought in contact with another body.

HEAT, INTERNAL ENERGY AND WORK

Internal energy of a system is defined as the total energy possessed by the system due to molecular motion and molecular configuration. It is represented by U. The energy due to molecular motion is called **internal kinetic energy** U_K. The motion includes translational, rotational and vibrational motion of the molecules. The energy due to molecular configuration is called **internal potential energy** U_P. Then,

$$\boxed{\text{Internal energy}, U = U_K + U_P}$$

Thus, the internal energy of a system is the sum of molecular kinetic and potential energies in the frame of reference relative to which the centre of mass of the system is at rest.

Internal Energy of an Ideal Gas

In an ideal gas, there are no molecular forces of attraction so that the intermolecular forces are zero and the gas does not possess intermolecular potential energy, thus $U_P = 0$.

Hence, internal energy of an ideal gas is just the sum of kinetic energies associated with various random motions (i.e. translational, rotational and vibrational) of its molecules. Thus, the internal energy of an ideal gas depends on its temperature.

Internal Energy of a Real Gas

In a real gas, the intermolecular forces are not negligible. The molecules of a real gas exert mutual force of attraction on one another. Therefore, a definite amount of work has to be done in changing the distance between molecules.

Thus, internal energy of a real gas is the sum of internal kinetic energy and internal potential energy of the molecules of the gas. It would obviously depend on both the temperature and volume of the gas.

(i) The internal energy is a macroscopic state variable. The internal energy depends on the state of the system that depends on the values of pressure, volume, temperature, mass, composition etc., when the container is at rest as shown in Fig. (a)

(a) Container is at rest
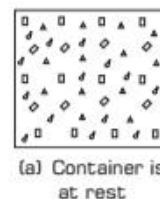
(ii) The internal energy depends on the state of the system, but not on the path taken to achieve that state.

(iii) The internal energy of a gas can vary the macroscopic state variables of the gas, varies.

(iv) In thermodynamics, the KE of the system as a whole is not relevant. It means if the container of the gas is moving as a whole with some velocity as shown in Fig. (b), the KE of the container is not to be included in internal energy.

(b) Container is moving
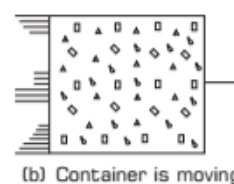
Heat

It is the energy that exchanged between a system and its environment because of the temperature difference between them. SI unit of heat is joule. The amount of heat Q given to a body to raise its temperature from T_i to T_f depends on mass, nature of substance and change in its temperature.

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

or   Change in heat, $\Delta Q = ms(T_f - T_i)$

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

Work

By work, we mean work done by the system or on the system. Suppose, a gas is confined in a cylinder with a movable piston, if p is pressure on the piston and A is area of piston, then force exerted by the gas on the piston of cylinder, $F = pA$

When the piston is pushed outward an infinitesimal distance dx, then the work done by the gas

$$dW = Fdx = pA\,dx = p\,dV \qquad [\because Adx = dV]$$
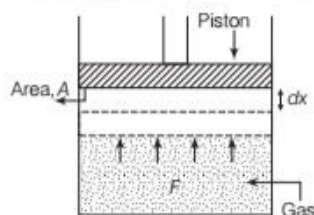
and for a finite volume change from V_i to V_f,

$$\text{Work done, } W = \int_{V_i}^{V_f} dW$$

$$\boxed{\text{Work done, } W = \int_{V_i}^{V_f} pdV}$$

Here, p could be variable or constant.

There are many ways to change the state of a gas. One way is represented by a plot between pressure of the gas and its volume and it is called an **indicator diagram**. The indicator diagram represents the variation of pressure (p) of the gas with the volume (V).

p-V diagram

On indicator diagram, the area bounded by p-V graph represents the work done
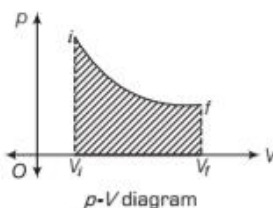
$$\text{Work} = \int_{V_i}^{V_f} pdV = \text{area under } p\text{-}V \text{ graph}$$

$$\text{From, } \Delta W = \int_{V_i}^{V_f} p\,dV$$

If system expands, $V_f > V_i$ i.e. W = positive

If system contracts, $V_f < V_i$ i.e. W = negative

Like heat, work done is also path dependent and so it is not a state function. In case of a cyclic process, work done is equal to the area enclosed under p-V diagram and it is positive, if cycle is clockwise and negative, if the cycle is anti-clockwise.

Ways to Change Internal Energy of a System

There are four ways to change the internal energy of a system.

  (i) By doing work on the system ($\Delta W = -$ ve).
  (ii) If system is doing some work ($\Delta W = +$ ve).
  (iii) If some heat energy is given to the system ($\Delta Q = +$ve).
  (iv) If some heat energy is taken out from the system. ($\Delta Q = -$ ve).

We will use these sign conventions for ΔQ and ΔW in the topics coming ahead.

HEAT AND WORK–TWO DIFFERENT MODES OF ENERGY TRANSFER

To understand the concept, let us perform the following experiment

  (i) Place a cylinder having some gas over a burner. Heat energy will flow from the burner to the gas. This will increase the internal energy of the gas.

  (ii) To push the piston of the cylinder containing gas in the upward direction, some work is done by the gas, due to which the internal energy of the gas decreases.

Experimental arrangement
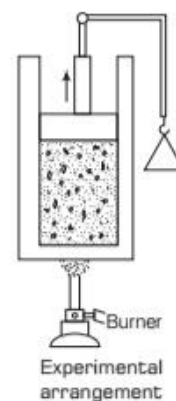
Note that both these things could happen in the reverse directions too.

If the gas, is in contact with a colder body then heat will flow from gas to the colder body and temperature of the gas will fall. Hence, internal energy of the gas will decrease. If the gas pushed the piston downwards, the work will be done on the gas. Therefore, the internal energy of the gas will increase.

Heat and work are two different modes to change the state of the system and to change the internal energy of the system.

Heat is the energy in transit. Heat is not a state variable of the system is described by internal energy of the system.

Hence, we can say that heat and work are not state variables. They are two modes of energy transfer that could change the internal energy of the system.

FIRST LAW OF THERMODYNAMICS AS ENERGY BALANCE

First law of thermodynamics is a statement of conservation of energy applied to any system in which energy transfer from or to the surroundings is taken into account.

It states that heat given to a system is either used in doing external work or it increases the internal energy of the system or both.

i.e. $\boxed{\text{Heat supplied, } \Delta Q = \Delta U + \Delta W}$
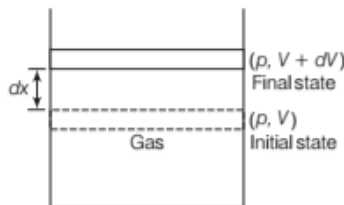
where,

ΔQ = Heat supplied to the system by the surroundings.

ΔW = Work done by the system on the surroundings

ΔU = Change in internal energy of the system.

ΔU depends only on the initial and final states.

Consider a gas in a cylinder with a massless and frictionless piston. Let the gas expands by a very small volume dV.

Experimental arrangement to prove first law of thermodynamics

Let p is pressure and V is volume of the gas. A is area of cross-section of the piston, dx is the distance moved by the piston. Let the volume expansion is dV.

So, the work done by the gas

dW = force × dx

or $dW = pA \times dx = p(A\,dx) = pdV$ $[\because A\,dx = dV]$

$\therefore$ $dW = pdV$

[For small displacement dx, the pressure is assumed to be constant.]

Thus, from first law $\Delta Q = \Delta U + pdV$

where,

ΔQ = heat transition between system and surroundings

ΔU = change in internal energy of the system.

EXAMPLE |1| Conversion of Water into Steam

1 g of water at 100°C is converted into steam of the same temperature. If the volume of steam is 1551 cm³, find out the change in internal energy of the water. Latent heat of steam = 2256×10^3 J/kg. Consider atm pressure.

Sol. Given, Mass of water, $m = 1\,g = 1 \times 10^{-3}$ kg

Hence, pressure is $p = 1.013 \times 10^5$ N/m²

Volume of steam, $V_s = 1551$ cm³ $= 1551 \times 10^{-6}$ m³

Volume of water, $V_w = \dfrac{\text{mass}}{\text{density}} = \dfrac{1 \times 10^{-3}}{10^3} = 2 \times 10^{-6}$ m³

First law of thermodynamics gives

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

$\Rightarrow$ $mL = \Delta U + p(V_s - V_w)$

$\therefore$ Change in internal energy is

$\Delta U = mL - p(V_s - V_w)$

$= 1 \times 10^{-3} \times 2256 \times 10^3 - 1.013 \times 10^5$

$\times (1551 \times 10^{-6} - 10^{-6})$

$= 2256 - 0.1013 \times 1550 \equiv 2099\,\text{J}$

EXAMPLE |2| Different Types of Phases

The quantities in the following table represent four different paths for same initial and final states. Find the values of a, b, c, d, e, f and g.

S. No.	Q (J)	W (J)	ΔU (J)
Path I	− 80	−120	d
Path II	90	c	e
Path III	a	40	f
Path IV	b	− 40	g

Sol. For path I, $\Delta Q = \Delta W + \Delta U \Rightarrow \Delta U = \Delta Q - \Delta W$

$= - 80 - (-120) = 40$ J
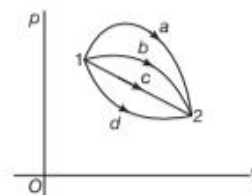
As, ΔU = a state function, so $d = e = f = g = 40$ J

Now for path II, $\Delta Q = \Delta W + \Delta U$

$90 = c + 40 \Rightarrow c = 50$ J

Similarly, $a = 80$ J, $b = 0$

EXAMPLE |3| Different Paths of System

Arrange four paths shown in ascending order on the basis of (i) change in internal energy (ii) work done by the gas (iii) magnitude of energy transferred or heat.

Sol. (i) As, ΔU depends on initial and final states but not on path, so for all a, b, c and d paths, ΔU is same.

(ii) Work done is given by area under curve and above volume axis so in ascending order, work done is d, c, b, a.

(iii) By first law, $\Delta Q = \Delta U + \Delta W$

and ΔU is same for all so, ΔQ is greatest for which ΔW is greatest. So, ascending order for ΔQ is d, c, b, a.

HEAT CAPACITY

If an amount of heat ΔQ is needed to change its temperature by ΔT, then **heat capacity** can be defined as

$$\boxed{\text{Heat capacity, } S = \frac{\Delta Q}{\Delta T}}$$

Heat capacity is numerically equal to the heat energy required to change the temperature of a body by unity. Its unit is J/K. Different amounts of heat may be needed for a unit rise in temperature at different temperatures.

Specific Heat Capacity

The amount of heat required to change the temperature of unit mass of a substance by unity is known as **specific heat capacity** of heat substance.

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

$$\boxed{\text{Specific heat capacity, } s = \frac{1}{m}\frac{\Delta Q}{\Delta T}}$$

where, s = specific heat capacity of the substance.

It depends on the nature of substance and its temperature. Its unit J/kg-K. Heat capacity per kg is known as **specific heat capacity**.

Molar Specific Heat Capacity

Heat capacity per mole is known as **molar specific heat capacity**.

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

$$\boxed{\text{Molar specific heat capacity, } C = \frac{1}{\mu}\frac{\Delta Q}{\Delta T}}$$

where, μ = number of moles.

The amount of heat required to raise the temperature of one gram mole of a substance through a unit is called **molar specific heat** capacity of the substance.

C depends on the nature of the substance, its temperature and the conditions under which heat is supplied. Its unit is J/mol-K.

Using the law of equipartition of energy, we can predict molar specific heat capacities of solids. In a solid consisting of N-atoms, the energy corresponding to vibration in each dimension about the mean position is given by

$$2 \times \frac{1}{2} K_B T = K_B T \qquad \ldots(i)$$

Then, the average energy in three dimensions is $3K_B T$. For one mole of a solid, the total energy is

$$U = 3K_B T \times N_A = 3RT \qquad [\because K_B N_A = R] \ldots(ii)$$

Now, at constant pressure

$$\Delta Q = \Delta U_{int} + p\,\Delta V \simeq \Delta U_{int}$$

Since, for a solid, ΔV is negligible.

Therefore, by using Eq. (ii)

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

Specific and molar heat capacities of some solids at room temperature and atmospheric pressure

Substance	Specific heat $(Jkg^{-1}K^{-1})$	Molar specific heat $(J\,mol^{-1}K^{-1})$
Aluminium	900.0	24.4
Carbon	506.5	6.1
Copper	386.4	24.5
Lead	127.7	26.5
Silver	236.1	25.5
Tungsten	134.4	24.9

SPECIFIC HEAT CAPACITY OF WATER

In old time, **calorie** is used as a unit of heat. Earlier it was defined as the amount of heat required to raise the temperature of 1 g of water by 1°C.

But later it was observed that specific heat of water varies slightly with temperature as shown in the figure below.
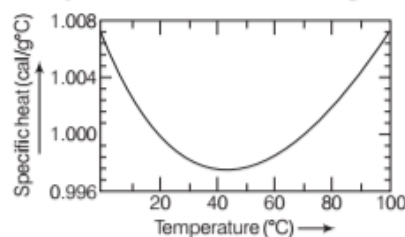
Variation of specific heat capacity of water with temperature

Specifically, one calorie is defined to be the amount of heat required to raise the temperature of 1 g of water from 14.5°C to 15.5°C.

As heat is a form of energy, hence joule, J is preferred to use the unit of heat, in SI unit, the specific heat capacity of water is 4186 J/kg-K or 4.186 J/g-K.

Mechanical Equivalent of Heat

Mechanical equivalent of heat is defined as the amount of work needed to produce 1 calorie of heat.

It is just a conversion factor.

1 calorie (heat energy) = 4.186 J ≃ 4.2 J

Specific heat capacities of gases

For gases, their specific heat capacities depends on the process or under which condition heat exchange between the gases and the sourrounding is taking place.

There are two main specific heat capacities for a gas and defined as,

(i) **Molar heat capacity at constant volume, (C_V) –**

The amount of heat required to increase the temperature of one mole of the gas by 1°C (or 1K) at constant volume is known as molar heat capacity at constant volume. It is denoted by C_V.

(ii) **Molar heat capacity at constant pressure, (C_p) –**

The amount of heat required to increase the temperature of one mole of the gas by 1°C (or 1 K) at constant volume is known as molar heat capacity at constant pressure. It is denoted by C_p.

Note

For a gas, $C_p > C_V$ always, because at constant pressure, more heat is required to increase the temperature of one mole of the gas by 1°C (or 1K) as compare to that of at constant volume.

Relation between C_p and C_V (Mayer's Formula)

We can establish the relation between specific heat capacity at constant volume (C_V) and specific heat capacity at constant pressure (C_p) of a gas.

For an ideal gas, the relation between C_p and C_V is

$$C_p - C_V = R \qquad \ldots(i)$$

This relation is known as **Mayer's Formula**.

To establish the relation, we begin with first law of thermodynamics for 1 mole of the gas

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

If heat ΔQ is absorbed at constant volume,

$\therefore$ $p\Delta V = 0$ and $\Delta Q = C_V \Delta T$ for one mole of a gas
$\Delta V = 0$

Then, $C_V = \left(\dfrac{\Delta Q}{\Delta T}\right)_V = \left(\dfrac{\Delta U}{\Delta T}\right)_V = \left(\dfrac{\Delta U}{\Delta T}\right) \qquad \ldots(ii)$

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

Now, heat ΔQ is absorbed at constant pressure, then
$$\Delta Q = C_p \Delta T$$
$$C_p = \left(\dfrac{\Delta Q}{\Delta T}\right)_p = \left(\dfrac{\Delta U}{\Delta T}\right)_p + p\left(\dfrac{\Delta V}{\Delta T}\right)_p$$

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

Now, by using Eq. (ii), we have

or $C_p = C_V + p\left(\dfrac{\Delta V}{\Delta p}\right)_p \qquad \ldots(iii)$

For one mole of an ideal gas, we can write $pV = RT$
If the pressure is kept constant

$$p\left(\dfrac{\Delta V}{\Delta T}\right)_p = R \qquad \ldots(iv)$$

From Eqs. (iii) and (iv), we get

$$\boxed{C_p - C_V = R}$$

Here, C_p and C_V are molar specific heat capacities of an ideal gas at constant pressure and volume, respectively and R is the universal gas constant.

The ratio of C_p and C_V is notified by γ.
$$\gamma = C_p / C_V$$
It is also known as heat capacity ratio, then

$$C_V = \dfrac{R}{r-1} \text{ and } C_p = \gamma\dfrac{R}{r-1}$$

EXAMPLE |4| Mixture of Two Gases

A gaseous mixture enclosed in a vessel consists of 1g mole of a gas $A\left(\gamma = \dfrac{5}{3}\right)$ and some amount of gas $B\left(\gamma = \dfrac{7}{5}\right)$ at a temperature T. The gases A and B do not react with each other and are assumed to be ideal.
Find number of gram moles of the gas B, if γ for the gaseous mixture is $\left(\dfrac{19}{13}\right)$.

Sol. For an ideal gas,
$$\dfrac{C_p}{C_V} = \gamma \text{ and } C_p - C_V = R$$

So, combining above equations, we get
$$C_V = \dfrac{R}{\gamma - 1}$$

$$(C_V)_A = \dfrac{R}{\dfrac{5}{2}-1} = \dfrac{3}{2}R$$

and $(C_V)_B = \dfrac{5}{2}R$

and $(C_V)_{mix} = \dfrac{R}{\dfrac{19}{13}-1} = \dfrac{13}{6}R$

Now, from conservation of energy
$$U_{mix} = U_A + U_B$$
or $\Delta U_{mix} = \Delta U_A + \Delta U_B$
$\Rightarrow (\mu_A + \mu_B)(C_V)_{mix}\Delta T = \mu_A(C_V)_A \Delta T + \mu_B(C_V)_B \Delta T$

$$\Rightarrow \quad (C_V)_{mix} = \frac{\mu_A (C_V)_A + \mu_B (C_V)_B}{\mu_A + \mu_B}$$

$$\Rightarrow \quad \frac{13}{6} R = \frac{1 \times \frac{3}{2} R + \mu_B \times \frac{5}{2} R}{1 + \mu_B}$$

$$\Rightarrow \quad 13 + 13\mu_B = 9 + 15\mu_B$$

$$\Rightarrow \quad \mu_B = 2 \, g\text{-mol}$$

EXAMPLE |5| Monoatomic Gas

Find molar specific heat for the process $p = \dfrac{a}{T}$ for a monoatomic gas. $\left(a = \text{constant}, C_V = \dfrac{3}{2} R\right)$

Sol. From first law of thermodynamics,

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

$$\Rightarrow \quad C = \frac{\Delta Q}{\Delta T} = \frac{\Delta W}{\Delta T} + \frac{\Delta U}{\Delta T}$$

$$\text{or} \quad C = \frac{\Delta W}{\Delta T} + C_V \qquad [\because \Delta U = C_V \Delta T]$$

$$C = \frac{p \Delta V}{\Delta T} + C_V \qquad [\because \Delta W = p \Delta V] \quad ...(i)$$

For the process,

$$pV = RT \qquad [\because \text{for monoatomic gas}, \mu = 1]$$

$$\Rightarrow \quad V = \frac{RT}{p} = \frac{RT^2}{a}$$

$$\Rightarrow \quad \frac{\Delta V}{\Delta T} = \frac{dV}{dT} = \frac{2RT}{a} \qquad ...(ii)$$

Substituting value of Eq. (ii) in Eq. (i), we get

$$= p\left(\frac{2RT}{a}\right) + C_V = \frac{a}{T}\left(\frac{2RT}{a}\right) + C_V \qquad \left[\because p = \frac{a}{T}\right]$$

$$\Rightarrow \quad C = 2R + C_V = 2R + \frac{3}{2} R = \frac{7}{2} R$$

# THERMODYNAMIC STATE VARIABLES AND EQUATION OF STATE

Every **equilibrium state** of a thermodynamic system is completely described by specific values of some macroscopic variables and these are called **state variables**. e.g. Pressure, volume, temperature and mass.

Equilibrium State

A system is not always in a equilibrium state but with time, it comes in mechanical and thermal equilibrium state.

e.g. A mixture of gases undergoing an explosive chemical reaction (e.g. a mixture of petrol vapour and air when ignited by a spark) is not an equilibrium state but with time the gas attains a uniform temperature and pressure and comes to thermal and mechanical equilibrium with its surroundings.
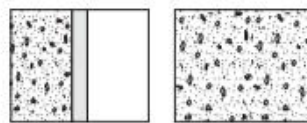
(a) Partition in the box is suddenly removed leading to free expansion of the gas
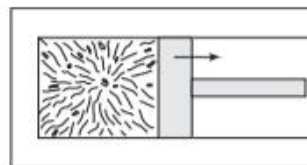
(b) A mixture of gases undergoing an explosive chemical reaction

Equation of State

The various state variables are not necessarily independent. The equation which represents the relationship between the state variables of a system is called its **equation of state**.

e.g. For an ideal gas, the equation of state is the ideal gas equation

$$pV = \mu RT$$

For a fixed amount of gas given, there are thus only two independent variables, say p and V or T and V. The pressure-volume curve for a fixed temperature is called an **isotherm**.

EXTENSIVE AND INTENSIVE STATE VARIABLES

The state variables are of two types such as extensive and intensive

Extensive State Variables

Extensive state variables indicate the **size** of the system.

Let us consider that a system in equilibrium is divided into two equal parts. The variable whose values get halved in each part are **extensive**. e.g. Internal energy (U), volume (V), total mass (M) are extensive variables.

Intensive State Variables

These are state variables that do not depend on the size of the system. Again consider a system in equilibrium divided into two equal parts. The variables that remain unchanged for each part are **intensive**.

e.g. Pressure (p), temperature (T) and density (ρ) are intensive variables.

Note
The extensive variables change with the size of the system, but the intensive variables do not change with size.

THERMODYNAMIC PROCESSES

When state of a system changes or the state variables changes with time, then this process is known as **thermodynamic process**.

Quasi-Static Process

Quasi-static process is a hypothetical concept. Practically, processes that are sufficiently slow are considered as quasi-static.

The system changes its variables (p, T, V) so slowly that it remains in thermal and mechanical equilibrium with its surroundings throughout. In a quasi-static process, at every stage, the difference in the pressure of the system and the external pressure is infinitesimally small. The same is true for the temperature difference between the system and its surroundings.

To take a gas from the state (p, T) to another state (p', T') *via* a quasi-static process, we change the external pressure by a very small amount, allow the system to equalise its pressure with that of the surroundings and continue the process infinitely slowly until the system achieves the pressure p'.
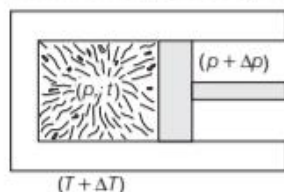
Changes in temperature and pressure in quasi-static process

Similarly, to change the temperature, we introduce an infinitesimal temperature difference between the system and the surrounding reservoirs and by choosing reservoirs of progressively different temperatures T to T'. The system achieves the temperature T'.

Note
The processes that do not involve accelerated motion of piston-large temperature gradient and pressure gradient are quasi-static.

Some Important Processes

(i) An **isothermal process** occurs at constant temperature.
   e.g. Freezing of water at 0°C to form ice at 0°C.
(ii) An **isobaric process** occurs at constant pressure.
   e.g. Boiling of water in a open container.

(iii) An **isochoric process** is one in which volume is kept constant, meaning that the work done by the system will be zero.
   e.g. Heat given to a system with fixed walls.

(iv) An **adiabatic process** does not allow transfer of heat by or to the system.
   e.g. Rapid compression, like filling of a cycle tube by a hand pump.

(v) **Cyclic and non-cyclic process** In cyclic process, initial and final states are same while in non-cyclic processes, they are different.

EXAMPLE |6| Examples of Various Processes

Give an example of each of given below
   (i) Isobaric process   (ii) Isochoric process
   (iii) Isothermal process   (iv) Adiabatic process

Sol. (i) **Isobaric process** Cooking in an open lid container.
   (ii) **Isochoric process** Cooking in a pressure cooker.
   (iii) **Isothermal process** Boiling of water at atmospheric pressure.
   (iv) **Adiabatic process** Expulsion of air from a bursted tyre (tube).

EXAMPLE |7| Condition of Adiabatic Process

How an adiabatic can be carried practically?

Sol. For an adiabatic process, $\Delta Q = 0$. So, if a process is carried very fast so that heat cannot transferred from system to surroundings and *vice-versa*, it is an adiabatic process.

Work Done in an Isothermal Process

For an isothermal process, temperature remains constant.

For an ideal gas, the equation of state is given by

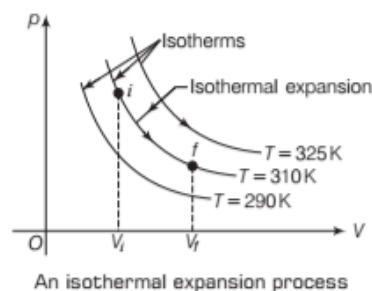$$pV = \text{constant}$$

So, gas follows Boyle's law

$$p_i V_i = p_f V_f, \text{ for isothermal process}$$

p-V Diagram

On a p-V diagram, an isotherm is a curve that connects points of same temperature.

An isothermal expansion process

Work Done

Work done in an isothermal process = area under p-V graph

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

$$= \mu RT \ln(V)_{V_i}^{V_f} = \mu RT \ln(V_f - V_i)$$

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

Work done, $\boxed{W_{iso} = 2.303\,\mu RT \log\left(\frac{V_f}{V_i}\right)}$

As temperature of ideal gas remains constant.

$\therefore \qquad\qquad\qquad \Delta U = 0$

So, by first law of thermodynamics

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

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

where, μ = number of moles, R = gas constant and T = temperature

V_f and V_i are the final and initial volumes of the gas, respectively.

i.e. Heat supplied in an isothermal change is used to do work against surroundings or if the work is done on the system, then the equal amount of heat energy will be liberate by the system.

Let us consider two cases for finding the nature of the work done.

Case I If $V_f > V_i$, then $W > 0$

Thus, it is an **isothermal expansion** which means the gas absorbs heat.

Case II If $V_f < V_i$, then $W < 0$

Thus, it is an **isothermal compression**, work is done on the gas by the environment and heat is released.

EXAMPLE |8| Work Done in Isothermal Process

Three moles of an ideal gas kept at constant temperature of 300 K are compressed from a volume of 4 L to 1 L. Calculate the work done in the process. Take R as 8.31 J/mol-K.

Sol. Given, $\mu = 3$, $T = 300$ K, $V_i = 4$ L, $V_f = 1$ L,

$\qquad R = 8.31$ J/mol-K, W = ?

Work done in isothermal process is given by

$$W = 2.303\,\mu RT \log\frac{V_f}{V_i}$$

$$= 2.303 \times 3 \times 8.31 \times 300 \log\frac{1}{4} = -1.037 \times 10^4 \text{ J}$$

WORK DONE IN AN ADIABATIC PROCESS

In an adiabatic process, there is no exchange of heat between system and the surroundings.

By first law, $\qquad \Delta Q = \Delta U + \Delta W \qquad$ ...(i)

For adiabatic process, $\quad \Delta Q = 0$

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

For adiabatic process,

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

where, $\qquad \gamma = \dfrac{C_p}{C_V}$

Thus, if we consider an ideal gas with the adiabatic range from (p_i, V_i) to (p_f, V_f), then

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

In the propagation of sound in air, the compression and rare fraction of air molecules comes under adiabatic process. The air molecules oscillates, so fast that neither the heat comes in nor comes out from the oscillating particles region. That is why oscillation of particles during sound wave propagation comes under adiabatic process.

Note

Relation between p and T; V and T in an adiabatic process
$$p^{1-\gamma} \cdot T^{\gamma} = \text{Constant} \quad \text{and} \quad V^{\gamma-1} \cdot T = \text{Constant}$$

p-V Diagram

On a p-V diagram, the process is represented by an adiabatic curve as shown.

An adiabatic expansion process
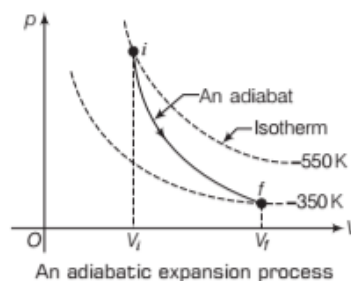
A curve representing an adiabatic process is called an **adiabat**. If we differentiate $pV^{\gamma} = $ constant, we get

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

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

So, slope of adiabatic curve $= -\gamma\left(\dfrac{p}{V}\right)$, which is γ times more than slope of an isotherm.

By definition of specific heat,

$$C = \frac{\Delta Q}{m\,\Delta T} = \frac{Q}{m\,\Delta T}, \Delta Q = 0 \text{ in adiabatic process.}$$

So, $\quad C = 0 \quad$ (adiabatic process)

So, specific heat of a gas in adiabatic compression or expansion is zero.

Work Done

Also, work done in an adiabatic process

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

$\because \qquad pV^\gamma = K \qquad\qquad$ [constant]

$\therefore \qquad p_i V_i^\gamma = p_f V_f^\gamma = K \qquad$ [constant]

where, $\quad pV^\gamma = \text{constant} = K$

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

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

$pV = \mu RT$, $p_i V_i = \mu RT_i$ and $p_f V_f = \mu RT_f$

$$\boxed{\text{Work done, } W = \frac{\mu R(T_i - T_f)}{\gamma-1}}$$

Now, by first law of thermodynamics

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

As, $\qquad \Delta Q = 0 \Rightarrow \Delta U = -\Delta W$

So, if work is done by the system, the internal energy and so the temperature of system falls i.e. $W > 0$, $T_f < T_i$. Conversely, if work is done on the system, the internal energy and so the temperature of system increases. i.e. $W < 0, T_f > T_i$

All nearly practical adiabatic processes occur so rapidly that no transfer of energy as heat occurs between the system and surroundings. e.g. Sudden bursting of bicycle tube and propagation of sound waves in air.

The p-V curves of an ideal gas for two adiabatic processes connecting two isotherms is shown in the figure

p-V curve of an ideal gas
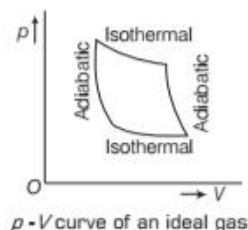
A cylinder containing one gram molecule of the gas was compressed adiabatically until its temperature lose from 27°C to 97°C. Calculate the work done and heat produced in the gas. Take γ as 1.5

Sol. Given, $T_i = 27°C = 27 + 273 = 300\,K$

$\qquad T_f = 97°C = 97 + 273 = 370\,K, \gamma = 1.5$

Work done in adiabatic compression is given by

$$W = \frac{R}{1-\gamma}(T_i - T_f) = \frac{8.31}{1-1.5}(300-370) = 1163.4\,J$$

Heat produced, $H = \dfrac{W}{J} = \dfrac{1163.4}{4.2} = 277$ cal

Work Done in an Isochoric Process

In case of an isochoric process, volume of the system remains constant. So, if heat is added to system, its pressure increases and if heat is extracted from the system, pressure will be reduced.

Equation of State

In this process, p and T changes but $V = $ constant. Gay-Lussac's law is obeyed.

$\Rightarrow \qquad p \propto T \Rightarrow \dfrac{p_1}{T_1} = \dfrac{p_2}{T_2}$

where, $V = $ constant

So, $\qquad \boxed{\text{Work done, } \Delta W = 0}$

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

From first law of thermodynamics, $\Delta Q = \Delta U$

Hence, in an isochoric process, the entire heat given to or taken from the system goes to change its internal energy and temperature of the system.

The change in temperature can be determined by the equation.

$$\boxed{\Delta U = \mu C_V\,\Delta T}$$

WORK DONE IN AN ISOBARIC PROCESS

When a thermodynamic system undergoes a physical change at constant pressure, then this thermodynamic process is known as **isobaric process**.
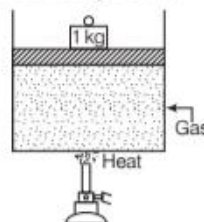
A simple arrangement to show isobaric process

e.g. A gas is heated in a piston cylinder arrangement with constant weight over the cylinder.

Suppose the pressure p of a gas remains constant and its volume changes from V_i to V_f, then the work done by the gas is

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

$$\boxed{\text{Work done}, W = \mu R(T_f - T_i)} \qquad [\because pV = \mu RT]$$

As the temperature of the gas changes, so its internal energy also changes. Hence, in an isobaric process, the absorbed heat goes partly to increase internal energy and partly to do work.

EXAMPLE |10| Raising the Temperature of Ideal Gas

If 70 cal of heat is required to raise the temperature of 2 mol of an ideal gas at constant pressure from 30°C to 35°C, calculate

(i) work done by the gas

(ii) increase in internal energy of gas.
Take R = 2 cal/mol-K.

Sol. (i) In isobaric process, $p = $ constant

and $\Delta W = $ work done $= p\Delta V$

$\qquad = nR(\Delta T) = 2 \times 2 \times (35 - 30) = 20$ cal

(ii) $\Delta U = \Delta Q - \Delta W$ [from first law]

$\qquad = 70 - 20 = 50$ cal

EXAMPLE |11| Isobaric Process

Find the ratio of $\dfrac{\Delta Q}{\Delta U}$ and $\dfrac{\Delta Q}{\Delta W}$ in an isobaric process. The

ratio of molar specific heats, $\dfrac{C_p}{C_V} = \gamma$.

Sol. In an isobaric process, $p = $ constant

$\therefore \qquad C = C_p$

and $\qquad \dfrac{\Delta Q}{\Delta U} = \dfrac{nC_p \Delta T}{nC_V \Delta T} = \dfrac{C_p}{C_V} = \gamma$

also $\qquad \dfrac{\Delta Q}{\Delta W} = \dfrac{\Delta Q}{\Delta Q - \Delta U}$

$\qquad = \dfrac{nC_p \Delta T}{nC_p \Delta T - nC_V \Delta T} = \dfrac{C_p}{C_p - C_V} = \dfrac{\gamma}{\gamma - 1}$

EXAMPLE |12| Ratio of C_p and C_V

3 mol of an ideal gas at 300 K is isothermally expanded to five times its initial volume and heated at this constant volume so that the pressure is raised to its initial value before expansion.

In the whole process, heat supplied to the gas is 83.14 kJ. Calculate ratio C_p / C_V for the gas. [$\log_e 5 = 1.61$ and $R = 8.31$ J mol^{-1} K^{-1}]

Sol. Process is shown in the indicator diagram.
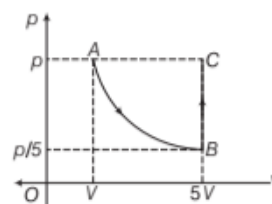
For isothermal process AB,

$\Delta W = \mu RT \log_e (V_f / V_i)$

$\qquad = 3 \times 8.31 \times 300 \times \log_e 5$

$\qquad = 12.03$ kJ

As for isothermal process, $\Delta T = 0$

$\Rightarrow \qquad \Delta U = 0$

and by first law, $\Delta Q = \Delta W = 12.03$ kJ

For isochoric process BC,

$V = $ constant $\Rightarrow \Delta W = 0$

$\Delta U = \mu C_V \Delta T = 3 C_V \Delta T$

Now, for process BC, $\dfrac{p_B}{T_B} = \dfrac{p_C}{T_C}$

$\Rightarrow \qquad \dfrac{P/5}{300} = \dfrac{P}{T_C} \Rightarrow T_C = 1500$ K

$\Rightarrow \qquad \Delta T_{BC} = T_C - T_B = 1500 - 300 = 1200$ K

So, $\Delta U = \mu C_V \Delta T = 3 \times C_V \times 1200 = 3.6\, C_V$ kJ

$\therefore \qquad (\Delta Q)_{\text{isochoric}} = 3.6\, C_V$ kJ

Now, given that $\Delta Q_{\text{process } ABC} = 83.14$ kJ

$\Rightarrow \qquad \Delta Q_{ABC} = \Delta Q_{\text{isothermal}} + \Delta Q_{\text{isochoric}}$

$\Rightarrow \qquad 83.14 = 12.03 + 3.6\, C_V \Rightarrow C_V = 19.75$ J/mol-K

and $\qquad C_p = C_V + R = 19.75 + 8.31$

$\qquad = 28.05$ J/mol -K

$\therefore \qquad \gamma = \dfrac{C_p}{C_V} = \dfrac{28.05}{19.75} = 1.42$

WORK DONE IN A CYCLIC PROCESS

A single process or a series of processes in which, after certain interchanges of heat and work, the system is restored to its initial state known as a **cyclic process**. As both initial and final states are same in a cyclic process, $\Delta U = U_f - U_i = 0$.

Clockwise cyclic process   Anti-clockwise cyclic prociess
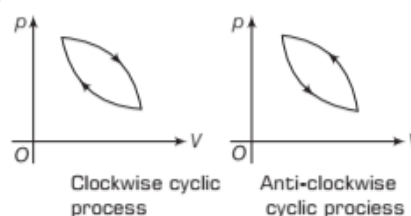
For a cyclic process, p-V graph is a closed curve and area enclosed by the curve is equal to the work done.

From first law of thermodynamics,

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

For cyclic process, $\Delta U = 0$ or $\Delta Q = \Delta W$

So, heat supplied to the system is converted into work done and *vice-versa*.

Let (V_1, p_1) shows the initial state of a gas and (V_2, p_2) shows the final state. The gas reached between A and B by both paths AB and BA.

Calculation of work done in a cyclic process
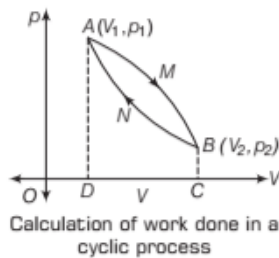
So, work done by the gas for expansion from A to B, is

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

Net work done by the gas in the cyclic process

$$W_{A \to B \to A} = W_1 + W_2$$
$$= \text{area } AMBCDA - \text{area } BNADCB$$
$$= \text{area } AMBNA$$

Hence, the work done in a cyclic process is equal to the area enclosed by the loop.

- If the cycle is clockwise, work done is positive and if the cycle is anti-clockwise, the work done is negative.
- Cyclic processes are of great importance or mechanical machines like engines and refrigerators operates in cycles; in which the system do work by using influx of heat and is restored to its initial state.
- A process in which the system do not return to its initial state after undergoing a series of change is known as non-cyclic process.

Summary of thermodynamic processes

p-V diagram to represent various thermodynamic processes
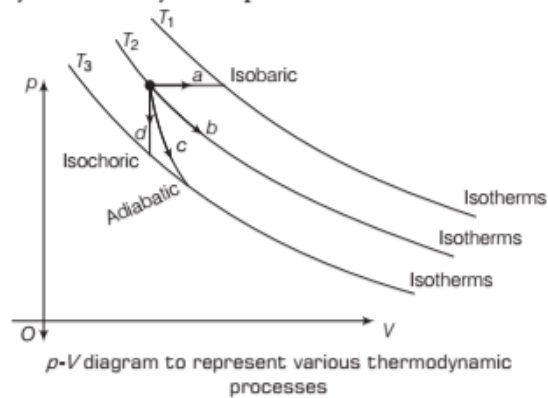
Thermodynamic Processes

Process	Constant Quantity	Path	Heat/Work/Internal energy
Isobaric	p	a	$\Delta Q = nC_p\Delta T$, $\Delta W = p\Delta V$ $\Delta U = nC_v\Delta T$
Isochoric	V	d	$\Delta Q = \Delta U = nC_v\Delta T$ $\Delta W = 0$
Isothermal	T	b	$\Delta Q = \Delta W = nRT\ln V_f/V_i$ $\Delta U = 0$
Adiabatic	pV^γ	c	$\Delta Q = 0$; $\Delta W = -\Delta U$

(iii) If in moving from A to B along a different path where, work done on the system is 400 J, how much heat does it absorb for this path?

Sol. (i) From first law of thermodynamics,

$$\Delta U_{AB} = \Delta Q_{AB} - \Delta W_{AB} = (400 - 100)\text{J} = 300 \text{ J}$$

(ii) As ΔU for a closed path is zero,

$$\Delta U_{AB} + \Delta U_{BA} = 0$$
$$\Delta U_{BA} = -\Delta U_{AB} = -300 \text{ J}$$
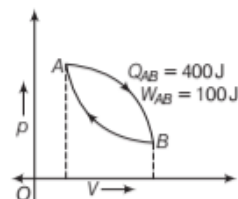
(iii) As ΔU_{AB} is same for any other path, so

$$\Delta U_{AB} = \Delta Q - \Delta W$$
$$300 \text{ J} = \Delta Q - (-400 \text{ J}) \Rightarrow \Delta Q = -100 \text{ J}$$

TOPIC PRACTICE 1

OBJECTIVE Type Questions

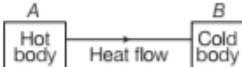**1.** If two systems are in thermal equilibrium with each other, it means their
   (a) masses are equal, temperatures may be unequal
   (b) temperatures are equal
   (c) masses and temperatures are equal
   (d) None of the above

Sol. (b) If two systems are in thermal equilibrium with each other, it means their temperatures must be same. Masses may be equal or unequal.

2. Choose the correct option.
   (a) Zeroth law gives the concept of temperature
   (b) Temperature measures the 'hotness' of the body
   (c) Heat flows from higher temperature to lower temperature until thermal equilibrium is attained
   (d) All of the above

Sol. (d)

   Heat flows from body A to body B because temperature of body A is higher. At thermal equilibrium, $T_A' = T_B'$

   $\left.\begin{array}{l} A \text{ in equilibrium with } C \\ B \text{ in equilibrium with } C \end{array}\right] \Rightarrow A$ in equilibrium with B

   zeroth law.

3. For isothermal expansion of an ideal gas,
   (a) $\Delta U = +$ ve   (b) $\Delta Q = +$ ve
   (c) $\Delta W = +$ ve   (d) Both (b) and (c)

Sol. (d) For isothermal expansion,
   $$\Delta U = 0 \Rightarrow \Delta Q = \Delta W$$
   Here, $\Delta W \rightarrow +$ ve $\Rightarrow \Delta Q \rightarrow +$ ve

4. Heat capacity of a substance depends on
   (a) the mass of the substance
   (b) the temperature of the substance
   (c) Both (a) and (b)
   (d) Neither (a) nor (b)

Sol. (c) S depends on the mass of the substance and its temperature.

   Heat capacity, $S = \dfrac{\text{Heat consumed by given mass}}{\text{Temperature raised}}$

   If given mass is increased, then S increases.

5. A system is provided with 200 cal of heat and the work done by the system on the surroundings is 40 J. Then, its internal energy
   (a) increases by 600 J   (b) decreases by 800 J
   (c) increases by 800 J   (d) decreases by 50 J

Sol. (c) Given, $dQ = +200\,\text{cal} = 200 \times 4.2 = 840\,\text{J}$, $dW = +40\,\text{J}$
   From first law of thermodynamics,
   $$dQ = dU + dW$$
   $$dU = dQ - dW = 840 - 40 = 800\,\text{J}$$
   So, the internal energy of the system increases by 800 J.

6. An ideal gas undergoes cyclic process $ABCDA$ as shown in given p-V diagram. The amount of work done by the gas is   **[NCERT Exemplar]**
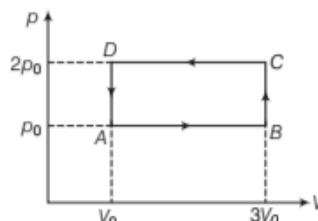
   (a) $6p_0 V_0$ (b) $-2p_0 V_0$ (c) $+2p_0 V_0$ (d) $+4p_0 V_0$

Sol. (b) Consider the p-V diagram given in the question.
   Work done in the process $ABCD$
   $$= \text{area of rectangle } ABCDA$$
   $$= (AB) \times BC = (3V_0 - V_0) \times (2p_0 - p_0)$$
   $$= 2V_0 \times p_0 = 2 p_0 V_0$$
   As the process is going anti-clockwise, hence there is a net compression in the gas. So, work done by the gas $= -2 p_0 V_0$.

VERY SHORT ANSWER Type Questions

7. Can a system be heated and its temperature remain constant?   **[NCERT Exemplar]**

Sol. If the system does work against the surroundings so that it compensates for the heat supplied, the temperature can remains constant.

8. Air pressure in a car tyre increases during driving. Explain.   **[NCERT Exemplar]**

Sol. During driving, temperature of the gas increases while its volume remains constant. So, according to Charles' law, at constant V, $p \propto T$. Therefore, pressure of gas increases.

9. An electric heater supplies heat to a system at a rate of 100 W. If the system performs work at a rate of 75 J/s. At what rate, is the internal energy increasing?   **[NCERT]**

Sol. Heat energy supplied per second by the heater
   $$\Delta Q = 100\,\text{W} = 100\,\text{J/s}$$
   Work done by the system $(\Delta W) = +75\,\text{J/s}$
   Rate of change in internal energy $(\Delta U) = ?$
   According to first law of thermodynamics,
   $$\Delta U = \Delta Q - \Delta W$$
   $$= 100 - 75 = 25\,\text{J/s}$$
   $$= 25\,\text{W}$$

10. If a gas is suddenly compressed, its temperature increases, why?

Sol. Because sudden compression of a gas is an adiabatic process. According to the first law of thermodynamics,

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

$$\because \qquad \Delta Q = 0$$

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

$\because \Delta W =$ negative because work done on the gas

Thus, ΔU increases and gas temperature rises.

11. Find the values of two molar specific heats of nitrogen. Given, $\gamma = 1.41$ and $R = 8.31 \, \text{J mol}^{-1}\text{K}^{-1}$.

Sol. Given, $R = 8.31 \, \text{J mol}^{-1}\text{K}^{-1}$ and $\gamma = 1.41$

We know, $C_V = \dfrac{R}{(\gamma - 1)} = \dfrac{8.31}{(1.41 - 1)} = 20.3 \, \text{Jmol}^{-1}\text{K}^{-1}$

$\because \qquad \dfrac{C_p}{C_V} = \gamma \Rightarrow C_p = C_V \cdot \gamma$

$$= 20.3 \times 1.41 = 28.623 \, \text{J/mol-K}$$

12. Write conditions for an isothermal process.

Sol. The conditions for an isothermal process are

(i) The walls should be diathermic.

(ii) The process should be quasi-static.

13. Why a gas is cooled when it expand?

Sol. When a gas expands, it does work on the surroundings. This work is done on the expense of internal energy and that is why its internal energy and so its temperature decreases.

14. Apply first law of thermodynamics for isothermal expansion of an ideal gas.

Sol. First law of thermodynamics gives, $\Delta Q = \Delta U + \Delta W$

For an isothermal expansion, $\Delta U = 0$.

So, $\qquad\qquad \Delta Q = \Delta W$

For an isothermal expansion of the ideal gas work done by the gas is equal to the heat given to the ideal gas.

15. Two isothermal curves do not intersect each other, why?

Sol. If two isothermal curves intersect, this implies that the pressure and volume of a gas are the same at two different temperatures, that's impossible.

16. When a bottle of cold carbonated drink is opened, a slight fog is formed around the opening, why?

Sol. In opening of bottle, adiabatic expansion of gas causes lowering of temperature.

17. Why air quickly leaking out of a balloon becomes cooler?

Sol. Leaking of air is adiabatic expansion and adiabatic expansion produces cooling.

SHORT ANSWER Type Questions

18. A person of mass 60 kg wants to lose 5 kg by going up and down a 10 m high stairs. Assume he burns twice as much fat while going up than coming down. If 1 kg of fat is burnt on expending 7000 kcal calories, how many times must he go up and down to reduce his weight by 5 kg?

[NCERT Exemplar]

Sol. Here, $m = 60 \, \text{kg}, g = 10 \, \text{m/s}^2, h = 10 \, \text{m}$

In going up and down once, number of kilocalories burnt

$$= (mgh + mgh/2) = \dfrac{3}{2}mgh$$

$$= \dfrac{3}{2} \times \dfrac{60 \times 10 \times 10}{4.2 \times 1000} = \dfrac{15}{7} \, \text{kcal}$$

Total number of kilocalories to be burnt for losing 5 kg of weight $= 5 \times 7000 = 35000 \, \text{kcal}$

$\therefore$ Number of times of the person has to go up and down the stairs $= \dfrac{35000}{15/7} = \dfrac{35 \times 7}{15} \times 10^3 = 16.3 \times 10^3 \, \text{times}$

19. A system goes from P to Q by two different paths in the p-V diagram as shown in figure. Heat given to the system in path 1 is 1000 J. The work done by the system along path 1 is more than path 2 by 100 J. What is the heat exchanged by the system in path 2? [NCERT Exemplar]
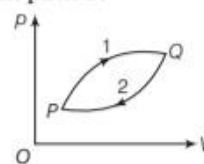
Sol. For path 1, Heat given $Q_1 = +1000 \, \text{J}$

Work done $\qquad\qquad = W_1$ [Let]

For path 2, Work done $W_2 = (W_1 - 100) \, \text{J}$

Heat given $\qquad\qquad Q_2 = ?$

As change in internal energy between two states for different path is same.

$$\Delta U = Q_1 - W_1 = Q_2 - W_2$$

$$1000 - W_1 = Q_2 - (W_1 - 100)$$

$$Q_2 = 1000 - 100 = 900 \, \text{J}$$

20. What amount of heat must be supplied to 2.0×10^{-2} kg of nitrogen (at room temperature) to raise its temperature by 45°C at constant pressure? (Molecular mass of $N_2 = 28$, $R = 8.3 \, \text{J mol}^{-1}\text{K}^{-1}$) [NCERT]

Sol. Here, mass of gas, $m = 2 \times 10^{-2} \, \text{kg} = 20 \, \text{g}$

Rise in temperature, $\Delta T = 45°C$

Heat required, $\Delta Q = ?$

Molecular mass, $M = 28$

Number of moles, $n = \dfrac{m}{M} = \dfrac{20}{28} = 0.714$

As nitrogen is a diatomic gas, molar specific heat at constant pressure is

$$C_p = \dfrac{7}{2}R = \dfrac{7}{2} \times 8.3 \, \text{J mol}^{-1}\text{K}^{-1}$$

As $\quad \Delta Q = nC_p \Delta T$

$\therefore \quad \Delta Q = 0.714 \times \dfrac{7}{2} \times 8.3 \times 45 \, \text{J} = 933.4 \, \text{J}$

21. A geyser heats water flowing at the rate of 3.0 L/min from 27°C to 77°C. If the geyser operates on a gas burner, what is the rate of consumption of the fuel if its heat of combustion is 4.0×10^4 J/g?. **[NCERT]**

Sol. Here, volume of water heated = 3.0 L/min

Mass of water heated, $m = 3000$ g/min

Rise in temperature, $\Delta T = 77 - 27 = 50°\text{C}$

Specific heat of water, $C = 4.2 \, \text{J g}^{-1}\,°\text{C}^{-1}$

Amount of heat used, $\Delta Q = mC\Delta T = 3000 \times 4.2 \times 50$

$\qquad\qquad = 63 \times 10^4 \, \text{J/min}$

Heat of combustion = 4×10^4 J/g

Rate of combustion of fuel = $\dfrac{63 \times 10^4}{4 \times 10^4}$

$\qquad\qquad = 15.75 \, \text{g/min}$

22. Two bodies at different temperatures T_1 and T_2 are brought in contact. Under what condition, they settle to mean temperature? (after they attain equilibrium) **[NCERT Exemplar]**
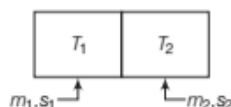
Sol. Let m_1 and m_2 are masses of bodies with specific heats s_1 and s_2, then if their temperature after they are in thermal equilibrium is T.

Then, if $T_1 > T > T_2$ and assuming no heat loss.

Heat lost by hot body = heat gained by cold body

$$m_1 s_1 (T_1 - T) = m_2 s_2 (T - T_2)$$

$\Rightarrow \quad \dfrac{m_1 s_1 T_1 + m_2 s_2 T_2}{m_1 s_1 + m_2 s_2} = T$ [equilibrium temperature]

So for, bodies to settle down to mean temperature,

$$m_1 = m_2 \quad \text{and} \quad s_1 = s_2$$

means bodies have same specific heat and have equal masses.

Then, $\quad T = \dfrac{T_1 + T_2}{2}$ [mean temperature]

23. A cylinder with a movable piston contains 3 moles of hydrogen at standard temperature and pressure. The walls of the cylinder are made of a heat insulator and the piston is insulated by having a pile of sand on it. By what factor, does the pressure of the gas increase if the gas is compressed to half its original volume? **[NCERT]**

Sol. As no heat is allowed to be exchanged, the process is adiabatic.

$\therefore \quad p_2 V_2^\gamma = p_1 V_1^\gamma \quad \text{or} \quad \dfrac{p_2}{p_1} = \left(\dfrac{V_1}{V_2}\right)^\gamma$

As $\quad V_2 = \dfrac{1}{2}V_1$ or $\dfrac{p_2}{p_1} = \left(\dfrac{V_1}{1/2\,V_1}\right)^{1.4} = 2^{1.4} = 2.64$

24. The initial state of a certain gas is (p_i, V_i, T_i). It undergoes expansion till its volume becomes V_f. Consider the following two cases

(i) The expansion takes place at constant temperature.

(ii) The expansion takes place at constant pressure.

Plot the p-V diagram for each case. In which of the two cases, is the work done by the gas more? **[NCERT Exemplar]**

Sol.
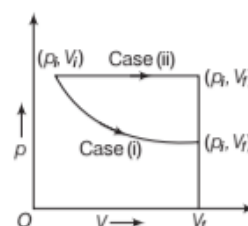
The p-V diagram for each case is shown in the figure.

In case (i) $p_i V_i = p_f V_f$, therefore process is isothermal.

In case (ii), pressure is constant, work done = area under the p-V curve, so work done is more when the gas expands at constant pressure.

25. When ice melts, then change in internal energy is greater than the heat supplied, why?

Sol. When ice melts, volume of water formed is less than that of ice. So, surroundings (environment) does work on the system (ice). And by first law,

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

$\Rightarrow \qquad \Delta U = \Delta Q - \Delta W$

(ΔW = negative as work is done on the system)

$\Rightarrow \qquad \Delta U > \Delta Q$

LONG ANSWER Type I Questions

26. Explain, why?

(i) 500 J of work is done on a gas to reduce its volume by compression adiabatically. What is the change in internal energy of the gas?

(ii) The coolant in a chemical or a nuclear plant , i.e. the liquid used to prevent the different parts of a plant from getting too hot should have high specific heat.

(iii) The climate of a harbour town is more temperate than that of a town in a desert at the same latitude. **[NCERT]**

Sol. **(i)** $\because$ process is adiabatic

$\therefore \qquad \Delta Q = 0$

Work done on the gas, $\Delta W = -500\text{J}$

According to the first law of thermodynamics.

$\Delta Q = \Delta U + \Delta W \Rightarrow \Delta U = -\Delta W = 500\text{J}$

(ii) This is because heat absorbed by a substance (coolant) is directly proportional to the specific heat of the substance.

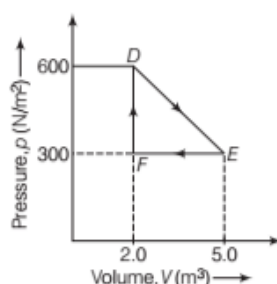**(iii)** This is because in a harbour town, the relative humidity is more than in a desert town. Hence, the climate of a harbour town is without extremes of hot and cold.

27. A thermodynamic system is taken from an original state D to an intermediate state E by the linear process shown in figure.

Its volume is then reduced to the original value from E to F by an isobaric process. Calculate the total work done by the gas from D to E to F. **[NCERT]**

Sol. From figure, change in pressure,

$$dp = DF = 600 - 300 = 300\ \text{Nm}^{-2}$$

Change in volume, $dV = EF = 5 - 2 = 3\ \text{m}^3$

Work done by the gas from D to E to F = area of ΔDEF

$$W = \frac{1}{2} \times EF \times DF = \frac{1}{2} \times 300 \times 3 = 450\text{J}$$

28. In changing the state of a gas adiabatically from an equilibrium state A to another equilibrium state B, an amount of work equal to 22.3 J is done on the system. If the gas is taken from state A to B via a process in which the net heat absorbed by the system is 9.35 cal, how much is the net work done by the system in the latter case? (Take, 1 cal = 4.19 J). **[NCERT]**

💡 According to first law of thermodynamics, if ΔQ heat energy is given (or taken) to a thermodynamic system which is partially utilised in doing work (ΔW) and remaining part increases (or decreases) the internal energy of the system.

Sol. Given, work done $(W) = -22.3\text{ J}$

Work done is taken negative as work is done on the system.

In an adiabatic change, $\Delta Q = 0$

Using first law of thermodynamics,

$$\Delta U = \Delta Q - W = 0 - (-22.3) = 22.3\text{ J}$$

For another process between states A and B,

Heat absorbed $(\Delta Q) = +9.35$ cal

$$= +(9.35 \times 4.19)\text{ J} = +39.18\text{ J}$$

Change in internal energy between two states *via* different paths are equal.

$\therefore \qquad \Delta U = 22.3\text{ J}$

$\therefore$ From first law of thermodynamics,

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

or $\qquad W = \Delta Q - \Delta U$

$$= 39.18 - 22.3 = 16.88\text{ J} = 16.9\text{ J}$$

29. A cycle followed by an engine (made of one mole of an ideal gas in a cylinder with a piston) is shown in figure. Find heat exchanged by the engine with the surroundings for each section of the cycle. $[C_V = (3/2)R]$
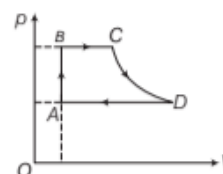
(i) AB : constant volume

(ii) BC : constant pressure

(iii) CD : adiabatic

(iv) DA : constant pressure **[NCERT Exemplar]**

Sol. **(i)** In figure, portion AB of the cycle involved increases in pressure/temperature of gas at constant volume. Therefore, the system gains heat from the surroundings.

$Q_{AB} = U_{AB}$ \hfill $[\because W = 0]$

$$= \frac{3}{2}R(T_B - T_A) = \frac{3}{2}(p_B V_B - p_A V_A)\ [\because \Delta U = nC_V \Delta T]$$

$$= \frac{3}{2}(p_B - p_A)V_A \hfill [\because V_B = V_A]$$

(ii) In the portion BC, the gas increases in volume at constant pressure. Heat required for this is gained from surroundings.

$$Q_{BC} = U_{BC} + W_{BC} = \frac{3}{2}(p_C V_C - p_B V_B) + p_B(V_C - V_B)$$

$$= \frac{5}{2}p_B(V_C - V_B) \hfill [\because p_C = p_B]$$

$$Q_{BC} = \frac{5}{2}p_B(V_C - V_A)$$

(iii) As CD represents an adiabatic change, therefore,

$$Q_{CD} = 0.$$

(iv) DA involves compression of gas from V_D to V_A at constant pressure p_A. Work is done on the gas (negative).

$$\Delta Q_{DA} = \Delta U_{DA} + \Delta W_{DA}$$
$$= \frac{3}{2}R(T_A - T_D) + p_A(V_A - V_D)$$
$$= \frac{3}{2}p_A(V_A - V_D) + p_A(p_A - V_D)$$
$$= \frac{5}{2}p_A(V_A - V_D)$$

30. Calculate the work done for adiabatic expansion of a gas.

Sol. Consider (say μ mole) an ideal gas, which is undergoing an adiabatic expansion. Let the gas expands by an infinitesimally small volume dV, at pressure p, then the infinitesimally small work done given by $dW = pdV$

The net work done from an initial volume V_1 to final volume V_2 is given by

$$W = \int_{V_1}^{V_2} pdV$$

For an adiabatic process, $pV^\gamma = \text{constant} = K$

$$p = \frac{K}{V^\gamma} = KV^{-\gamma}$$

$$\therefore \quad W = \int_{V_1}^{V_2} (KV^{-\gamma})dV = K\left[\frac{V^{-\gamma+1}}{-\gamma+1}\right]_{V_1}^{V_2}$$

$$= \frac{KV_2^{-\gamma+1} - KV_1^{-\gamma+1}}{(1-\gamma)}$$

For an adiabatic process,
$$K = p_1 V_1^\gamma = p_2 V_2^\gamma$$

$$\Rightarrow \quad W = \frac{p_2 V_2^\gamma \cdot V_2^{-\gamma+1} - p_1 V_1^\gamma \cdot V_1^{-\gamma+1}}{(1-\gamma)}$$

$$= \frac{1}{(1-\gamma)}(p_2 V_2 - p_1 V_1)$$

For an ideal gas, $p_1 V_1 = \mu RT_1$ and $p_2 V_2 = \mu RT_2$. So, we have

$$W = \frac{1}{(1-\gamma)}[\mu RT_2 - \mu RT_1] = \frac{\mu R}{(\gamma-1)}[T_1 - T_2]$$

31. Consider one mole of perfect gas in a cylinder of unit cross-section with a piston attached (figure). A spring (spring constant k) is attached (unstretched length L) to the piston and to the bottom of the cylinder. Initially, the spring is unstretched and the gas is in equilibrium.
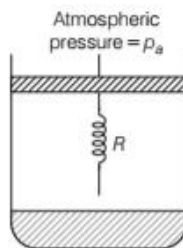
A certain amount of heat Q is supplied to the gas causing an increase of volume from V_0 to V_1.

(i) What is the initial pressure of the system?

(ii) What is the final pressure of the system?

(iii) Using the first law of thermodynamics, write down a relation between Q, p_a, V, V_0 and k.

Sol. (i) $p_i = p_a$

(ii) $p_f = p_a + \frac{k}{A}(V - V_0)$

(iii) According to first law of thermodynamics,
$$\Delta Q = \Delta U + \Delta W \text{ where,}$$

$$\Delta U = C_V(T - T_0), \Delta W = p_a(V - V_0) + \frac{1}{2}k(V - V_0)^2$$

$$\Delta Q = p_a(V - V_0) + \frac{1}{2}k(V - V_0)^2 + C_V(T - T_0)$$

where, $T_0 = p_a V_0 / R$,

$$\Rightarrow \quad T = [p_a + (K/A) \times (V - V_0)]V/R$$

32. Consider a p-V diagram in which the path followed by one mole of perfect gas in a cylindrical container is shown.
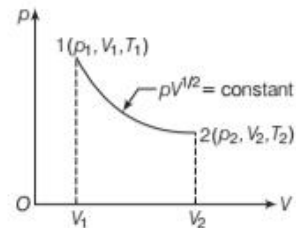
(i) Find the work done when the gas is taken from state 1 to state 2.

(ii) What is the ratio of temperatures T_1/T_2, if $V_2 = 2V_1$?

(iii) Given the internal energy for one mole of gas at temperature T is $(3/2)RT$, find the heat supplied to the gas when it is taken from states 1 to 2, with $V_2 = 2V_1$. **[NCERT Exemplar]**

Sol. (i) Work done by the gas (let $pV^{1/2} = A$),

$$\Delta W = \int_{V_1}^{V_2} pdV = A\int_{V_1}^{V_2} \frac{dV}{\sqrt{V}} = A\left[\frac{\sqrt{V}}{1/2}\right]_{V_1}^{V_2}$$

$$= 2A(\sqrt{V_2} - \sqrt{V_1})$$

$$= 2p_1 V_1^{1/2}[V_2^{1/2} - V_1^{1/2}]$$

(ii) Since, $T = pV/nR = \frac{A}{nR} \cdot \sqrt{V}$

Thus, $\frac{T_2}{T_1} = \sqrt{\frac{V_2}{V_1}} = \sqrt{2}$

(iii) Then, the change in internal energy,

$$\Delta U = U_2 - U_1 = \frac{3}{2}R(T_2 - T_1) = \frac{3}{2}RT_1(\sqrt{2} - 1)$$

$$\Delta W = 2A\sqrt{V_1}(\sqrt{2} - 1) = 2RT_1(\sqrt{2} - 1)$$

According to first law of thermodynamics,
$$\Delta Q = \Delta U + \Delta W \Rightarrow \Delta Q = (7/2)RT_1(\sqrt{2} - 1)$$
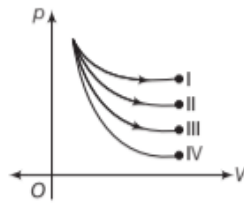
LONG ANSWER Type II Questions

33. In the given p-V diagrams, **[NCERT Exemplar]** Find which curve represents
  (i) isothermal process,
  (ii) adiabatic process for
    (a) monoatomic
    (b) diatomic
    (c) triatomic gas.

Sol. For isothermal process, pV = constant

For adiabatic process, pV^{γ} = constant

$$\gamma = \frac{5}{3} \text{ for monoatomic gas} = 1.66$$

$$\gamma = \frac{7}{5} = 1.4 \text{ for diatomic gas}$$

$$\gamma = \frac{8}{6} = 1.33 \text{ for triatomic gas}$$

and slope increases with γ so,
For Ist, $\gamma = 1$, an isotherm
For IInd, $\gamma = 1.33$
For IIIrd, $\gamma = 1.4$
For IVth, $\gamma = 1.66$
So, graph I is isothermal,
Graph II is triatomic adiabatic,
Graph III is diatomic adiabatic,
Graph IV is monoatomic adiabatic.

34. Consider that an ideal gas (n moles) is expanding in a process given by $p = f(V)$, which passes through a point (V_0, p_0). Show that the gas is absorbing heat at (p_0, V_0), if the slope of the curve $p = f(V)$ is larger than the slope of the adiabat passing through (p_0, V_0).

Sol. Slope of $p = f(V)$, curve at $(V_0, p_0) = f(V_0)$

Slope of adiabat at (V_0, p_0)

$$= K(-\gamma) V_0^{-1-\gamma} = -\gamma p_0/V_0$$

Now, heat absorbed in the process $p = f(V)$

$$dQ = dU + dW = nC_V dT + pdV$$

Since, $T = (1/nR) pV = (1/nR) V f(V)$

$$\therefore \quad dT = (1/nR)[f(V) + V f'(V)] dV$$

Thus, $\left.\dfrac{dQ}{dV}\right|_{V=V_0} = \dfrac{C_V}{R}[f(V_0) + V_0 f'(V_0)] + f(V_0)$

$$= \left[\frac{1}{\gamma-1} + 1\right] f(V_0) + \frac{V_0 f'(V_0)}{\gamma-1}$$

$$= \frac{\gamma}{\gamma-1} p_0 + \frac{V_0}{\gamma-1} f'(V_0)$$

Heat is absorbed when $dQ/dV > 0$ when gas expands, that is when $\gamma p_0 + V_0 f'(V_0) > 0$

$$f'(V_0) > -\gamma p_0/V_0$$

35. A cycle followed by a machine (made of one mole of perfect gas in a cylinder with a piston) is shown in figure
A to B : volume constant
B to C : adiabatic
C to D : volume constant
D to A : adiabatic
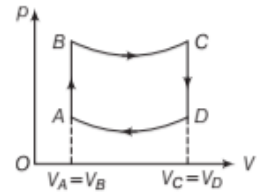
$$V_C = V_D = 2V_A = 2V_B$$

  (i) In which part of the cycle, heat is supplied to the machine from outside?
  (ii) In which part of the cycle, heat is being given to the surrounding by the machine?
  (iii) What is the work done by the machine in one cycle? Write your answer in term of p_A, p_B, V_A.
  (iv) What is the efficiency of the machine?

Take, $\gamma = \dfrac{5}{3}$ for the gas and

$$C_V = \frac{3}{2} R \text{ for one mole}$$

[NCERT Exemplar]

Sol. (i) A to B because $T_B > T_A$, as $p \propto T$ [$\because V$ constant]
(ii) C to D because $T_C > T_D$, as $p \propto T$ [$\because V$ constant]
(iii) $W_{AB} = \int_A^B pdV = 0$ and $W_{CD} = 0$ [$\because V$ constant]

Similarly, $W_{BC} = \int_B^C pdV = K\int_B^C \dfrac{dV}{V^{\gamma}} = K\left[\dfrac{V^{-\gamma+1}}{-\gamma+1}\right]_{V_B}^{V_C}$

[$\because pV^r = K$]

$$= \frac{1}{1-\gamma}(p_C V_C - p_B V_B)$$

Similarly, $W_{DA} = \dfrac{1}{1-\gamma}(p_A V_A - p_D V_D)$

Now, $p_C = p_B\left(\dfrac{V_B}{V_C}\right)^{\gamma} = 2^{-\gamma} p_B$ [$\because V_C = 2V_B$]

Similarly, $p_D = p_A 2^{-\gamma}$

Total work done $= W_{BC} + W_{DA}$

$$= \frac{1}{1-\gamma}[p_B V_B(2^{-\gamma+1}-1) - p_A V_A(2^{-\gamma+1}-1)]$$

$$= \frac{1}{1-\gamma}(2^{1-\gamma}-1)(p_B - p_A)V_A \quad [\because V_A = V_B]$$

$$= \frac{3}{2}\left[1 - \left(\frac{1}{2}\right)^{2/3}\right](p_B - p_A)V_A$$

(iv) Heat supplied during process A to B

$$dQ_{AB} = dU_{AB}$$

$$Q_{AB} = \frac{3}{2} nR(T_B - T_A) = \frac{3}{2}(p_B - p_A) V_A$$

$$\text{Efficiency} = \frac{\text{Net work done}}{\text{Heat supplied}} = \left[1 - \left(\frac{1}{2}\right)^{2/3}\right]$$

36. What is a cyclic process? What is change in internal energy of the system in a cyclic process? In changing the state of a gas adiabatically from an equilibrium states A to B, an amount of 40.5 J of work is done on the system. If the gas is taken from states A to B via a process in which net heat absorbed by the system is 12.6 cal. How much is the net work done by the system in the later case? (1 cal = 4.19 J) **[NCERT]**

Sol. A cyclic process restores the system back to its initial state after completion of the cycle.
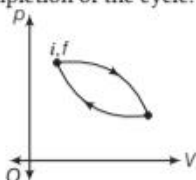
As internal energy is a state function, so its value at initial point is same as that at final point (initial state is same as that of final state).
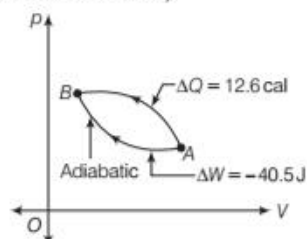
For adiabatic process $A \rightarrow B$,
$\Delta Q = 0$, so by first law of thermodynamics,

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

or $\qquad \Delta U = -\Delta W = -(-40.5) = 40.5$ J

For another process, $A \rightarrow B$,

$$\Delta Q = +12.6 \text{ cal}$$
$$= 12.6 \times 4.19 \text{ J} = 52.8 \text{ J}$$

and by first law of thermodynamics,

$$\Delta Q = \Delta W + \Delta U$$
$$\Rightarrow \qquad \Delta W = \Delta Q - \Delta U$$
$$\Rightarrow \qquad \Delta W = 52.8 - 40.5 = 12.3 \text{ J}$$

[as ΔU is a state function, ΔU_{AB} is same for this process also]

ASSESS YOUR TOPICAL UNDERSTANDING

OBJECTIVE Type Questions

1. If a system is in thermodynamic equilibrium with its surroundings, it means
   (a) temperature of system and surroundings must be same
   (b) pressure, volume and temperature of system and surroundings must be same
   (c) pressure, volume and temperature of system and surroundings may be different
   (d) None of the above

2. According to Zeroth law, which physical quantity must have same value for the two systems to be in thermal equilibrium?
   (a) Pressure
   (b) Temperature
   (c) Volume
   (d) Composition

3. Specific heat capacity depends on
   (a) nature of the substance
   (b) on its mass
   (c) on its temperature
   (d) Both (a) and (c)

4. An ideal gas having molar specific heat capacity at constant volume is $\frac{3}{2}R$, the molar specific heat capacities at constant pressure is
   (a) $\frac{1}{2}R$
   (b) $\frac{5}{2}R$
   (c) $\frac{7}{2}R$
   (d) $\frac{9}{2}R$

5. If 150 J of heat is added to a system and the work done by the system is 110 J, then change in internal energy will be
   (a) 40 J
   (b) 110 J
   (c) 150 J
   (d) 260 J

6. An ideal gas undergoes four different processes from the same initial state (figure). Four processes are adiabatic, isothermal, isobaric and isochoric. Out of 1, 2, 3 and 4 which one is adiabatic?

[NCERT Exemplar]
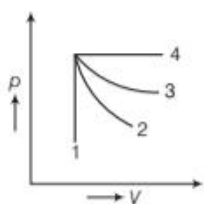
(a) 4   (b) 3
(c) 2   (d) 1

Answers

1. (a)	2. (b)	3. (d)	4. (b)	5. (a)
6. (c)				

VERY SHORT ANSWER Type Questions

7. What is meant by free expansion?

8. State why a gas can only expand at constant temperature, if a certain quantity of heat is supplied to it.

9. Is it possible to convert internal energy into work?

SHORT ANSWER Type Questions

10. Generally, a gas has two specific heat capacities, why? and which one is greater, explain it?

11. State the process in which air pressure in a car tyre increases during driving. Explain why?

12. Two samples of a gas initially at the same temperature and pressure are compressed from a volume V to a volume $V/2$. One sample is compressed isothermally and the other adiabatically. In which sample is the pressure greater? Justify.

LONG ANSWER Type I Questions

13. Explain the limitations of the first law of thermodynamics.

14. (i) Why does a gas have two molar specific heats?
(ii) Which one is greater and why?
(iii) What is the difference between the two molar specific heats and what is their ratio?

15. A monoatomic ideal gas $\left(\gamma = \dfrac{5}{3}\right)$ initially at 17°C is suddenly compressed to one-eight of its original volume.
Find the final temperature after compression.   **[Ans. 887°C]**

LONG ANSWER Type II Questions

16. Two containers P and Q of equal volume are connected to each other with a stopcock. The temperature and pressure in P is standard and in evacuated with no gas in it. Both the containers are thermally insulated. The stopcock is suddenly opened. Answer the following questions.
(i) What are the final pressures of the gases P and Q?
(ii) What is the change in internal energy of the gas in P?

17. A gas is expanded twice in a way so that the volume becomes twice the initial value. In first case, gas is expanded isothermally while in second case gas is expanded adiabatically.

(i) In which case, is the pressure is greater and why?
(ii) Which work done is more and why?

18. Figure shows a process PQR performed on an ideal gas. Find the net heat given to the system during the process.
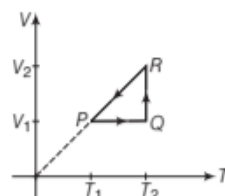
$$\text{Ans. } nR\left[T_2 \ln \frac{V_2}{V_1} - (T_2 - T_1)\right]$$

|TOPIC 2|
Second Law of Thermodynamics

SECOND LAW OF THERMODYNAMICS

There are many processes which are based on energy conservation but not possible in nature.

e.g. A ball lying on a floor could jump upto some height by itself gaining some heat energy from the ground. This process is possible according to first law (energy conservation) but not actually possible in nature.

It means that some additional basic principle of nature forbids the above process, even though it satisfy the energy conservation. The principle that put a restriction on the first law of thermodynamics is known as the **second law of thermodynamics.**

The second law of thermodynamics gives a fundamental limitation to the efficiency of a heat engine and the coefficient of performance of a refrigerator. Two statements of Kelvin-Planck and Clausius put restrictions on the possibility of perfect heat engine and perfect refrigerator, respectively.

KELVIN-PLANCK'S STATEMENT

No process is possible whose sole result is the absorption of heat from a reservoir and the complete conversion of the heat into work.

CLAUSIUS STATEMENT

No process is possible whose sole result is the transfer of heat from a colder object to a hotter object.

PMM1 AND PMM2

Any device that violates the first law of thermodynamics (by creating energy) is called a perpetual motion machine of the first kind (PMM1) and the device that violates the second law is called a perpetual motion machine of the second kind (PMM2).

EXAMPLE |1| Conversion of Heat into Work
Is it possible to convert all the heat extracted from a hot body into work?

Sol. No, heat cannot be converted into work completely because a part of heat is rejected and remaining part is converted into work.

REVERSIBLE AND IRREVERSIBLE PROCESS

Reversible Process

A process which could be reserved in such a way that the system and its surrounding returns exactly to their initial states with no other changes in the universe is known as **reversible process.**

e.g. If heat is absorbed in the direct process, then same amount of heat should be given out in the reverse process. If work is done on the working substance in the direct process, then the same amount of work should be done by the working substance in the reverse process.

The conditions for reversibility are

(i) There must be complete absence of dissipative forces such as friction, viscosity, electric resistance etc.

(ii) The direct and reverse processes must take place infinitely slowly.

(iii) The temperature of the system must not differ appreciably from its surroundings.

Some examples of reversible process are

(i) All isothermal and adiabatic changes are reversible if they are performed very slowly.

(ii) When a certain amount of heat is absorbed by ice, it melts. If the same amount of heat is removed from it, the water formed in the direct process will be converted into ice.

(iii) An extremely slow extension or contraction of a spring without setting up oscillations.

(iv) When a perfectly elastic ball falls from some height on a perfectly elastic horizontal plane, the ball rises to the initial height.

(v) Very slow evaporation or condensation.

It should be remembered that the conditions mentioned for a reversible process can never be realised in practice. Hence, a reversible process is only an ideal concept. In actual process, there is always loss of heat due to friction, conduction radiation, etc.

Ideal Engine is Practically not Possible

Reversibility is the rule of nature. It means that a change happened in the universe cannot be exactly reversed. That is why, any engine cannot have 100% efficiency. If we could eliminate all the resistive forces, the efficiency of an engine could be maximised.

For future, some trains are proposed that will move in a vacuum tunnel to eliminate the air friction and hence to increase the efficiency of the engine.

Irreversible Process

Any process which is not reversible exactly is an **irreversible process**. All natural processes such as conduction, radiation, radioactive decay etc., are irreversible processes. All practical processes such as free expansion, Joule-Thomson expansion, electrical heating of a wire are also irreversible.

Irreversibility arises mainly from two causes

(i) Many processes (like diffusion of gases, decay of organic matter) take the system to non-equilibrium states.

(ii) Many processes involve the dissipative forces like friction, viscosity, inelasticity, etc.

Some examples of irreversible processes are given below

(i) When a steel ball is allowed to fall on an inelastic lead sheet, its kinetic energy changes into heat energy by friction. The heat energy raises the temperature of lead sheet. No reverse transformation of heat energy occurs.

(ii) The sudden and fast stretching of a spring may produce vibrations in it. Now, a part of the energy is dissipated. This is the case of irreversible process.

(iii) Sudden expansion or contraction and rapid evaporation or condensation are examples of irreversible processes.

(iv) The passage of an electric current through a resistor is irreversible.

(v) Heat transfer between bodies at different temperatures is also irreversible.

(vi) Joule-Thomson effect is irreversible because on reversing the flow of gas, a similar cooling or heating effect is not observed.

CARNOT ENGINE

Carnot engine is an ideal heat engine proposed by **Sadi Carnot** in 1824. The reversible engine which operates between two temperatures of source (T_1) and sink (T_2) is known as **Carnot heat engine**.

The designed engine is a theoretical engine which is free from all the defects of a practical engine. This engine cannot be realised in actual practice, however, this can be taken as a standard against which the performance of an actual engine can be judged.
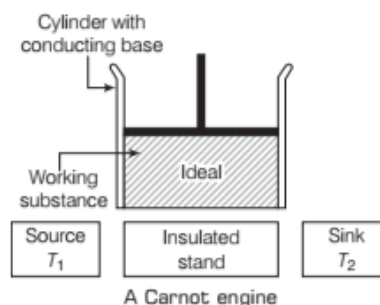
A Carnot engine

The main parts of Carnot engine are as follows

Cylinder

The cylinder has conducting base and insulating walls. It consists an ideal gas as a working substance insulating and frictionless piston is attached with it as shown in the figure.

Source

It is a hot reservoir at a temperature T_1 with conducting walls. It has infinite thermal capacity. Any amount of heat can be taken from it without changing the temperature.

Sink

It is a cold reservoir at temperature T_2. It has infinite thermal capacity so any amount of heat can be rejected to it without changing the temperature.

Working Substance

We use an ideal gas as a working substance in the cylinder.

Insulating Stand

The base of the cylinder could be placed on the insulating stand, to isolate it completely from the surroundings.

Carnot Cycle

As the engine works, the working substance of the engine undergoes a cycle known as **Carnot cycle**.

The Carnot cycle consists of the following four strokes

First Stroke (Isothermal Expansion)(Curve AB)

The cylinder containing one mole of an ideal gas as working substance allowed to expand slowly at the constant temperature T_1 by putting it on the source.

Various processes in Carnot cycle

Work done = heat absorbed by the system

$$W_1 = Q_1 = \int_{V_1}^{V_2} p\, dV$$

$$= RT_1 \log_e\left(\frac{V_2}{V_1}\right) = \text{area of } ABGEA$$

Second Stroke (Adiabatic Expansion) (Curve BC)

The cylinder is then placed on the non-conducting stand and the gas is allowed to expand adiabatically till the temperature falls from T_1 to T_2.

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

Third Stroke (Isothermal Compression) (Curve CD)

The cylinder is placed on the sink and the gas is compressed at constant temperature T_2.

Work done = heat released by the system

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

$$= RT_2 \log_e \frac{V_3}{V_4} = \text{area } CDFH$$

Fourth Stroke (Adiabatic Compression) (Curve DA)

Finally, the cylinder is again placed on non-conducting stand and the compression is continued so that gas returns to its initial stage.

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

$$= \frac{R}{\gamma - 1}(T_1 - T_2) = \text{area of } ADFEA$$

Efficiency of Carnot Cycle (Engine)

The efficiency of engine is defined as the ratio of work done to the heat supplied, i.e.

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

Net work done during the complete cycle

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

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

or

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

Since, points B and C lie on same adiabatic curve

$$\therefore \quad T_1 V_2^{\gamma - 1} = T_2 V_3^{\gamma - 1}$$

or

$$\frac{T_1}{T_2} = \left(\frac{V_3}{V_2}\right)^{\gamma - 1} \qquad \ldots(i)$$

Also, points D and A lie on the same adiabatic curve

$$\therefore \quad T_1 V_1^{\gamma - 1} = T_2 V_4^{\gamma - 1}$$

or

$$\frac{T_1}{T_2} = \left(\frac{V_4}{V_1}\right)^{\gamma - 1} \qquad \ldots(ii)$$

From Eqs. (i) and (ii), we get

$$\frac{V_3}{V_2} = \frac{V_4}{V_1}$$

or

$$\frac{V_3}{V_4} = \frac{V_2}{V_1}$$

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

So,

$$\boxed{\text{Efficiency of Carnot engine, } \eta = 1 - \frac{T_2}{T_1}}$$

- The efficiency of the Carnot engine depends only on the temperatures of source and sink.
- The efficiency of Carnot engine does not depend on the nature of the working substance.
- The efficiency of Carnot engine will be 100%, if the temperature of the sink is 0 K. As practically, we cannot attain a sink at 0 K, so it is not possible to have 100% efficiency.

Carnot Theorems

According to Carnot theorem,

(i) A heat engine working between the two given temperatures T_1 of hot reservoir i.e. source and T_2 of cold reservoir i.e. sink cannot have efficiency more than that of the Carnot engine.

(ii) The efficiency of the Carnot engine is independent of the nature of working susbtance.

We can prove the part (ii) of Carnot theorem as below.

Suppose a reversible Carnot engine R and an irreversible heat engine I, working between the same source T_1 and same sink T_2 as shown in figure.

Reversible and irreversible heat engine act together

Suppose the two engines are coupled in such a way that irreversible engine I acts like a heat engine and reversible Carnot engine R acts like a refrigerator. In one complete cycle, the engine I absorbs heat Q_1 from the source, deliver work W' and release the balance $(Q_1 - W')$ to the sink. The engine R returns the same heat Q_1 to the source when work W is done on it in one full cycle. Therefore, it would take heat $(Q_1 - W)$ from the sink as shown in figure.

Let us assume that the efficiency of reversible engine R is less than that of I, i.e. $\eta_R < \eta_I$.

For Q_1, $W < W'$ and $(Q_1 - W) > (Q_1 - W')$

Thus, the coupled I-R system on whole extracts heat $(Q_1 - W) - (Q_1 - W') = (W' - W)$ from the sink and delivers the same amount of work $(W' - W)$ in one cycle without any change in the source. So, it is against the second law of thermodynamics.

Hence, the assertion $\eta_I > \eta_R$ is wrong. No engine can have efficiency greater than that of the Carnot engine. Thus, this proves the first part of Carnot theorem.

Coefficient of Performance of Carnot Engine

For Carnot refrigerator, $\dfrac{Q_1}{Q_2} = \dfrac{T_1}{T_2}$

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

So, $\boxed{\text{Coefficient of performance, } \beta = \dfrac{T_2}{T_1 - T_2}}$

where, T_1 = temperature of surrounding,
T_2 = temperature of cold body.

It is clear that $\beta = 0$ when $T_2 = 0$, i.e. the coefficient of performance will be zero, if the cold body is at the temperature equal to absolute zero.

EXAMPLE |2| Carnot Cycle

Consider a Carnot cycle operating between $T_1 = 500$ K and $T_2 = 300$ K producing 1 kJ of mechanical work per cycle. Find the heat transferred to/by the engine by/to the reservoir. **[NCERT Exemplar]**

Sol. Here, $T_1 = 500$ K, $T_2 = 300$ K, $W = 1$ kJ = 1000 J

As, efficiency, $\eta = \dfrac{W}{Q} = \dfrac{T_1 - T_2}{T_1}$

So, heat transferred to engine by the hot reservoir in cycle

$Q_1 = \dfrac{W T_1}{T_1 - T_2} = \dfrac{1000 \times 500}{500 - 300} = 2500$ J or 2.5 kJ

and heat transferred by the engine to the cold reservoir in one cycle

$Q_2 = Q_1 - W = 2.5$ kJ $- 1$ kJ $= 1.5$ kJ

EXAMPLE |3| Power Consumed in Carnot Cycle

A refrigerator has to transfer an average of 263 J of heat per second from temperature $-10°$ C to $25°$ C. Calculate the average power consumed, assuming no energy losses in the process.

Sol. Given, $Q_2 = 263$ J/s, $T_2 = -10°$ C $= -10 + 273 = 263$ K

and $T_1 = 25°$ C $= 25 + 273 = 298$ K,

$\beta = \dfrac{Q_2}{W} = \dfrac{T_2}{T_1 - T_2}$

$\Rightarrow$ Average power, $W = \dfrac{Q_2(T_1 - T_2)}{T_2} = \dfrac{263\,(298 - 263)}{263}$

$= 35$ J / s $= 35$ W

EXAMPLE |4| Coefficient of Performance of Carnot Engine

A Carnot engine takes 10^6 cal of heat from a source at 827°C and exhaust it to a sink 27°C. How much work does it gives or output? What is engine efficiency? Also, find out the coefficient of performance of the engine, if it is used in reverse direction.

Sol. Given, $T_1 = 827 + 273 = 1100$ K

$T_2 = 27 + 273 = 300$ K, $Q_1 = 10^6$ cal

$Q_2 = \dfrac{T_2}{T_1} \times Q_1 = \dfrac{300}{1100} \times 10^6 = 2.72 \times 10^5$ cal

Efficiency $(\eta) = \left(1 - \dfrac{T_2}{T_1}\right) \times 100\% = \left(1 - \dfrac{300}{1100}\right) \times 100$

$= 72.72\%$

As, $\beta = \dfrac{T_2}{T_1 - T_2}$ = coefficient of performance

$= \dfrac{300}{1100 - 300} = \dfrac{300}{800} = 0.375$

EXAMPLE |5| Freezing of Water

A Carnot engine with ideal gas is used for freezing water which is at 0°C. The engine is operated by a 600 W electric motor having an efficiency of 50%. Find time to freeze 25 kg of water. Take 25°C and 0°C as the source and sink. Latent heat of ice $= 333 \times 10^3$ Jkg^{-1}.

Sol. Given, $\qquad T_1 = 273$ K,

$$T_2 = 25 + 273 = 298 \text{ K}$$
$$L = 333 \times 10^3 \text{ J kg}^{-1}$$

Efficiency of electric motor = 50%
Find out the used power of the engine.

$$= 50\% \text{ of } 500 \text{ W} = 250 \text{ W}$$

Coefficient of performance, $\beta = \dfrac{Q_2}{W} = \dfrac{T_2}{T_1 - T_2}$

Heat extracted from water in unit time.

$$Q_2 = \dfrac{T_2}{T_1 - T_2} \times W = \dfrac{273}{298 - 273} \times 250 = 2730.0 \text{ Js}^{-1}$$

Total heat extracted from 25 kg water to freeze it into ice,

$$Q = mL = 25 \times 333 \times 10^3 \text{ J}$$
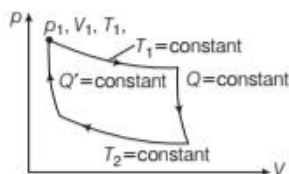
Total time taken in freezing water into ice

$$= \dfrac{Q}{Q_2} = \dfrac{25 \times 333 \times 10^3}{2730} = 3049.45 \text{ s}$$

| TOPIC PRACTICE 2 |

1. Carnot engine is a
(a) irreversible
(b) petrol engine
(c) reversible
(d) diesel engine

Sol. (c) Process starts from p_1, V_1, T_1 and reverses back to p_1, V_1, T_1 after doing work (given by area enclosed). Here p, V, T reverse back, work done is not reversed back.

Carnot engine is a reversible engine working between two temperatures.

2. According to second law of thermodynamics,
(a) a heat engine cannot have efficiency equal to 1
(b) a refrigerator (or heat pump) could have infinite value of coefficient of performance
(c) a heat engine can convert heat fully in to work
(d) heat can flow from cold to hot body

Sol. (a) Second law puts limitation on the efficiency of a heat engine and on the coefficient of performance of a refrigerator. Heat engine cannot have efficiency equal to 1 and a refrigerator cannot have infinite value of coefficient of performance.

3. According to Carnot, which type of engine working between two temperatures T_1 and T_2 have maximum efficiency?
(a) Reversible engine
(b) Irreversible engine
(c) External combustion engine
(d) Diesel engine.

Sol. (a) For reversible engine, according to Carnot, efficiency is maximum.

4. The efficiency of a Carnot's engine working between steam point and ice point is
(a) 26.81%
(b) 29%
(c) 30%
(d) 10%

Sol. (a) $T_1 = (100 + 273) = 373$ K
$$T_2 = (0 + 273) = 273 \text{ K}$$

Efficiency $(\eta) = 1 - \dfrac{T_2}{T_1} = 1 - \dfrac{273}{373} = \dfrac{100}{373}$

$$\% \eta = \dfrac{100}{373} \times 100 = 26.81 \%$$

VERY SHORT ANSWER Type Questions

5. Can a ship be moved with the energy of the sea water?

Sol. No, a ship cannot be moved in a sea by the use of the energy of sea water because refrigerator is against the second law of thermodynamics.

6. Is reversible process possible in nature?

Sol. A reversible process is never possible in nature because of dissipative forces and condition for a quasi-static process is not practically possible.

7. What are the forces which make any process irreversible?

Sol. All sorts of dissipative forces, e.g. force of friction, viscous drag, electrical resistance, non-elasticity, thermal radiation, convection etc., make a real process irreversible.

8. On what factors, the efficiency of a Carnot engine depends?

Sol. The efficiency of a carnot engine depends, on the temperature of source of heat and the sink.

9. If the temperature of the sink is increased, what will happen to the efficiency of Carnot engine?

Sol. Efficiency, $\eta = 1 - \dfrac{T_2}{T_1}$

By increasing T_2, the efficiency of the Carnot engine will decrease.

10. Find the efficiency of the Carnot engine working between boiling point and freezing point of water.

Sol. Efficiency of Carnot engine, $\eta = 1 - \dfrac{T_2}{T_1}$

$$= 1 - \dfrac{273 \text{ K}}{373 \text{ K}} = \dfrac{100}{373}$$

$$= 0.268 = 26.8\%$$

11. Can we design a reversible Carnot engine in practice?

Sol. No, we cannot design an ideal Carnot engine in practice.

12. Which thermodynamic law put restrictions on the complete conversion of heat into work?

Sol. According to second law of thermodynamics, heat energy cannot converted into work completely.

13. What type of process is a Carnot cycle?

Sol. Carnot cycle is a reversible cyclic process through which heat is converted into mechanical work.

SHORT ANSWER Type Questions

14. Consider a Carnot cycle operating between $T_1 = 500$ K and $T_2 = 300$ K producing 1 kJ of mechanical work per cycle. Find the heat transferred to the engine by the reservoirs.

[NCERT Exemplar]

Sol. As we know, $\quad \dfrac{Q_2}{Q_1} = \dfrac{T_2}{T_1} = \dfrac{3}{5}$

$$\because \qquad 1 - \dfrac{Q_2}{Q_1} = 1 - \dfrac{T_2}{T_1}$$

$$\Rightarrow \qquad \dfrac{Q_1 - Q_2}{Q_1} = \dfrac{500 - 300}{500} \qquad [\because Q_1 - Q_2 = W]$$

$$\Rightarrow \qquad \dfrac{W}{Q_1} = \dfrac{2}{5}$$

$$\therefore \qquad Q_1 = 10^3 \times \dfrac{5}{2} = 2500 \text{ J}$$

15. A Carnot engine is operating between 600 K and 200 K. Consider that the actual energy produced is 2 kJ per kilocalorie of heat absorbed. Compare the real efficiency with the efficiency of Carnot engine.

Sol. Given, $T_1 = 600$ K, $T_2 = 200$ K

Efficiency of Carnot engine,
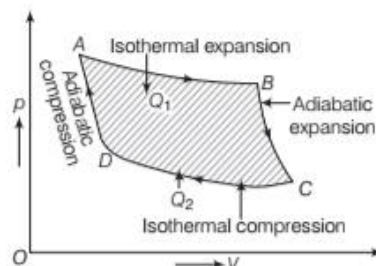
$$\eta = \dfrac{T_1 - T_2}{T_1} = \dfrac{600 - 200}{600}$$

$$= \dfrac{400}{600} = \dfrac{2}{3} = 66\%$$

Real efficiency $= \dfrac{\text{Energy output}}{\text{Energy input}} = \dfrac{2}{1 \times 4.2} = 0.47 = 47\%$

$$\therefore \quad \dfrac{\text{Real efficiency}}{\text{Carnot engine efficiency}} = \dfrac{47}{66} = 0.71$$

16. Draw p-V diagram of a Carnot cycle.

Sol. p-V diagram for Carnot cycle

17. Under what condition, an ideal Carnot engine has 100% efficiency?

Sol. Efficiency of a Carnot engine is given by $\eta = \left(1 - \dfrac{T_2}{T_1}\right)$

where, $T_2 = $ temperature of sink

and $T_1 = $ temperature of sink source.

So, for $\eta = 1$ or 100%, $T_2 = 0$ K or heat is rejected into a sink at 0 K temperature.

LONG ANSWER Type I Questions

18. Temperatures of the hot and cold reservoirs of a Carnot engine is raised by equal amounts. How the efficiency of the Carnot engine affected?

Sol. Let the initial temperatures of hot and cold reservoirs were T_1 and T_2. The efficiency of the Carnot engine is given by

So, initially $\qquad \eta = \dfrac{T_1 - T_2}{T_1} \qquad$ ...(i)

As given the temperature of both the reservoirs is raised by equal amount t, so $T_1' = T_1 + t$ and $T_2' = T_2 + t$. The final efficiency of the Carnot engine will be

$$\eta' = \dfrac{T_1' - T_2'}{T_1'} = \dfrac{(T_1 + t) - (T_2 + t)}{(T_1 + t)}$$

$$= \dfrac{T_1 - T_2}{(T_1 + t)} \qquad \text{...(ii)}$$

Dividing Eq. (ii) by Eq. (i), we have

$$\dfrac{\eta'}{\eta} = \dfrac{\left(\dfrac{T_1 - T_2}{T_1 + t}\right)}{\left(\dfrac{T_1 - T_2}{T_1}\right)} = \dfrac{T_1}{T_1 + t} \qquad \text{...(iii)}$$

As $\eta' < \eta$, i.e. the efficiency of Carnot engine decreases.

19. Two Carnot engines A and B are operated in series. The first one A receives heat at 900 K and rejects it to a reservoir at temperature T. The second engine B operates on this reservoir and rejects heat to a reservoir at 400 K. Calculate temperature T when
  (i) efficiencies of both A and B are equal.
  (ii) the work outputs of both A and B are equal.

Sol. (i) Efficiency of A = efficiency of B
$$\eta_A = \eta_B$$
$$\Rightarrow \quad 1 - \frac{T}{900} = 1 - \frac{400}{T}$$
$$\Rightarrow \quad T^2 = 900 \times 400$$
$$\Rightarrow \quad T = 600 \text{ K}$$

(ii) Let the first engine take Q_1 heat as input at temperature, $T_1 = 800$ K and gives out heat Q_2 at temperature T_0. The second engine receive Q_2 as input and give is out heat Q_3 at temperature $T_3 = 300$ K to the sink.

Work done by first (A) engine = work done by second (B) engine.

Thus, $\quad Q_1 - Q_2 = Q_2 - Q_3$

Dividing both sides by Q_1
$$1 - \frac{Q_2}{Q_1} = \frac{Q_2}{Q_1} - \frac{Q_3}{Q_1}$$
$$\Rightarrow \quad 1 - T/T_1 = \frac{Q_2}{Q_1}\left(1 - \frac{Q_3}{Q_2}\right)$$
$$\Rightarrow \quad 1 - T/T_1 = \frac{T}{T_1}(1 - T_3/T)$$
$$\Rightarrow \quad T_1/T - 1 = 1 - \frac{T_3}{T} \Rightarrow \frac{T_1}{T} + \frac{T_3}{T} = 2$$
$$\Rightarrow \quad \frac{1}{T}(T_1 + T_3) = 2 \Rightarrow T = \frac{T_1 + T_3}{2}$$
$$\Rightarrow \quad T = \frac{900 + 400}{2} = 650 \text{ K}$$

20. Find out whether these phenomena are reversible or not.
  (i) Waterfall and (ii) Rusting of iron.

Sol. (i) **Waterfall** The falling of water cannot be reversible process. During the water fall, its potential energy convert into kinetic energy of the water.
On striking the ground, some part of potential energy converts into heat and (sound not possible that heat and the sound). In nature, it automatically convert the kinetic energy and potential energy so that the water will rise back so waterfall is not a reversible process.
(ii) **Rusting of iron** In rusting of iron, the iron become oxidised with the oxygen of the air as it is a chemical reaction, it cannot be reversed.

LONG ANSWER Type II Questions

21. Two cylinders A and B of equal capacity are connected to each other via a stopcock. A contains a gas at standard temperature and pressure. B is completely evacuated. The entire system in thermally insulated. The stopcock is suddenly opened.

Answer the following
  (i) What is final pressure of the gas in A and B?
  (ii) What is the change in internal energy of the gas?
  (iii) What is the change in temperature of the gas?
  (iv) Do the intermediate states of the system (before settling to the final equilibrirum state) lie on its p-V-T surface?   **[NCERT]**

Sol. (i) Let capacity of each cylinder be V and atmospheric pressure be p.
$$p_1 = p$$
Initial volume of gas = Volume of the cylinder A
$$\therefore \quad V_1 = V$$
When stopcock is opened, then volume available for gas becomes $2V$
$$\therefore \quad V_2 = 2V$$
Final pressure (p_2) = ?

As system is thermally insulated, therefore there is no change in temperature during the process and hence it is an isothermal process.

For an isothermal process (according to Boyle's law),
$$p_1 V_1 = p_2 V_2$$
or
$$p_2 = p_1 \frac{V_1}{V_2} = p \times \frac{V}{2V}$$
$$= \frac{p}{2} = \frac{1}{2} \text{ atm}$$
$$= 0.5 \text{ atm}$$

(ii) Change in internal energy, $\Delta U = 0$, as no work is done on or by the gas.

(iii) Change in temperature of the gas is zero as gas does no work in expansion.

(iv) No, because free expansion of gas is rapid and cannot be controlled. The intermediate states are non-equilibrium states and do not satisfy the gas equation. Therefore, the intermediate state of the gas does not be on the p-V-T surface.

22. Explain with the suitable example that a reversible process must be carried slowly and a fast process is necessarily irreversible.

Sol. A reversible process must pass through equilibrium states which are very close to each other so that when process is reversed, it passes back through these equilibrium states.

Then, it is again decompressed or it passes through same equilibrium states, system can be restored to its initial state without any change in surroundings.

e.g. If a gas is compressed as shown
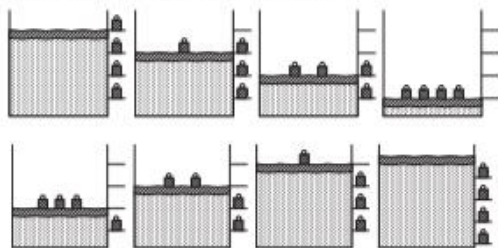
But a reversible process can proceeds without reaching equilibrium in intermediate states.

Expansion   Compression
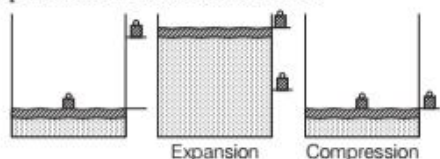
23. The efficiency of a Carnot engine is 1/2. If the sink temperature is reduced by 100°C, then engine efficiency becomes 2/3. Find
  (i) sink temperature
  (ii) source temperature
  (iii) Explain, why a Carnot engine cannot have 100% efficiency?

Sol. (i) Efficiency, $\eta = 1 - \dfrac{T_2}{T_1}$

where, T_2 = sink temperature
T_1 = source temperature.

$$1 - \dfrac{T_2}{T_1} = \dfrac{1}{2} \qquad\qquad \text{...(i)}$$

$$1 - \left(\dfrac{T_2 - 100}{T_1}\right) = \dfrac{2}{3} \qquad\qquad \text{...(ii)}$$

From Eq. (i), $\dfrac{T_2}{T_1} = \dfrac{1}{2}$ and Eq. (ii)

$$\dfrac{T_2 - 100}{T_1} = \dfrac{1}{3}$$

On dividing, we get

$$\dfrac{T_2}{T_2 - 100} = \dfrac{3}{2} \ \Rightarrow\ T_2 = 300\text{K}$$

(ii) Substituting in Eq. (i), $T_1 = 600\text{ K}$

(iii) As efficiency, $\eta_2 \ \Rightarrow\ 1 - \dfrac{T_2}{T_1}$

$\therefore$ It equals to 1 only when $\dfrac{T_2}{T_1} = 0$ or $T_2 = 0\text{K}$

But absolute zero is not possible.

24. Two Carnot engines A and B are operated in series. The first one A receives heat at 800 K and rejects to a reservoir at temperature T K. The second engine B receives the heat rejected by the first engine and in turn rejects to a heat reservoir at 300 K. Calculate the temperature T K for the following cases.
  (i) When the outputs of the two engines are equal.
  (ii) When the efficiencies of the two engines are equal.

Sol. **For engine A,** $T_1 = 800\text{ K}, T_2 = T\text{ K}$

Efficiency, $\qquad \eta_A = 1 - \dfrac{T_2}{T_1} = 1 - \dfrac{T}{800}$

Also, $\qquad\qquad \dfrac{Q_2}{Q_1} = \dfrac{T_2}{T_1} = \dfrac{T}{800}$

Work output, $W_A = Q_1 - Q_2 = \eta_A \times Q_1$

$$\left[\because \eta_A = 1 - \dfrac{Q_2}{Q_1}\right]$$

or $\qquad\qquad W_A = \left(1 - \dfrac{T}{800}\right)Q_1$

For engine B, $T_1' = T\text{ K}, T_2' = 300\text{ K}$

Efficiency, $\qquad \eta_B = 1 - \dfrac{T_2'}{T_1'} = 1 - \dfrac{300}{T}$

Work output, $W_B = Q_1' - Q_2' = \eta_B \times Q_1' = \left(1 - \dfrac{300}{T}\right)Q_1'$

Since, the engine B absorbs the heat rejected by the engine A, so

$$Q_1' = Q_2 \quad \therefore\ W_B = \left(1 - \dfrac{300}{T}\right)Q_2$$

(i) When outputs of the two engines are equal,
$\qquad W_A = W_B$

or $\qquad \left(1 - \dfrac{T}{800}\right)Q_1 = \left(1 - \dfrac{300}{T}\right)Q_2$

or $\qquad \left(1 - \dfrac{T}{800}\right) = \left(1 - \dfrac{300}{T}\right)\dfrac{Q_2}{Q_1} = \left(1 - \dfrac{300}{T}\right)\dfrac{T}{800}$

On solving, we get $T = 550\text{ K}$

(ii) When the efficiencies are equal, $\eta_A = \eta_B$

or $\qquad\qquad 1 - \dfrac{T}{800} = 1 - \dfrac{300}{T}$

or $\qquad\qquad T^2 = 24 \times 10^4$

$\therefore \qquad\qquad T = 489.9\text{ K}$

OBJECTIVE Type Questions

1. Reversibility is not possible because of
   (a) resistive force present everywhere
   (b) every process around us is Quasi-static
   (c) gases are viscous.
   (d) gases have density

2. Which condition is true for an ideal Carnot engine which have 100% efficiency?
   (a) Temperature of sink source $T_1 = 0K$
   (b) Temperature of sink $T_2 = 0K$
   (c) Temperature of sink source $T_1 = 1.0\,K$
   (d) None of the above

Answers
   1. (a) | 2. (b)

VERY SHORT ANSWER Type Questions

3. What is the significance of second law of thermodynamics ?

4. How is the efficiency of a Carnot engine affected by the nature of the working substance?

SHORT ANSWER Type Question

5. A Carnot engine takes in a thousand kilocalories of heat from a reservoir at 827°C and exhausts it to a sink at 27°C.
   (i) How much work does it perform?
   (ii) What is the efficiency of the engine?
   [**Ans.** (i) 2.720×10^5 cal (ii) 72.72 %]

LONG ANSWER Type I Questions

6. An ideal Carnot engine takes heat from a source at 317°C, does some external work and delivers the remaining energy to a heat sink at 117°C. If 500 kcal of heat is taken from the source.
   (i) How much work is done?
   (ii) How much heat is delivered to the sink?
   [**Ans.** (i) 710 kg (ii) 331 kcal]

7. A Carnot engine absorbs 6×10^5 cal at 227°C. Calculate work done per cycle by the engine if its sink is maintained at 127°C. [**Ans.** 5.04×10^5 J]

LONG ANSWER Type II Questions

8. Heat cannot flow itself from a body at lower temperature to a body at higher temperature, is a consequence of which law of thermodynamics?

9. (i) Explain second law of thermodynamics.
   (ii) Write a paragraph explaining Carnot engine efficiency (η) and its relation with temperature.

SUMMARY

- **Thermodynamics** It is the branch of physics which deals with the study of transformation of heat energy into other forms of energy.
- **System** Thermodynamic system is an assembly of an extremely large number of particles so that the assembly has a certain value of pressure, volume and temperature.
- **Surroundings** Everything outside the system which has a direct effect on the system.
- **Boundary** A system is separated from its surroundings.
- **A thermodynamic** system is said to be in thermodynamical equilibrium when macroscopic variables that characterise the system do not change with time.
- Two systems are said to be in thermal equilibrium with each other if they are at the same temperature.
- **Zeroth law of thermodynamics** If two systems A and B are separately in thermal equilibrium with a third system C, then A and B are in thermal equilibrium with each other.
- **Heat** It is the energy that is transferred between a system and its environment.
$$\Delta Q = ms(T_f - T_i)$$
- **Internal energy** The total energy possessed by the system due to molecular motion and molecular configuration, i.e,
$$U = U_k + U_p$$

- Work done by or on the system is given by $\quad W = \int_{V_i}^{V_f} p\, dV$

  where, V_i = initial volume of gas, $\quad V_f$ = final volume of gas, $\quad p$ = pressure
- **Heat capacity** An amount of heat ΔQ is needed to change its temperature ΔT. Its unit is J/K.

  $$S = \frac{\Delta Q}{\Delta T}$$
- **Specific heat capacity** The amount of heat required to change the temperature of unit mass of a substance by unity. Its unit is J/kg-K.

  $$S = \frac{1}{m}\frac{\Delta Q}{\Delta T}$$
- **Molar specific heat capacity** The amount of heat required to raise the temperature of one gram mole of a substance through a unit degree.

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

  Its unit is J/mol-K
- The relation between C_p and C_V is given by, $C_p - C_V = R$
- **First law of thermodynamics** The heat given to system is either used in doing work (ΔW) or it increases the internal energy (ΔU) the system, i.e. $\Delta Q = \Delta U + \Delta W$
- When state of a system changes or the state variables changes with time, then this process is known as thermodynamic system.
- The processes that do not involve accelerated motion of piston-large temperature gradient and pressure gradient are quasi-static.
- An **isothermal process** occurs at constant temperature and work done in an isothermal process is given by the following equation.

  $$W = 2.303\,\mu RT \log\left(\frac{V_f}{V_i}\right)$$
- An isobaric process occurs at constant pressure and work done is an isobaric process is given by the following equation.

  $$W = \mu R(T_f - T_i)$$
- An **isochoric process** is one in which volume is kept constant, meaning that the work done by the system will be zero.
- An adiabatic process does not allow transfer of heat by or to the system and work done in this process is given by the following equation

  $$W = \frac{\mu R(T_i - T_f)}{\gamma - 1}$$
- In cyclic process, initial and final states are same while in non-cyclic processes, they are different.
- **Kelvin-Planck statement** No process is possible whose sole result in the absorption of heat from a reservoir and the complete conversion of heat into work.
- **Clausius statement** No process is possible whose sole result is the transfer of heat from a colder object to hotter object.
- **Carnot engine** The reversible engine which operates between two temperatures of source and sink.
- Carnot cycle consists four strokes and each stroke having own work which is given by the following equations.

  $$W_1 = RT_1 \log_e \frac{V_2}{V_1}, \qquad W_2 = (T_1 - T_2)\frac{R}{\gamma - 1}(T_1 - T_2)$$
  $$W_3 = RT_2 \log_e \frac{V_3}{V_4}, \qquad W_4 = \frac{R}{\gamma - 1}(T_1 - T_2)$$
- **Carnot's theorem**
  (i) A heat engine working between the two given temperature T_1 of hot reservoir, i.e. source and T_2 of cold reservoir, i.e. sink cannot have efficiency of more than that of Carnot engine.
  (ii) The efficiency of the Carnot engine is independent of the nature of working substance.
- Coefficient of performance of Carnot engine is given by the following equation.

  $$\beta = \frac{T_2}{T_1 - T_2}$$
- where, T_1 = temperature of surroundings and T_2 = temperature of cold body

CHAPTER PRACTICE

OBJECTIVE Type Questions

1. According to first law of thermodynamics
   (a) any process that involves energy conservation is possible in nature
   (b) $\Delta Q = \Delta U + \Delta W$
   (c) Both (a) and (b)
   (d) Neither (a) nor (b)

2. $(\Delta Q - \Delta W)$ is
   (a) path dependent
   (b) path independent
   (c) equal to ΔU
   (d) Both (b) and (c)

3. Mechanical equivalent of heat is equal to the amount of
   (a) work done to produce 1 cal heat
   (b) a conversion factor between calorie and joule
   (c) Both (a) and (b)
   (d) Neither (a) nor (b)

4. Choose the state variable from the given options.
   (a) Heat
   (b) Work
   (c) Internal energy
   (d) All of these

5. A mixture of gases undergoing explosive chemical reaction
   (a) is not in equilibrium state during explosion
   (b) may have variable temperature and pressure values during explosion
   (c) finally the gas will attained equilibrium state with its surroundings
   (d) All of the above

6. A gas is expanded isothermally from volume V_1 to V_2 at a constant temperature T, the work done by the gas in this expansion is
   (a) $\mu RT \log \dfrac{V_1}{V_2}$
   (b) $\mu RT \times \dfrac{V_1}{V_2}$
   (c) $\mu RT \log \dfrac{V_2}{V_1}$
   (d) $\mu RT \times \dfrac{V_2}{V_1}$

7. For Carnot engine, which process should be chosen to take the working substance from T_1 to T_2 or *vice-versa* ?
   (a) Isochoric
   (b) Isothermal
   (c) Adiabatic
   (d) Isobaric

ASSERTION AND REASON

Direction (Q. Nos. 8-15) *In the following questions, two statements are given- one labelled Assertion (A) and the other labelled Reason (R). Select the correct answer to these questions from the codes (a), (b), (c) and (d) as given below*
   (a) Both Assertion and Reason are true and Reason is the correct explanation of Assertion.
   (b) Both Assertion and Reason are true but Reason is not the correct explanation of Assertion.
   (c) Assertion is true but Reason is false.
   (d) Assertion is false but Reason is true.

8. **Assertion** Thermodynamics deals with the concepts of heat and temperature.
   Reason The temperature of an ideal gas depends on its molecular kinetic energy.

9. **Assertion** If the temperature of two systems is not same it means that they must not be in thermodynamic equilibrium.
   Reason If the temperature of two systems is same, it means that they must be in thermal equilibrium.

10. **Assertion** By doing some work on the system, we can change the internal energy of a system.
    Reason If work is done by the system, its internal energy may decrease.

11. **Assertion** Specific heat capacity and molar specific heat capacity both have same units.
    Reason Specific heat capacity and molar specific heat capacity both do not depend on mass.

12. **Assertion** State variables are required to specify the equilibrium state of the system.
    Reason Pressure is an intensive state variable.

13. **Assertion** In isothermal process for ideal gas, change in internal energy is zero.
    Reason No heat is supplied to system or rejected by system, in an isothermal process.

14. **Assertion** First law of thermodynamics is based on energy conservation.
    Reason Second law of thermodynamics put limitations on first law.

15. Assertion Reversible Carnot engine with one particular substance can not be more efficient than the one using another substance.

Reason Efficiency of Carnot engine = T_2/T_1.

CASE BASED QUESTIONS

Direction (Q. Nos. 16-17) *These questions are case study based questions. Attempt any 4 sub-parts from each question.*

16. Equilibrium State

An equilibrium state of a gas is completely specified by the values of pressure, volume, temperature and mass (and composition, if there is a mixture of gases). A gas allowed to expand freely against vacuum is not an equilibrium state. During the rapid expansion, pressure of the gas may not be uniform throughout. Similarly, a mixture of gases undergoing an explosive chemical reaction is not an equilibrium state, again its temperature and pressure are not uniform. Now consider following system.

Diathermic walls and piston

An ideal gas initially at thermodynamic and mechanical equilibrium
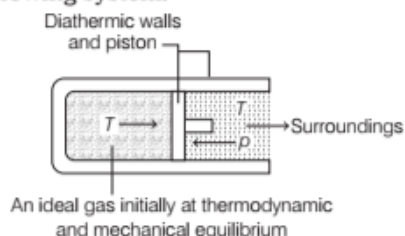
(i) If the external pressure is reduced suddenly, then
(a) the gas will expand suddenly which has non-equilibrium intermediate stages
(b) the piston will accelerate outwards
(c) Both (a) and (b)
(d) Neither (a) nor (b)

(ii) If a finite temperature difference exists between system and surroundings.
(a) there will be a rapid exchange of heat between system and surroundings with non-equilibrium intermediate stages
(b) after sometime the temperature and pressure of surroundings and system will become same
(c) Both (a) and (b)
(d) Neither (a) nor (b)

(iii) Choose the correct option.
(a) Thermodynamics is a microscopic science
(b) Thermodynamics results based on molecular description of the molecules of the gas
(c) p, V and T are state variables
(d) Q is a state variable

(iv) The internal energy of the given system could be changed
(a) by extracting heat from the system
(b) by doing work done on the system
(c) if system do some work on the surroundings
(d) All of the above

(v) A mixture of gases undergoing explosive chemical reaction
(a) is in equilibrium state during explosion
(b) have constant temperature and pressure values during explosion
(c) finally the gas will attained equilibrium state with its surroundings
(d) Both (b) and (c)

17. First Law of Thermodynamics

First law of thermodynamics is a statement of conservation of energy applied to any system in which energy transfer from or to the surroundings is taken into account.

It states that heat given to a system is either used in doing external work or it increases the internal energy of the system or both.

i.e. Heat supplied, $\Delta Q = \Delta U + \Delta W$

where, ΔQ = heat supplied to the system by the surroundings,

ΔW = work done by the system on the surroundings

and ΔU = change in internal energy of the system.

(i) For an ideal gas, internal energy depends on
(a) only molecular kinetic energy
(b) only potential energy of the molecules
(c) Both kinetic and potential energies of the molecules
(d) None of the above

(ii) The internal energy of a system could be changed
(a) by extracting heat from the system
(b) by doing work done on the system
(c) if system do some work on the surroundings
(d) All of the above

(iii) $(\Delta Q - \Delta W)$ is
(a) path dependent
(b) path independent
(c) equal to ΔU
(d) Both (b) and (c)

(iv) Using first law of thermodynamics, which is true for isothermal expansion of an ideal gas,
(a) $\Delta U = +$ ve
(b) $\Delta Q = +$ ve
(c) $\Delta W = +$ ve
(d) Both (b) and (c)

(v) A system is provided with 200 cal of heat and the work done by the system on the surroundings is 40J, then its internal energy
(a) increases by 600 J
(b) decreases by 800 J
(c) increases by 800 J
(d) decreases by 50 J

Answers

1. (c)		2. (d)		3. (c)		4. (c)		5. (d)	
6. (c)		7. (c)		8. (b)		9. (d)		10. (a)	
11. (d)		12. (b)		13. (c)		14. (b)		15. (c)	
16. (i) (c)	(ii) (c)	(iii) (c)	(iv) (d)	(v) (c)					
17. (i) (a)	(ii) (d)	(iii) (d)	(iv) (d)	(v) (c)					

VERY SHORT ANSWER Type Questions

18. When work done is positive?

19. Is it possible to increase the temperature of a gas without heating it?

20. What is a thermodynamic system?

21. What do you mean by an adiabatic wall and a diathermic wall?

22. Can a system be heated and its temperature remains constant?

23. Find value of specific heat of a gas in isothermal process.

SHORT ANSWER Type Questions

24. Which one a solid, a liquid or a gas of same mass and at the same temperature has greatest internal energy? Give reason.

25. Why water at the base of a waterfall is slightly warmer than the top?

26. Two blocks of same metal having masses 5 g and 10 g collide against a target with same velocity. If total energy is used in heating the balls, which will attain higher temperature?

27. Why is conversion of heat into work not possible without a sink at lower temperature?

28. Explain coolant fluid used in a chemical plant or in a car radiator should have high specific heat. Is water a suitable coolant?

LONG ANSWER Type I Questions

29. Find work done during the cyclic process shown in indicator diagram.

$$\left[\text{Ans. } \pi \left(\frac{V_2 - V_1}{2} \right) \left(\frac{p_2 - p_1}{2} \right) \right]$$

30. Draw indicator diagram for an adiabatic process. Find the slope of an adiabatic at any point.

31. Two identical samples of a gas are at a pressure p_1 and volume V_1. The two samples are allowed to expand so as to acquire a volume V_2. But one sample expands isothermally while the other expands adiabatically. In which case, more work is done and why?

32. State second law of thermodynamics. Write a difference between heat engine and refrigerator.

33. Milk is poured into a cup of tea and is mixed with a spoon. Is this an example of a reversible process? Give reason.

34. Define reversible process. Write two characteristics of reversible process.

LONG ANSWER Type II Questions

35. What is Carnot engine? On what factors does it depend? Define also the efficiency of a Carnot engine.

36. A Carnot cycle is performed by 1 mole of air ($r = 1.4$) initially at 327°C. Each stage represents a compression or expansion in the ratio 1 : 6. Calculate
(i) the lowest temperature
(ii) network done during each side
(iii) efficiency of the engine
Take, $R = 8.31$ J/mol-K

[**Ans.** (i) 20° C (ii) 457232 J (iii) 51.2%]

37. Explain the construction and various operations for Carnot heat engine working between two temperatures. Hence, derive the relation coefficient of performance and efficiency of refrigerator.

38. What do you understand by reversible and irreversible processes? Give example what are the necessary conditions for a process to be reversible.

39. Find the V-T and T-p diagrams for cyclic process on p-V diagram.