

This module is designed to help you to:

- explain that thermodynamic changes can take place under a variety of conditions, leading to different types of thermodynamic processes;
- distinguish between reversible and irreversible processes;
- examine that a reversible process can only be idealized and cannot be achieved in practice;
- explain how a reversible process can be approximated by a quasistatic process;
- explain how the work done by/on a gas, during a thermodynamic change, can be calculated;
- explain the meanings of the terms isochoric, isobaric, isothermal and adiabatic processes
- draw graphs between different pairs of state variables (from P , V and T) for different thermodynamic processes;
- explain the meaning of the term cyclic process and give examples of the same;
- give examples of practical situations that can correspond to the different thermodynamic processes defined above.

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12.2.1 Introduction

In the previous module you learnt about thermodynamic systems. You also learnt about thermodynamic state, which essentially means an equilibrium state in which the thermodynamic variables describing the state do not change with time. In this module we shall talk about changes

of such variables with time, and such a change is called a thermodynamic process. We shall learn to distinguish between reversible and irreversible processes. We shall further understand that a reversible process can only be idealized and can't be achieved in practice. Since all natural processes are irreversible, we shall learn to adopt mathematical techniques for handling natural processes from the thermodynamic point of view.

We shall learn about processes where one or the other variable (pressure, volume or temperature) attached with the system remains constant. We shall learn to calculate the work done on or by a system and also heat absorbed or evolved during a process. We shall give special emphasis to cyclic processes.

12.2.2 Thermodynamic processes

When the thermodynamic variables associated with a thermodynamic system undergo change from one set of equilibrium values to another, the system is said to have gone through a thermodynamic process. A thermodynamic system can undergo various processes during which work is done by (or on) the system and energy transfer takes place as heat. We now study these processes.

Note: In the study of thermodynamic processes, some students (particularly the students who may not have opted for mathematics along with physics) may find the steps involving integration challenging, so special attention must be paid to these steps. Key points of these processes should also be emphasized upon.

Let us choose an ideal gas as our system. Consider a gas in thermal and mechanical equilibrium with its surroundings. The pressure of the gas in that case equals the external pressure and its temperature is the same as that of its surroundings. Suppose that the external pressure is suddenly reduced. The gas will expand rapidly and during the process it will pass through non-equilibrium states. Non-equilibrium states are the ones where the thermodynamic variables like pressure, volume and temperature do not remain invariant. In the same way, if a finite temperature difference exists between the gas and its surroundings, there will be an exchange of heat during which the gas may again pass through non-equilibrium states. In due course, the gas

will settle to an equilibrium state with well-defined temperature and pressure values; equal to those of the surroundings. We call these the initial and final equilibrium states.

Now, the question is about what happens during the intervening situation which we call the thermodynamic process. And how to handle the values of the thermodynamic variables during the process which make them compatible with mathematical operations. We shall see that a process will be depicted in the form of what is known as an indicator diagram (like pressure vs. temperature, pressure vs. volume, etc. graphs). In order to draw such a graph (say a P - T graph) we should be aware of the exact values of P and T during the process. This is possible if and only if the intermediate states through which the system passes are all equilibrium states. From the example cited above, we have realized that it is not possible in practice. Then, what is the way out? Let us explore.

12.2.3 Reversible and irreversible processes

If the thermodynamic system undergoes a process between an initial state i to a final state f so that all the intermediate states are equilibrium states, such that the process can be traced back from f to i along the same path, then the process is said to be reversible, otherwise it is irreversible.

The rapidity with which a natural process proceeds does not allow it to be called reversible. But unless it is reversible, the intermediate states are not in equilibrium. Since non-equilibrium states do not have well defined pressure and temperature values, how can we figure out the points on the P - T graph? Our inability to do so means that we are not able to draw the graph, which subsequently means that we shall not be able to analyze the process mathematically.

Thus, in order to be tenable to mathematical operations, we need a process to be reversible. But can such a process be realized in practice? Let us do a thought experiment. We would like to raise the temperature of a body from T_1 to T_2 . Let there be one intermediate equilibrium state having temperature $\frac{T_1+T_2}{2}$. Then, we have achieved one intermediate equilibrium state by dividing the given temperature range into two equal ranges. For having two intermediate equilibrium states, we shall need to have three equal ranges; for three intermediate equilibrium states we shall need four equal ranges and so on. Thus for n intermediate equilibrium states we shall need to divide the given range into $(n + 1)$ ranges. But for making all the intermediate states equilibrium, n should be equal to infinity, which establishes the very fact that a reversible process can only be idealized and can never be achieved in practice.

So, we have run into a deadlock. On one hand, unless the process is reversible, we cannot subject it to mathematical operation, and on the other hand all natural processes are irreversible. So, shall we not be able to treat the natural processes? Let us discuss that now.

One way to break this imbroglio is to imagine an idealized process, which is carried out so slowly that at every stage the system passes through states, each of which is a very close approximation to an equilibrium state, so that its pressure and temperature values are always very nearly well defined. Such a process is known as a quasistatic process. It has to be remembered that a quasistatic process is a hypothetical concept. In practice, processes that are sufficiently slow and do not involve rapid expansion, or large temperature/pressure/volume changes, are reasonable approximations to an ideal ‘quasistatic’ process. In our study of various thermodynamic processes, we shall assume these processes to be ‘quasistatic’.

There is yet another way, which gets facilitated by the use of thermodynamic functions like internal energy. Through the ‘Let Us Reflect’ Question No. Q.12.1.3 we got introduced to the concept of internal energy as being a state function. The change in the value of internal energy between two states is independent of the process connecting the initial and final states. The same happens with every other function of state. Thus if the working of a problem be so organized that it ultimately reduces to determining the change of the value of a state function, then while working out the same we shall mentally replace the actual irreversible process occurring between an initial state i to a final state f by a reversible process occurring between the same initial and final states, work out the change in the value of the state function following the reversible path, and claim the change along the irreversible path to be the same.

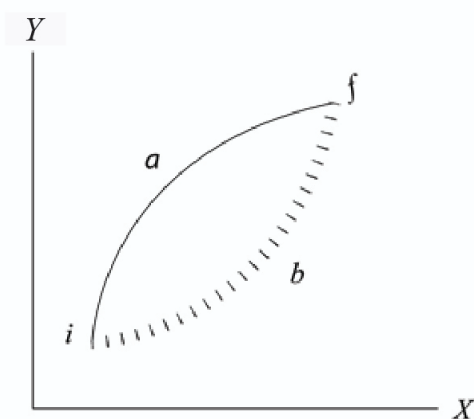


Fig. 12.2.1 Reversible and irreversible paths on an indicator diagram involving two variables X and Y

In this connection, refer to Fig. 12.2.1. It depicts a thermodynamic process on an indicator diagram with two thermodynamic variables X and Y . It shows two paths - one continuous (iaf), which is reversible, and the other discontinuous (ibf), which is irreversible and imaginary. The latter is the actual process, while the former is the mental replacement. Let F be a thermodynamic function, and we have

$$\Delta F(\text{along } iaf) = \Delta F(\text{along } ibf) \quad (12.2.1)$$

Now that we have developed the mathematical formalism of thermodynamic processes, let us take up the most illustrative example of work done by a gas.

Practical examples of reversible and irreversible process

All reversible processes, strictly speaking, are idealized quasi-static processes (i.e. processes that proceed in either direction) at an infinitely slow (approaching zero) rate). All practical processes, therefore, are, strictly speaking, irreversible in nature.

We can, however, approximately think of practical processes –like the conversion of ice into water, water into steam, inflation and deflation of a balloon as (approximately) reversible processes. They are, however, not reversible (in reversible processes the system and the surroundings come back to exactly the same state as before) in the strict sense of the term.

Practical processes, which we cannot reverse, are to be (commonly and easily) viewed as irreversible processes. Thus, the conversion of milk into curd, the burning out of a match stick and the squeezing out of tooth paste from a tube (by a person) are simple practical examples of processes that cannot be reversed. We can think of many more such processes as practical examples of irreversible processes.

We, however, need to remember that all practical processes are, strictly speaking, irreversible processes. A reversible process is an idealization that can be approached but not (strictly) attained.

12.2.4 Work done by an ideal gas

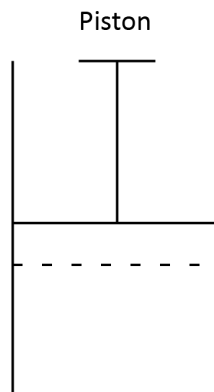


Fig.12.2.2 Gas in a cylinder pushed by a piston handle

A gas is taken in a cylinder fitted with an air-tight piston as shown in Fig 12.2.2. The piston is pushed by a handle.

Let the pressure applied be P , and let the cross-sectional area of the cylinder and the piston be α .

For an infinitesimal displacement dx , the change in volume $= dV$, say

If the applied force $= F$, the work done $dW = Fdx$

$$dW = P\alpha dx = PdV$$

So, for a change in volume from V_1 to V_2 , the work done is

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

So, the work done by an ideal gas is given by

$$W = \int_{V_1}^{V_2} PdV \quad (12.2.2)$$

where V_1 is the initial volume and V_2 is the final volume. It is a general equation where the work done by a gas can be calculated from the changes in the pressure and volume of the gas.

If gas expands, dV is positive and the work is done by the gas. On the other hand, if the gas is compressed, dV is negative and work is done on the gas.

PV diagrams

If we plot P along the y -axis and V along the x -axis, what we obtain is called a PV diagram (Fig.12.2.3). A process is represented by a curve on this PV diagram. From the significance of Definite Integral, we understand that the area under the curve gives the work done by the gas during the process.

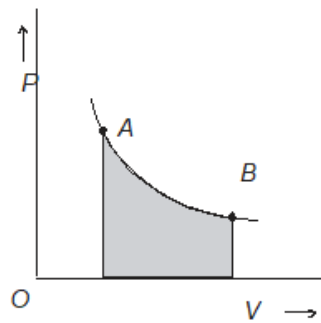


Fig.12.2.3 The shaded area in the PV diagram represents the work done

It can be easily noticed from the PV diagram that the work done by the gas in going from a state $A(P_1, V_1)$ to $B(P_2, V_2)$ depends on the path, that is, it is different for different paths. For example, in Fig.12.2.4 work done will be more for path 1 as compared to path 2 (area under curve 1 is more than the area under curve 2).

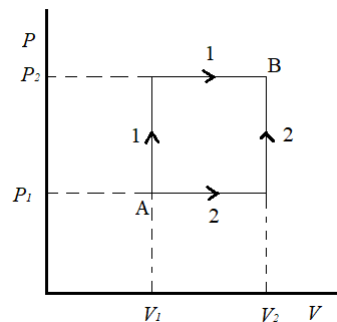


Fig.12.2.4 Two paths shown on a PV diagram

12.2.5 Isochoric process

In an isochoric process, the volume (of the system) remains constant. Isochoric processes can, therefore, be represented by a vertical line on the PV diagram (Fig.12.2.5).

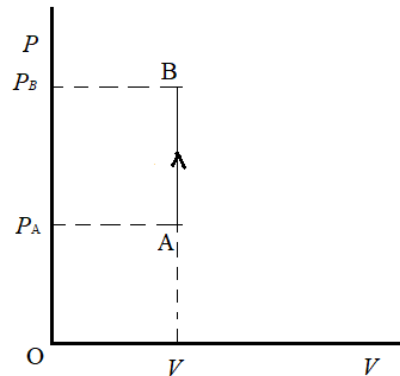


Fig.12.2.5 *PV diagram for an isochoric process*

If V is constant, from Eq(12.2.2) we find that $\Delta W = 0$. In an isochoric process, therefore, no work is done by the gas (or on the gas).

For this process, we shall see from the first law of thermodynamics (Module 3) reduces to

$$\Delta Q = \Delta U \quad (12.2.3)$$

The heat absorbed by the gas goes entirely to change its internal energy and its temperature.

When a gas, put in a closed metallic vessel (preferably made from a metal with a low value for its coefficient of volume expansion) is heated/cooled, we can think of the changes in its temperature and pressure as taking place under (nearly) isochoric conditions. We can, therefore, think of such changes as isochoric changes.

A reasonably good example of an isochoric change may be the filling of air/nitrogen in the present-day tubeless car tyres. Here the volume of the tyre remains nearly constant while the pressure (and temperature) of the gas, filled in it, can keep on changing.

12.2.6 Isobaric process

In isobaric processes, the pressure remains constant. Isobaric processes can, therefore, be represented by a horizontal line on a PV diagram (Fig.12.2.6).

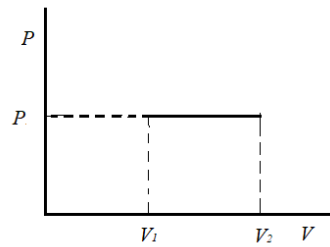


Fig.12.2.6 *PV diagram for isobaric process*

In Eq(12.2.3), since P is constant, it can be taken out of integral. The work done by the gas is, therefore,

$$W = P(V_2 - V_1) = \mu R (T_2 - T_1) \quad (12.2.4)$$

where symbols have their usual meanings. In this process, since temperature changes, the internal energy also changes. The heat absorbed goes partly to increase internal energy and partly to do work. We, therefore, say that, as per the first law of thermodynamics (explained further in Module 3), for an isobaric process we have,

$$\Delta Q = \Delta U + \Delta W \quad (12.2.5)$$

When a system is made to change its volume, under normal atmospheric conditions, the change is an isobaric change. During such a change, we can think of the pressure of the system to remain (nearly) constant at a value equal to that of the surrounding atmospheric pressure. Such a change in volume would usually be accompanied by a change in temperature.

In our day-to-day life, the changes we observe are all under (nearly) constant atmospheric pressure conditions. Such usual changes – say the melting of ice in an open vessel or the boiling of water (for making tea, say) can, therefore, be thought of as isobaric changes.

12.2.7 Isothermal process

A process, in which the temperature of the system remains constant throughout, is called an isothermal process. Since T is fixed, ideal gas equation gives

$$PV = \text{constant} \quad (12.2.6)$$

On the PV diagram, a plot of the above equation is called an isotherm (Fig.12.2.7).

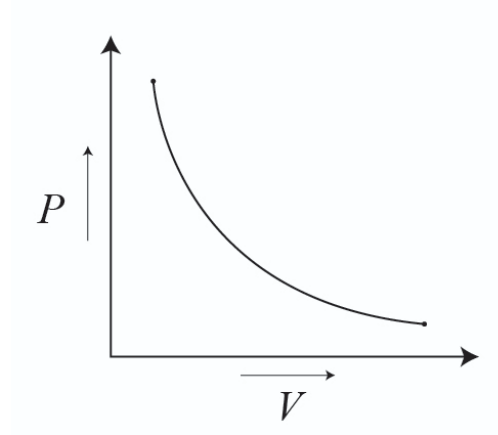


Fig.12.2.7 *PV diagram for isothermal expansion of an ideal gas*

Suppose an ideal gas goes isothermally (at temperature T) from its initial state (P_1, V_1) to the final state (P_2, V_2). Work done by the gas during the isothermal process is the area under the curve between V_1 and V_2 ; it is given by

$$\begin{aligned}
 W &= \int_{V_2}^{V_1} P dV = \int_{V_2}^{V_1} \frac{\mu RT}{V} dV \\
 W &= \mu RT \int_{V_2}^{V_1} \frac{dV}{V} = \mu RT \ln V \Big|_{V_2}^{V_1} \\
 W &= \mu RT \ln \frac{V_2}{V_1}
 \end{aligned} \tag{12.2.7}$$

If $V_2 > V_1$, $W > 0$; that is, in an isothermal expansion, work is done by the gas on its surroundings. On the other hand, if $V_2 < V_1$, $W < 0$, that is, in an isothermal compression, work is done on the gas by the surroundings.

Since temperature is fixed, there is no change in the internal energy of the ideal gas (that internal energy of an ideal gas changes only when there is a change in its temperature), that is, $\Delta U = 0$. Hence, the first law of thermodynamics (Eq 12.2.5), takes the form

$$\Delta Q = \Delta W \tag{12.2.5a}$$

Thus during an isothermal process, the heat supplied to the system (ΔQ) equals the work done by the system (ΔW) on its surroundings.

We can think of a gas, contained in a conducting cylinder. This cylinder can exchange heat with the surrounding. The changes in pressure and volume of the gas would then take place at (nearly) constant value of temperature. Such changes can, therefore, be thought of as (nearly) isothermal changes.

The simple Boyle's law verification apparatus, used in the laboratory, may be thought of as a set-up in which the pressure and volume changes of the gas take place under isothermal conditions. The process of 'blowing up' of a balloon also takes place under (nearly) isothermal conditions. For an isothermal change, we can also use a set up (like a thermostat) in which the temperature remains constant.

12.2.8 Adiabatic process

If during a process, the system is insulated from the surroundings and no heat flows between the system and the surroundings, the process is known as an adiabatic process.

The relationship between P and V , for an adiabatic process for an ideal gas, is given by

$PV^\gamma = \text{constant}$, where γ is the ratio of its two specific heat capacities (principal or molar)

(i) at constant pressure and (ii) at constant volume, $\gamma = \frac{c_p}{c_v}$.

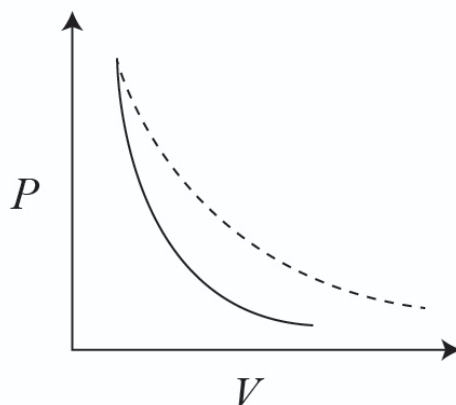


Fig. 12.2.8 *PV diagram for adiabatic process*

The dotted line is the replica of Fig 12.2.8. The continuous line actually represents the adiabatic curve. Work done, in an adiabatic change by an ideal gas from a state (P_1, V_1, T_1) to a state (P_2, V_2, T_2) , is given by

$$W = \frac{1}{1-\gamma} [P_2 V_2 - P_1 V_1] = \frac{\mu R(T_1 - T_2)}{(\gamma - 1)} \quad (12.2.8)$$

If work is done by the gas in an adiabatic process ($W > 0$), then $T_2 < T_1$, that is, the temperature of the gas decreases. (This is often used as a way to achieve low temperatures). On the other hand, if work is done on the gas ($W < 0$), we get $T_2 > T_1$, that is, the temperature of the gas rises.

In an adiabatic process, the system is insulated from the surroundings and heat absorbed or released is zero, that is, $\Delta Q = 0$. From first law of thermodynamics we obtain

$$\Delta W = -\Delta U \quad (12.2.5b)$$

Thus, in this case, Eq(12.2.5) takes the form of Eq(12.2.5b).

We, therefore, see that work done by the gas results in a decrease in the internal energy (and hence its temperature) of an ideal gas.

An adiabatic process, in the strict sense of the term, is difficult to achieve/observe in actual practice. We can, however, think of closed containers (or containers with tightly fitting lids) made up of very good heat insulating materials. Any change in the thermodynamic variables of the state of a gas, put in such a system, may be thought of taking place under (nearly) adiabatic conditions.

The thermos flask, often used in daily life, is a container in which very little heat is allowed to enter/leave the container over a time of a few hours. For this time duration, the changes, if any, in the fluid, put in the thermos flask, may be thought of as taking place under adiabatic conditions.



Let Us Reflect

Q.12.2.1 Derive the expressions for the work done during an adiabatic process, as given by Eq(12.2.8)

Q.12.2.2 Show that in Fig 12.2.8, the adiabatic curve is steeper than the isothermal curve.



Answers

A.12.2.1 With symbols usual meanings

$$W = \int_1^2 P dV$$

$$PV^\gamma = \text{a constant} = k, \text{ say}$$

$$\therefore W = k \int_1^2 V^{-\gamma} dV$$

$$= K \left[\frac{V^{-\gamma+1}}{1-\gamma} \right]_1^2$$

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

$$K = P_2 V_2^\gamma = P_1 V_1^\gamma$$

$$\therefore W = \frac{P_2 V_2 - P_1 V_1}{1-\gamma} = \frac{P_1 V_1 - P_2 V_2}{\gamma - 1}$$

$$\text{Again, } P_1 V_1 - P_2 V_2 = \mu R (T_1 - T_2)$$

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

$$\therefore W = \frac{\mu R}{\gamma - 1} (T_1 - T_2) = C_v (T_1 - T_2)$$

A.12.2.2 For the isotherm, $PV = \text{a constant}$

$$\therefore d(PV) = 0$$

$$\text{Or } PdV + VdP = 0$$

$$\therefore \frac{dP}{dV} = -\frac{P}{V} \quad (12.2.9)$$

And for the adiabatic curve.

$$d(PV^\gamma) = 0$$

$$\text{Or } VdP + \gamma V^{\gamma-1}PdV = 0$$

$$\text{Or } VdP + \gamma PdV = 0$$

$$\therefore \frac{dP}{dV} = -\frac{\gamma P}{V}. \quad (12.2.10)$$

Since, $\gamma > 1$. From Eqs(12.2.9) and (12.2.10) the adiabatic curve is steeper than the isothermal curve.

12.2.9 Cyclic process

In a cyclic process, the sequence of operations on the system is carried out in such a manner that the system finally returns to its initial state Fig.(12.2.9). Because the process starts and finishes at the same point, the change in internal energy is zero in a cyclic process; (that is $\Delta U = 0$ for a cyclic process). From the first law of thermodynamics, we get

$$\Delta Q = \Delta W$$

The heat supplied to the system (ΔQ) equals the work done by the system ΔW on its surroundings

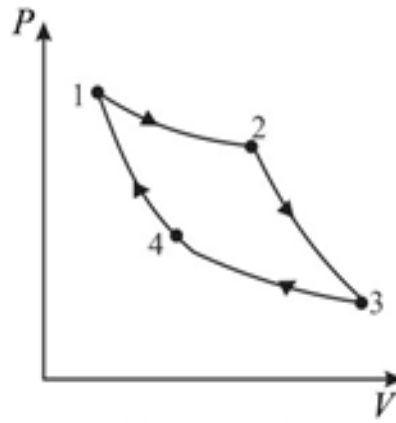


Fig: 12.2.9 *PV diagram of a cyclic process*

A cyclic process, as we know, is a process in which a system comes back to its initial condition (i.e. has the same ‘final’ values of its state variables as were their ‘initial’ values) after going through a change/ a series of changes.

We can think of any oscillating /vibrating system, (having negligible loss of energy through dissipative forces) as an example of a cyclic process. A gas, put in a container, whose (closing) piston is being made to move by, say, an oscillating spring, can be (nearly) regarded as undergoing a cyclic process. We, of course, need to have the piston moving in the (smooth) container with negligible loss of energy through dissipative forces, (like the force of friction).



Let Us Reflect

Q.12.2.3 Cyclic process, followed by an engine (made of one mole of perfect gas in a cylinder with a piston) is shown in Fig.12.2.10. The different steps of this cycle are carried out as per the following sequence:

A to B : volume constant

B to C : adiabatic change

C to D : volume constant

D to A : adiabatic change

$$\text{Also } V_C = V_D = 2V_A = 2V_B$$

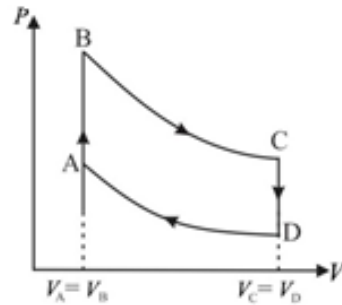


Fig: 12.2.10

- In which part of the cycle heat is supplied to the engine from the surrounding?
 - In which part of the cycle heat is being given to the surrounding by the engine?
 - What is the work done by the engine in one cycle for 1 mole? Write your answer in terms of P_A , P_B , and V_A .
- [$\gamma = \frac{5}{3}$ for the gas] also ($c_v = \frac{3}{2}R$)



Answers

A.12.2.4

The cycle is $A \rightarrow B \rightarrow C \rightarrow D \rightarrow A$

$A \rightarrow B$ and $C \rightarrow D$ are isochoric (work done = 0)

$B \rightarrow C$ and $D \rightarrow A$ are adiabatic (Heat exchange = 0)

Total work done = $(\Delta W)_{BC} + (\Delta W)_{DA}$

a) For $A \rightarrow B$, $\Delta W = 0$.

So, $\Delta Q = \Delta U$

$$\therefore \Delta Q = C_v T = C_v (T_B - T_A)$$

$$= \frac{C_v}{R} (P_B V_B - P_A V_A) = \frac{3}{2} V_A (P_B - P_A)$$

$P_B > P_A$. So, ΔQ is +ve

So, heat is taken in during $A \rightarrow B$.

b) Again for $C \rightarrow D$, $\Delta W = 0$, So, $\Delta Q = \Delta U$

$$\therefore \Delta Q = C_v T = C_v (T_D - T_C)$$

$$= \frac{C_v}{R} (P_D V_D - P_C V_C) = \frac{3}{2} V_C (P_D - P_C)$$

$P_D > P_C$, So, ΔQ is -ve.

So, heat goes out of the system during $C \rightarrow D$.

(c)

$$(\Delta W)_{BC} = \frac{P_B V_B - P_C V_C}{\gamma - 1} = \frac{P_B V_B - P_C V_C}{\frac{2}{3}} = \frac{3}{2} V_B (P_B - 2P_C)$$

$$\text{Now, } P_B V_B^\gamma = P_C V_C^\gamma$$

$$\therefore \frac{P_B}{P_C} = \left(\frac{V_C}{V_B} \right) = 2^{\frac{5}{3}},$$

$$\therefore P_C = \frac{P_B}{2^{\frac{5}{3}}}$$

$$\therefore (\Delta W)_{BC} = \frac{3}{2} V_A (P_B - \frac{2}{2^{5/3}} P_B) = \frac{3}{2} V_A P_B (1 - 2^{-5/3})$$

$$\therefore (\Delta W)_{BC} = (0.56) V_A P_B$$

Proceeding in the same manner, we get

$$(\Delta W)_{DA} = \frac{3}{2} V_A P_A (2^{-2/3} - 1) = - (0.56) V_A P_A$$

$$\Delta W = (0.56)(V_A P_B - V_A P_A) = (0.56) V_A (P_B - P_A)$$

12.2.12 Summary

- A process is reversible if it can be reversed such that both the system and the surroundings return to their original states, with no other change anywhere else in the universe .
- Reversible processes are idealized quasi-static processes with no dissipative factors such as friction , viscosity etc.
- Isothermal process is a process in which a system undergoes changes without change in temperature,i.e. $\Delta T = 0$.
- Isobaric process is a process in which a system undergoes changes without change in pressure ,i.e. $\Delta P = 0$.

- Isochoric process is a process in which a system undergoes changes without change in volume i.e. $\Delta V = 0$.
- Adiabatic process is a process in which a system undergoes changes without addition or removal of heat from the system i.e. $\Delta Q = 0$.
- In a cyclic process, the sequence of operations on the system is carried out in such a manner that the system finally returns to its initial state.

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