

Physics-02 (Keph_201203)

1. Details of Module and its structure

Module Detail	
Subject Name	Physics
Course Name	Physics 02 (Physics Part 2, Class XI)
Module Name/Title	Unit 8, Module 3, First Law of Thermodynamics Chapter 12, Thermodynamics
Module Id	keph_201203_eContent
Pre-requisites	Internal energy, work, heat, thermodynamic system, open, closed and isolated systems, surroundings, macroscopic variables, equilibrium state, thermal equilibrium, temperature, path functions and state functions,
Objectives	After going through this module, the learner will be able to <ul style="list-style-type: none">• State the first law of thermodynamics• Apply the mathematical relation between internal energy, work and heat• Understand the relevance of the first law to gases• Extract information from PV indicator diagrams.• Identify different types of thermodynamic processes• Differentiate between reversible and irreversible processes
Keywords	First law of thermodynamics, internal energy, work and heat, PV indicator diagram, thermodynamical processes

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1. UNIT SYLLABUS

Unit 8: Thermodynamics

SYLLABUS

Chapter 12: Thermodynamics

Thermal equilibrium, definition of temperature (Zeroth law of thermodynamics), heat, work and internal energy. First law of thermodynamics, isothermal and adiabatic processes. Second law of thermodynamics: reversible and irreversible processes, Heat engine and refrigerator.

2. MODULE-WISE DISTRIBUTION OF UNIT SYLLABUS 6 MODULES

The above unit is divided into six modules for better understanding.

Module 1	<ul style="list-style-type: none"> • Thermal equilibrium • Heat exchange • Zeroth law of thermodynamics • Daily life observations
Module 2	<ul style="list-style-type: none"> • Relation between work and internal energy • Work on solids, liquids & gas • Relation between heat and internal energy • Molecular nature of heat and work
Module 3	<ul style="list-style-type: none"> • First law of thermodynamics • Relation between internal energy work and heat absorbed or released by a body • Relevance of first law to gases • P-V indicator diagram • Thermodynamic processes Isothermal, adiabatic, isobaric, isochoric, reversible and irreversible
Module 4	<ul style="list-style-type: none"> • Second law of thermodynamics • Heat engines • Carnot cycle • Efficiency of engines
Module 5	<ul style="list-style-type: none"> • Refrigerator • Heat machines -devices that produce heat geyser, toaster, stove –devices that operate on using internal energy
Module 6	<ul style="list-style-type: none"> • Understanding the thermal effect of heat and thermodynamics • Problem solving in thermodynamics

MODULE 3

3. WORDS YOU MUST KNOW

Molar specific heat capacity of a gas at constant volume: heat required to raise the temperature of one mole of a gas by unity, keeping its volume constant.

Molar specific heat capacity of a gas at constant pressure: heat required to raise the temperature of one mole of a gas by unity, keeping its pressure constant.

Thermodynamic system: Part of the universe that is center of attentions

Surroundings: everything in immediate or far environment of the system.

Boundary: surface separating the system from surroundings

Isolated system: system that can exchange neither energy nor matter with the surroundings

Closed system: system that can only exchange energy with the surroundings

Equilibrium state: a thermodynamic system is in equilibrium state if all the macroscopic variables that describe the system do not change in time and space.

Path function: Quantity whose magnitude depends on the path between the initial and final points/ states.

State Function: quantity whose magnitude depends only on the initial and final points/states and not on the path.

Internal energy: Sum of the potential and kinetic energies of molecules of the system, assuming centre of mass of the system to be at rest

Thermodynamic work: work that brings a change in the random motion of the molecules of a thermodynamic system and hence can change its internal energy.

Heat: energy in transit which is transferred due to temperature difference, without the need for any bulk movement of the system or its parts.

4. INTRODUCTION

A child has 20 wooden blocks in his play box. At the end of each day his mother counts the blocks, looks around for the missing ones and put them back in the box. One day the child gets angry and forbids her to poke her nose into his box! Forbidden to look inside the box, the mother finds an ingenious way. She weighs the box once with all the blocks

and then, looks for variations in its mass every day. The variation in mass alerts her about the missing blocks!

First law of thermodynamics is that ingenious tool which lets us track the changes in the internal energy of a system without having to count the energy of each molecule of the system.

In this module, we learn the law and its application to different thermodynamic processes.

5. FIRST LAW OF THERMODYNAMICS

Statement:

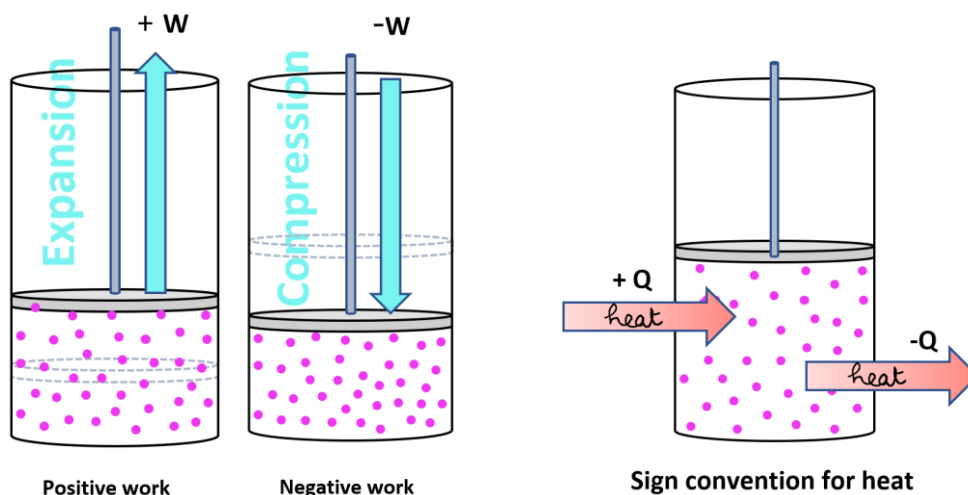
For a closed system, the change in internal energy is equal to the difference between the heat added to the system and the work done by the system, i.e.

$$\Delta U = Q - W$$

Here, ΔU is the change in internal energy; Q is the heat added and W is the work done by the system.

Points to note:

- There are only two ways of changing the internal energy of a system – either through work or through heat. This is like our bank balance, which can be changed through two instruments – either cash or a cheque!
- All the three quantities ΔU , Q and W must be in same units.
- Q is positive when the heat is gained by the system. W is positive when work is done by the system.



6. DIFFERENT INTERPRETATIONS OF THE FIRST LAW

There exists, for every thermodynamic system, a property called internal energy:

Heat (Q) and work (W) are path functions but their difference $Q - W$ is not a path function! If $Q - W$ depends only on the initial and final states and not on the process through which system passes from initial to final state, it means $Q - W$ must represent a state variable. This points to existence of a state variable for every thermodynamic system, namely, internal energy.

The law of conservation of energy applied to thermodynamics:

Law of conservation of energy in mechanics states that energy of an isolated system always remains conserved. The first law is the law of conservation of energy as applied to a closed system. It allows energy transaction with the surrounding by heating as well by doing work.

Energy of the universe is constant.

It follows from the fact the universe is an isolated system. An isolated system cannot exchange energy with the surroundings – neither as work nor as heat. Hence $Q - W = 0 = \Delta U$.

A bookkeeping device:

Processes in nature and in technology involve transformation of energy from one form to another. The first law provides a bookkeeping tool by which one keeps track of energy as it moves through successive transformations. The law tells us energy can neither be created nor be destroyed. If some energy in one form or one place disappears, the same amount must show up in another form or another place. For example, if a closed system loses some internal energy, we can always find it in the surroundings. It may have been given to the surroundings partly as heat and partly through work, but the energy given to the surroundings in different forms must always add up to the energy lost by the system.

Perpetual motion machine is an impossibility.

The law identifies as feasible, the processes in which energy is conserved and can be accounted for by the equation $\Delta U = Q - W$ and puts a restriction on the processes that do not conform to energy conservation equation. A perpetual motion machine proposes to run forever without any

energy source i.e. it is expected to perform work forever, by drawing on its internal energy, without any supply of heat or work. The experimental evidence for first law is the fact that even though countless have tried it, no one has succeeded in making a perpetual motion machine.

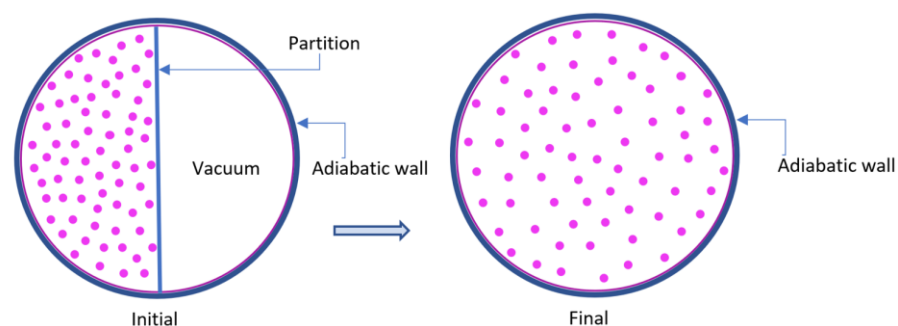
7. RELEVANCE OF THE FIRST LAW FOR GASES

We know that on applying heat to systems in any state its internal energy changes, the dimensions change (solids, liquids and gases expand on heating) the expansion in solids and liquids is small, so work done on or by them is very small. Gases on the other hand may be allowed to expand, depending upon whether they are in an enclosure of fixed volume or when the enclosure volume can be changed.

The first law of thermodynamics has the following implications for ideal gases:

There is no change in internal energy of a gas during free expansion with no heat exchange.

When a gas expands in vacuum, it is called free expansion. During free expansion into vacuum, the gas does not have to push against anything (there is no external pressure on it to push against) and hence work done $W = P \Delta V = 0$ as $P = \text{external pressure} = 0$.



Free expansion of a gas

When a gas sealed in an adiabatic container, expands in vacuum, adiabatic walls prohibit any heat exchange, hence $Q = 0$. From first law, we get,

$\Delta U = Q - W = 0$. Hence, the internal energy of a gas remains constant in free expansion with no heat exchange.

The internal energy of an ideal gas is independent of its volume if the temperature is kept constant.

Internal energy of a system is expected to depend on its pressure, volume and temperature but for ideal gases, the internal energy depends only on absolute temperature. Many

experiments have shown that when an ideal gas undergoes a free expansion, its temperature does not change. We just learnt how internal energy U remains constant during free expansion even though pressure P and volume V of the gas change. Since there is no change in U even when P and V change while T remains constant, we can conclude that U depends only on absolute temperature T , not on P or V .

For an ideal gas, molar specific heat capacities are related as $C_P - C_V = R$

Let us increase the temperature of n moles of an ideal gas by ΔT .

If volume of gas is kept constant, the heat required,

$$Q_1 = n C_V \Delta T$$

Work done by gas

$$W_1 = P \Delta V = 0 \quad \text{since volume is constant}$$

$$\text{From first law, } \Delta U_1 = Q_1 - W_1 = n C_V \Delta T$$

If the pressure of the gas (instead of volume) is kept constant

$$\text{Heat required for raising the temperature} = Q_2 = n C_P \Delta T$$

The gas will expand to keep the pressure constant. For volume changes ΔV , work done by gas $W_2 = P \Delta V$

$$\text{From first law, } \Delta U_2 = Q_2 - W_2 = n C_P \Delta T - P \Delta V$$

From ideal gas equation, $PV = nRT$

$$\text{Differentiating, } P \Delta V + V \Delta P = n R \Delta T$$

For constant pressure, $\Delta P = 0$, hence $P \Delta V = n R \Delta T$

$$\text{So, } \Delta U_2 = n C_P \Delta T - P \Delta V = n C_P \Delta T - n R \Delta T$$

Since the internal energy of an ideal gas depends only on temperature, for equal change in temperature ΔT , the change in internal energy must be same.

$$\text{Hence, } \Delta U_1 = \Delta U_2$$

$$\text{Or, } n C_V \Delta T = n C_P \Delta T - n R \Delta T$$

$$\text{Or, } C_P - C_V = R$$

This relation is called Meyer's formula.

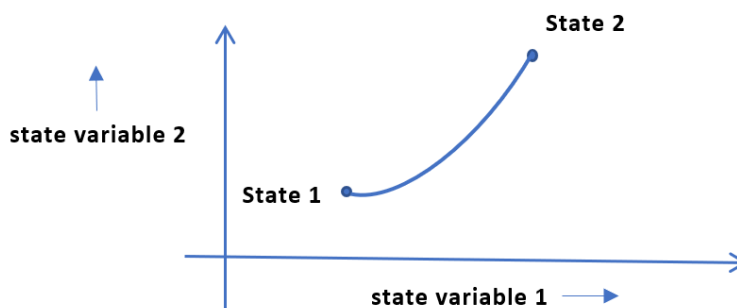
C_P is greater than molar specific heat at constant volume C_V , because heat must now be supplied not only to raise the temperature of the gas but also for the gas to do work, as in this case the volume changes.

8. THERMODYNAMIC PROCESS

A thermodynamic process is any operation or process that brings about a change in the equilibrium state of a thermodynamic system. Expansion, compression, heating, cooling etc. are some thermodynamic processes. Changes taking places inside our body, a pressure cooker and an engine are also thermodynamic processes.

The **initial state** of the system is defined by values of state variables (pressure, temperature, volume, number of moles) of the system before the change takes place. The **final state** of the system is defined by the values of state variables (pressure, temperature, volume, number of moles) of the system after the change has taken place. A process is said to have taken place whenever there is a change in any one or more of the state variables.

The locus of series of states through which a system passes during a process is called the **path of the process**. The figure below depicts the path of a process in which a system goes from state 1 to state 2.



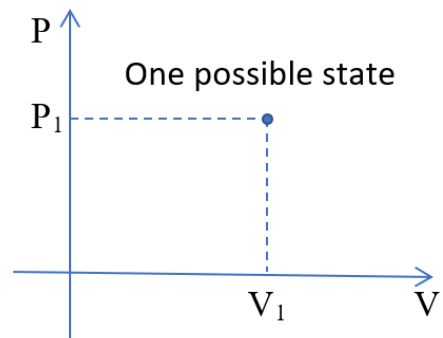
Thermodynamic process = Change in equilibrium state

9. P-V INDICATOR DIAGRAMS

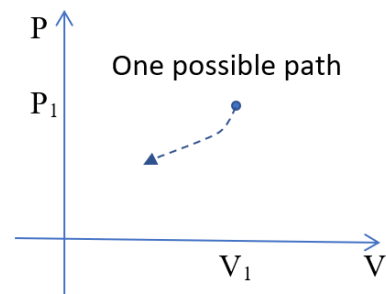
Pressure-Volume diagram (P-V diagrams) is a graphical representation of the state of a thermodynamic system using variables pressure and volume.

Consider a gas in a cylinder with a tightly fitting yet movable piston. We can do work on the gas by pressing the piston downward, and we can heat up the gas by placing the cylinder in a bath of boiling water. When subjected to these thermodynamics processes, the pressure and volume of the gas can change.

These changes are easily visualized by plotting a P-V diagram. Pressure is taken along the vertical axis and the volume, along the horizontal axis. A point on a P-V diagram corresponds to a set of pressure and volume coordinates and hence represents a specific state of the gas.



Every point on a PV diagram represents a different state of the gas. (one for every possible volume and pressure). As a gas goes through a thermodynamics process, the state of the gas shifts around on the PV diagram, tracing out a path as it moves. (see figure below).

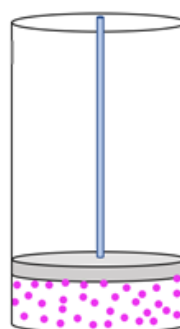
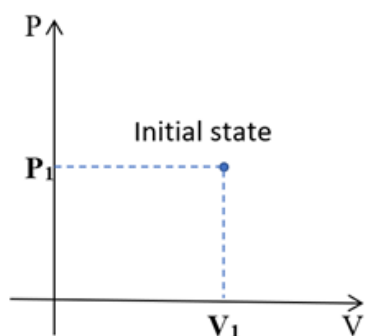


By decoding the information shown in P-V diagram, we can determine the change in internal energy of the gas ΔU , the heat exchanged Q and the work done W .

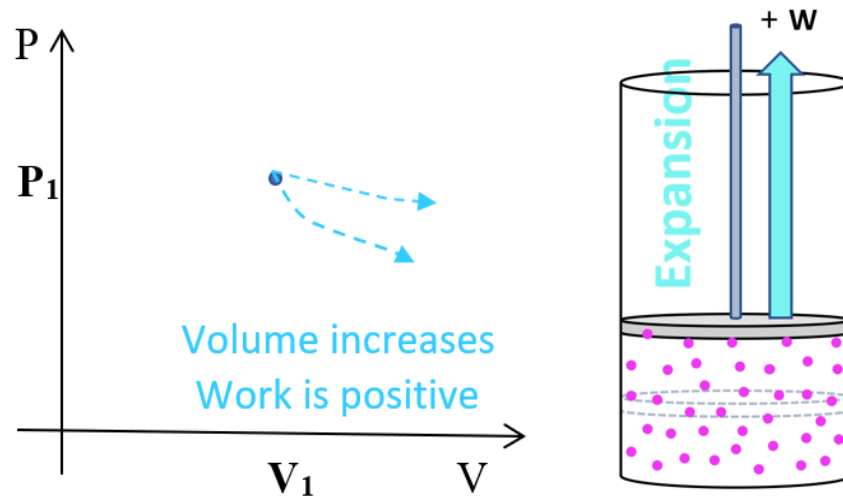
Deciphering information from P-V diagram:

A. Sign of work done:

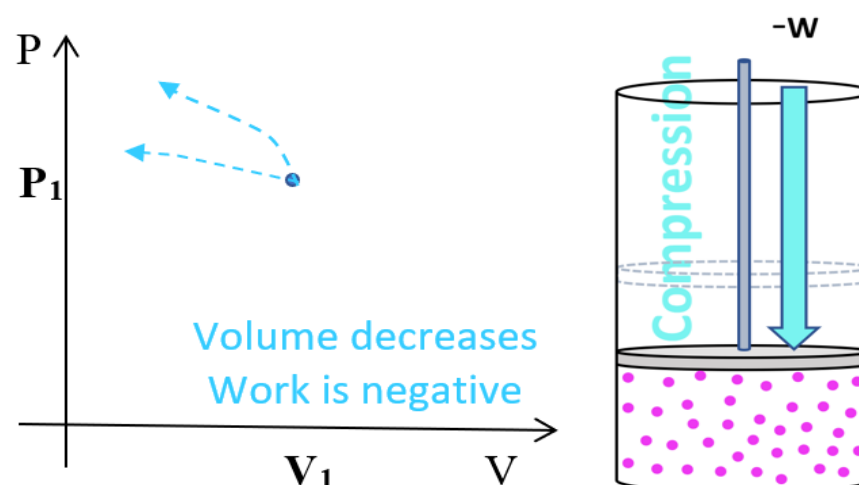
- Start from the initial state of the gas.



If the state shifts rightward on the P-V diagram, work done is positive. If the gas expands, pushing the piston upward, the volume of the gas increases, so on the P-V diagram, the state shifts to the right towards larger volume. Also, expansion means positive work done by the gas.

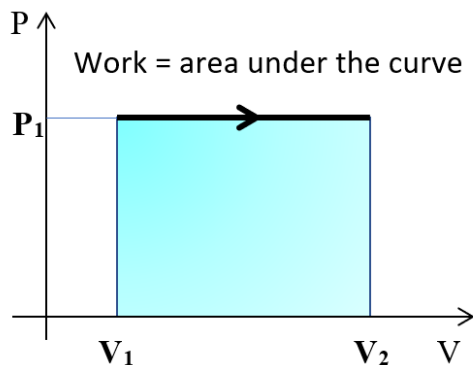


If the state shifts leftward on the P-V diagram, work done is negative. If the piston is pushed down, the volume of the gas decreases. So in the P-V diagram, the state shifts to the left towards smaller volume. Also, compression means negative work done on the gas.

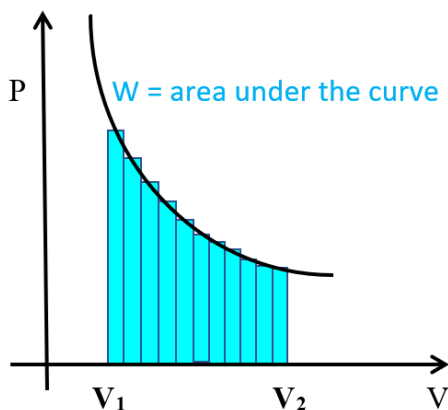


B. Magnitude of work done:

Magnitude of work done during a thermodynamic process is equal to the area under the curve.



$$\begin{aligned}
 W &= F \Delta x \\
 &= PA \Delta x \\
 &= P\Delta V \\
 &= P (V_2 - V_1) \\
 &= \text{height} \times \text{width of the rectangle} \\
 &\quad \text{on PV diagram}
 \end{aligned}$$



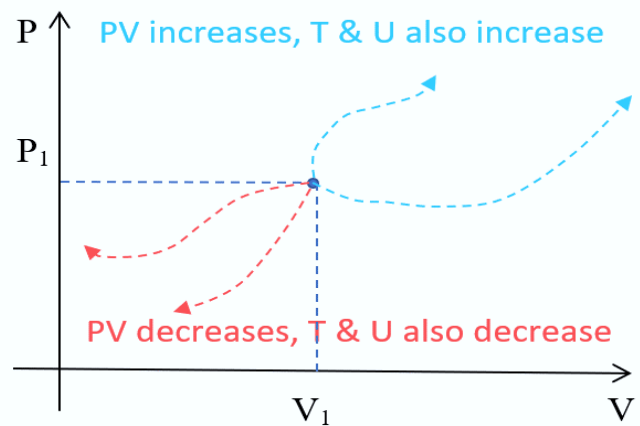
Work done = sum of areas of all rectangles

$$\begin{aligned}
 &= \int_{V_1}^{V_2} P \, dV
 \end{aligned}$$

C. Sign of ΔU

- Start from the initial state of the gas.
- If the final state on the P-V diagram ends up further right and up compared to the initial state, ΔU is positive. But if the final state ends up further left and down with respect to the initial state, ΔU is negative.

This is because internal energy is directly proportional to temperature and for an ideal gas, $PV = nRT$. So, for fixed amount of gas, $U \propto T \propto PV$. Hence, if the product PV increases, temperature T and internal energy U must also increase. This is indicated in blue on the PV diagram. Pink lines show the decrease in product PV , hence a decrease in temperature and internal energy.



If the final state ends up further left and up or, further right and down, the nature of change in product PV cannot be determined at a glance. In such a case, the exact values of P and V must be read on the graph axes to determine whether the product PV has increased or decreased or remained same

D. Sign of heat Q

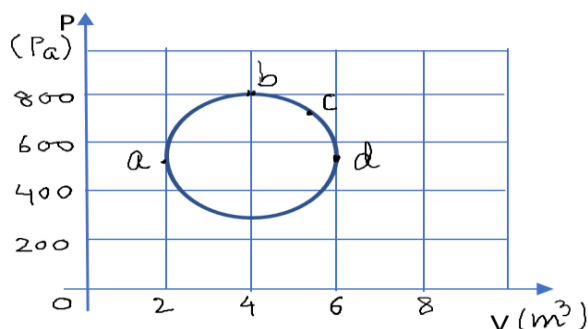
First use P - V diagram to determine the sign of W and ΔU as discussed above.

Then use $Q = \Delta U + W$ from the first law of thermodynamics to find the sign of Q .

CHECK YOUR UNDERSTANDING

EXAMPLE:

An ideal gas undergoes a process represented by the circle in the P - V Diagram, as shown in figure. At which of the following points the gas has the highest temperature?



- i. a
- ii. b
- iii. c
- iv. d

SOLUTION:

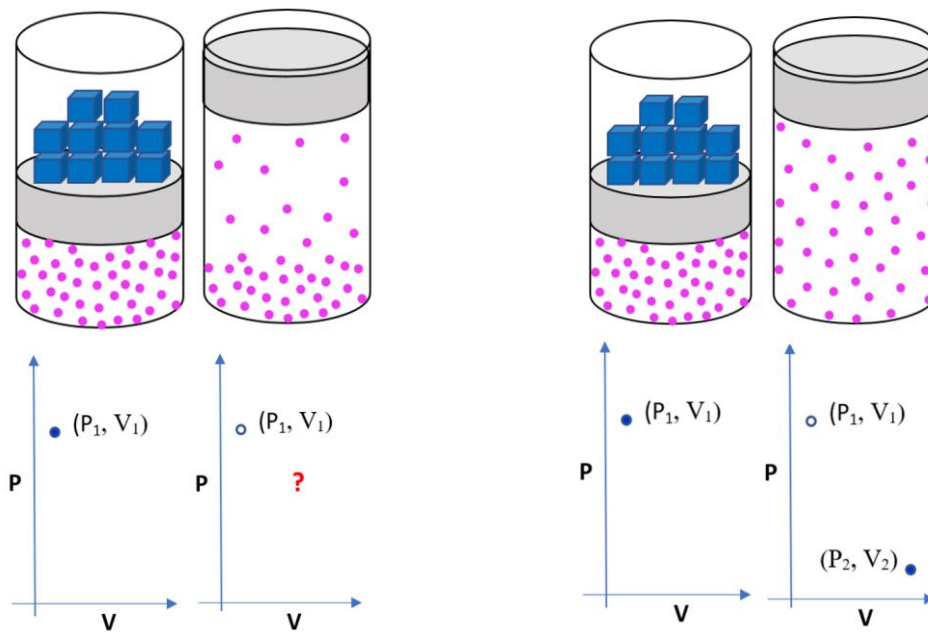
(iii.) c (Hint: product PV has maximum value at highest T)

10. QUASI-STATIC PROCESS:

A process so slow that the system is always in (or very close to) an equilibrium state. Quasi means almost and static means the thermodynamic properties/variables static with time.

All processes in thermodynamics must be quasi-static. Only infinite slowness of a process enables a system to have consistent value of a state variable throughout the system. Recall that the state of a system can be described only when the value of any state variable is constant in time and space.

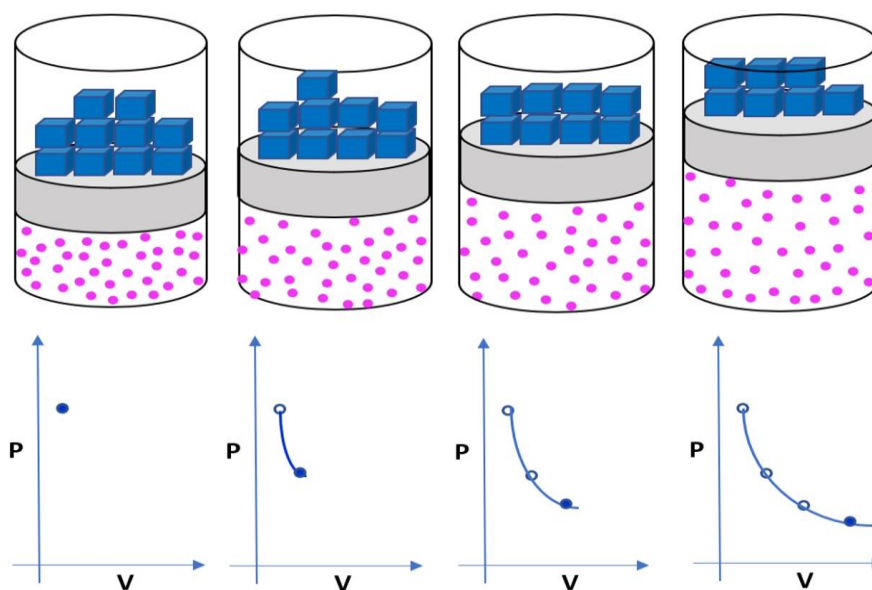
Consider a gas enclosed in a cylinder fitted with a movable piston. Many weights are kept on the piston. The piston is stationary, being push down by the weights and being pushed up by the gas by an equal amount. Its state is described by say (P_1, V_1) which can be depicted as a point on a P-V indicator diagram. If all the weights are suddenly removed, the piston rushes up due to the push by the gas. This happens so fast that the pressure near the piston reduces quickly whereas the pressure at the bottom still has the original value. The molecules at the bottom don't even realize that the weights at the top have been removed! There is a time in which pressure of the gas is not well defined, having different values at different places. The gas is not in equilibrium anymore and its state cannot be depicted as a point on the P-V diagram! Only after a long time the gas settles down to a single pressure throughout, say P_2 and its final state can be marked as a point on P-V indicator diagram again.



A sudden process – state variables not defined

A sudden process – state variables defined after a long time

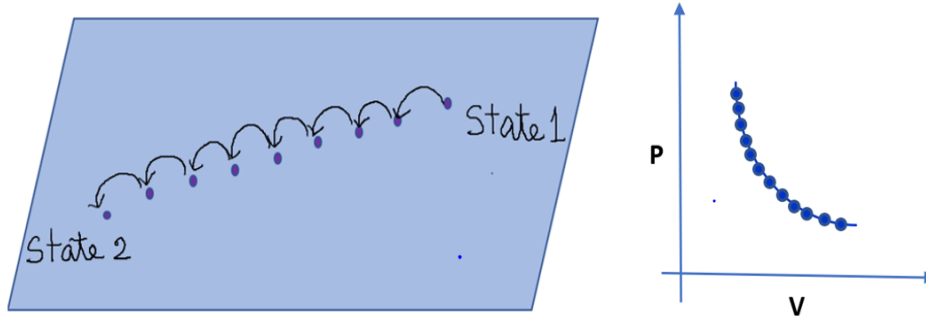
Instead, if we remove the weights one at a time and every time, give the gas sufficient time to equalize the pressure everywhere, the gas passes through a series of near equilibrium states during its journey from initial to final state. This allows us to define the state of the system at each instant during the process and deal with the process mathematically. The series of equilibrium states can be depicted as points in the P-V indicator diagram. (See figure below).



Quasi-static process – A series of near equilibrium states

In quasi-static process, conditions in the surroundings (pressure, temperature etc.) must be changed infinitesimally (like reducing the external pressure by removing weights, grain by grain!) so that the system needs to change only infinitesimally to achieve a new equilibrium state. In other words, the process must be infinitesimally slow, by changing conditions in the surroundings so infinitesimally that the system is always near equilibrium.

Quasi static is an idealized process where each point on the indicator diagram is an equilibrium state. It is a standard to which an actual process can be approximated and referred. We shall henceforth deal with quasi-static processes only, except when stated otherwise.



Representation of a thermodynamic system undergoing quasi-static process

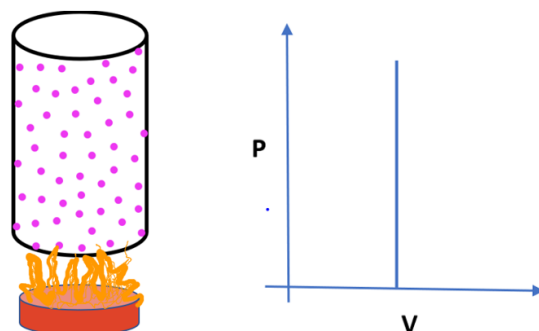
11. SOME THERMODYNAMIC PROCESSES & FIRST LAW

a. Isochoric process:

A process in which the volume of the system is kept constant i.e. $\Delta V = 0$.

Examples: 1. a gas heated in a rigid container 2. Processes in an individual biological cell are nearly isochoric.

Indicator diagram: For a system undergoing isochoric process, P-V indicator diagram is a straight line, perpendicular to volume axis. (If heat is added, pressure increases and vice-versa.)



An isochoric process

Work done in isochoric process:

The work done in isochoric process is zero. $W = \int P dV = 0$, since $dV = 0$.

Application of first law:

From first law, $\Delta U = Q - W$

Since $W = 0$, $\Delta U = Q$

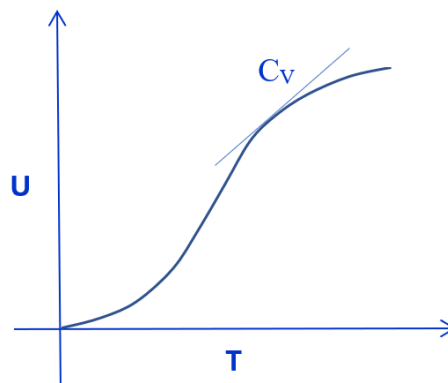
Also, $Q = n C_V \Delta T$

So, $\Delta U = n C_V \Delta T$

For one mole of matter, $C_V = \Delta U/\Delta T = \text{slope of } U \text{ vs } T \text{ graph}$

Also, $C_V = dU/dT$ if the slope of U vs T graph is variable

This implies: 1. in an isochoric process, all the heat gained by the system goes entirely to change its internal energy and its temperature 2. By measuring the heat required for a given change in temperature, we can measure the corresponding change in internal energy of a system. 3. For a given amount of heat absorbed, the change in temperature is determined by the specific heat of the system at constant volume. 4. Molar specific heat capacity of the system at constant volume is the slope of internal energy versus temperature graph.



b. Isobaric process:

A process in which the pressure is kept constant i.e. $\Delta P = 0$.

EXAMPLES: 1. Boiling water in an open vessel 2. A solid moth ball in a linen closet sublimating into an insect repelling gas,

Indicator diagram: For a system undergoing isobaric process, P-V indicator diagram is a straight line, parallel to volume axis.

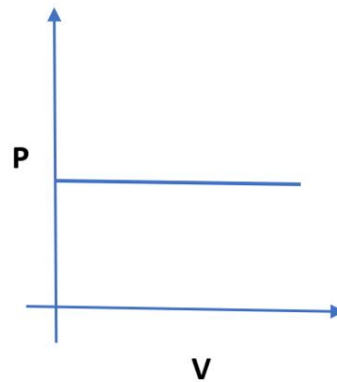


Photo credit: User: Yuksing Linked source: <https://www.flickr.com/photos/84622188@N00/503050990>

Water boiling in an open vessel: an isobaric process

Work done in isobaric process:

- For an ideal gas, work done in an isobaric process $W = P (V_2 - V_1)$.
Derivation: Suppose an ideal gas from its initial state (V_1, T_1) to a final state (V_2, P_2) at fixed pressure P . The work done by the gas

$$W = \int dW = \int P dV = nRT \int_{V_1}^{V_2} \frac{dV}{V} = P (V_2 - V_1) = nR (T_2 - T_1)$$

Application of first law:

From the first law $\Delta U = Q - W$ or $Q = W + \Delta U = P (V_2 - V_1) + \Delta U$

Also, $Q = n C_p (T_2 - T_1)$

This implies: 1. in an isobaric process, internal energy changes since the temperature changes. 2. The heat absorbed by the gas goes partly to increase internal energy and partly utilized for doing work 3. For a given amount of heat absorbed, the change in temperature is determined by the specific heat capacity of the gas at constant pressure.

c. Isothermal process:

A process in which the temperature of the system is kept constant i.e. $\Delta T = 0$.

In isothermal process, not only the initial and final temperatures are same, but the temperature is the same at each and every moment during the process.

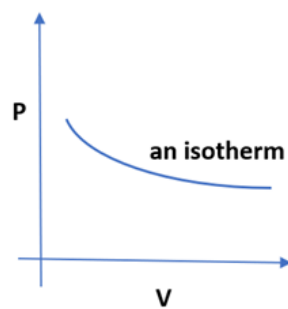
Consider this:

Boiling water in the open air, 2. Condensation, 3. all the changes that food undergoes in the refrigerator are isothermal as a constant temperature is maintained in it. 4. Expansion of a gas in a metallic cylinder placed in a large reservoir of fixed temperature.

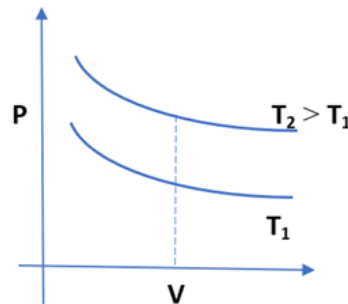
Indicator diagram: For an ideal gas undergoing isothermal process, P-V indicator diagram is a rectangular hyperbola. From ideal gas equation,

$$PV = \text{Constant for fixed temperature i.e. } P \propto 1/V.$$

The graph line is called an **isotherm**. An isotherm is higher at a higher temperature since the pressure of an ideal gas at a given volume is higher at higher temperature.

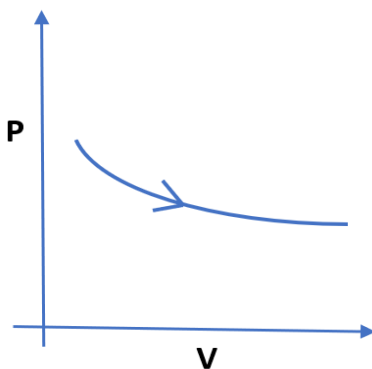


PV = constant

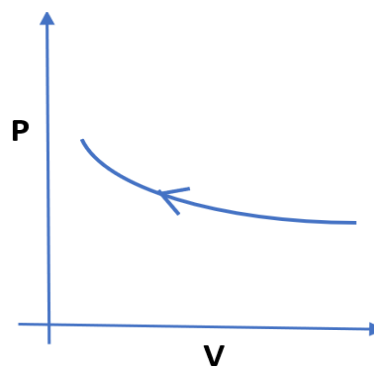


Isotherms at different temperatures

An isotherm can represent an isothermal compression or isothermal expansion by using an arrow.



Isothermal expansion



Isothermal compression

Work done in isothermal process:

- For an ideal gas, work done in an isothermal process $W = nRT \ln(V_2/V_1)$.

Derivation: Suppose an ideal gas goes isothermally (at temperature T) from its initial state (P_1, V_1) to a final state (P_2, V_2) . At any intermediate state with pressure P and volume change from V to $V + dV$, the work done

$$dW = P dV$$

Integrating for entire process, $W = \int dW = \int P dV = nRT \int_{V_1}^{V_2} dV/V = nRT \ln\left(\frac{V_2}{V_1}\right)$

- For non-ideal gases and other systems, work can be calculated as area under the graph in P-V diagram.

Application of first law:

For an ideal gas, the internal energy depends only on its temperature. Hence, for an isothermal process $\Delta U = 0$

From first law, $\Delta U = Q - W = 0$

Or, $Q = W$

That implies:

1. **In isothermal expansion all the heat gained by the gas is utilized in doing work on the surroundings.** Since the system uses all the energy it gained as heat, in doing work on surroundings, its temperature does not change.
2. **Isothermal process must be extremely slow to maintain constant temperature at all moments.** In practice, when the piston is pushed down, it must be done so slowly that heat has time to conduct out of the system.
3. **The product PV remains the same at each point on PV diagram** since $PV = nRT$ and T is constant at each point.
4. **Internal energy of the system is constant at all instants.**

d. Adiabatic process:

A process in which there is no exchange of heat or matter with the surroundings i.e. $Q = 0$.

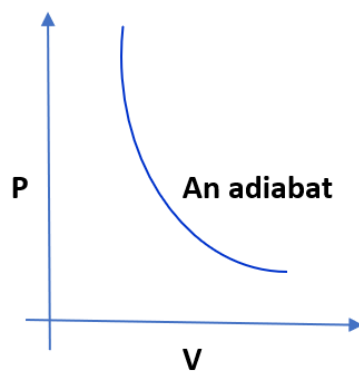
Processes happening very rapidly are nearly adiabatic since there is no time for heat exchange with the surroundings. For an adiabatic process to occur, the system must be completely insulated from surroundings. No heat exchange does not imply no temperature change.

EXAMPLES:

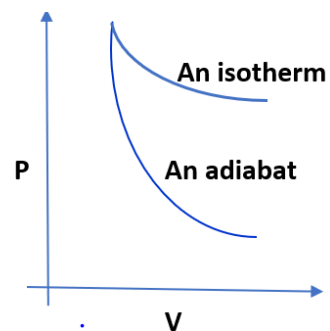
1. Vigorous shaking of tea in a thermos flask.
2. Adiabatic heating in Earth's atmosphere when an air mass descends on mountain slopes in katabatic or chinook wind.
3. Adiabatic cooling in Earth's atmosphere with orographic lifting during formation of lenticular clouds
4. Adiabatic demagnetization used for reaching one millionth of a degree above absolute zero.
5. Propagation of sound through air

Indicator diagram: For an ideal gas undergoing isothermal process, P-V indicator diagram is a curve. For adiabatic process of an ideal gas, $PV^\gamma = K = \text{Constant}$ ($\gamma = C_P/C_V$) i.e. $P \propto 1/V^\gamma$.

The graph line is called an **adiabat** i.e. an adiabat is steeper than an isotherm.

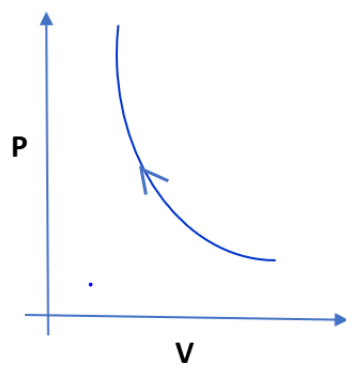


$PV^\gamma = \text{Constant} = K$

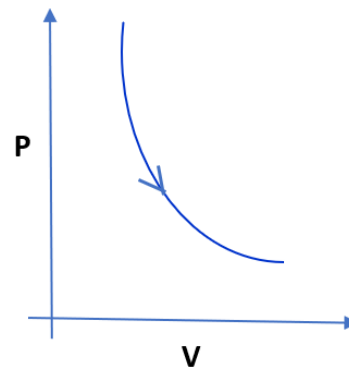


An adiabat is steeper than an isotherm

An adiabat can represent adiabatic compression or adiabatic expansion with an arrow.



Adiabatic compression



Adiabatic expansion

Work done in adiabatic process:

For an ideal gas, work done in an adiabatic process

$$W = \frac{nR(T_1 - T_2)}{(\gamma - 1)}$$

Derivation: Suppose an ideal gas goes adiabatically from its initial state (P_1, V_1, T_1) to a final state (P_2, V_2, T_2). At any intermediate state with pressure P and volume change from V to $V + dV$.

The work done during this volume change = $dW = P dV$

$$\begin{aligned} \text{Integrating for entire process, } W &= \int dW = \int P dV = \frac{KV^{-\gamma+1}}{(1-\gamma)} \Big|_{V_1}^{V_2} \\ &= \frac{K}{(1-\gamma)} \left[\frac{1}{V_2^{-\gamma+1}} - \frac{1}{V_1^{-\gamma+1}} \right] \\ &= \frac{1}{(1-\gamma)} \left[\frac{K}{V_2^{-\gamma+1}} - \frac{K}{V_1^{-\gamma+1}} \right] \\ &= \frac{1}{(1-\gamma)} \left[\frac{P_2 V_2^\gamma}{V_2^{-\gamma+1}} - \frac{P_1 V_1^\gamma}{V_1^{-\gamma+1}} \right] \\ &= \frac{1}{(1-\gamma)} [P_2 V_2 - P_1 V_1] \\ &= \frac{nR(T_1 - T_2)}{(\gamma - 1)} \end{aligned}$$

Application of first law:

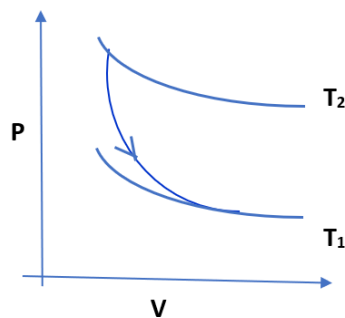
For an ideal gas, in an adiabatic process $Q = 0$

From first law, $\Delta U = Q - W = 0 - \frac{nR(T_1 - T_2)}{(\gamma - 1)}$

Or, $\Delta U = -W = \frac{nR(T_2 - T_1)}{(\gamma - 1)}$

That implies:

1. In adiabatic expansion, no heat is exchanged but temperature can still change.
2. The temperature of the gas drops as the gas uses its internal energy to perform work.
3. An adiabatic process takes the system from one isotherm to another (see figure below)



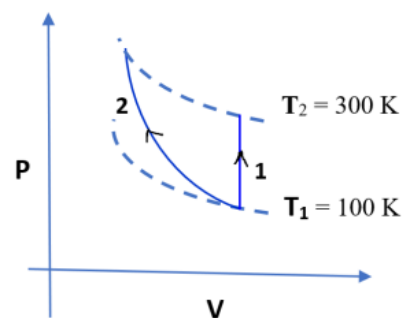
An adiabat operates between two isotherms

4. Adiabatic process must be very fast to not allow heat to escape. This is exact opposite of isothermal processes which must be very slow to allow time for heat to escape!

CHECK YOUR UNDERSTANDING

EXAMPLE:

An ideal gas is initially at temperature 100 K. It is taken to 300 K through two different processes 1 and 2 as shown in P-V diagram.



Answer the following.

- a. Name the two processes.
- b. In which process is the change in internal energy greater?

- c. In which process is the work done greater?
- d. In which process is the heat exchange greater?
- e. What is the ratio of heat exchanged in process 1 and the work done in process 2?

SOLUTION:

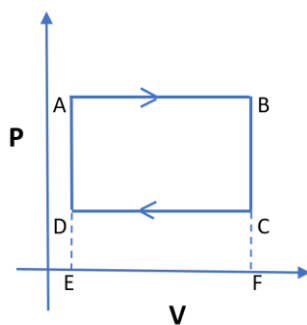
- a. Process 1 – isochoric, process 2 – adiabatic
- b. Equal change
- c. Process 2
- d. Process 1
- e. 1:1

e. Cyclic process:

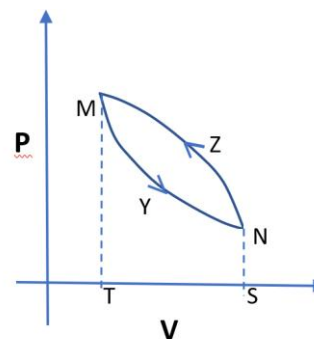
A process in which the system returns to its initial state after a series of intermediate processes and hence, $\Delta U = 0$.

Examples: processes in 1. Heat engine 2. Refrigerator 3. Air conditioner

Indicator diagrams: For a cyclic process, P-V diagram is a closed path. It is clockwise when expansion curve is above the compression curve. It is anticlockwise when the compression curve is above the expansion curve.



A cyclic process with positive work



A cyclic process with negative work

Work done in cyclic process:

Work done in clockwise cyclic process is positive whereas it is negative for anticlockwise cyclic process.

Work in cyclic process is summation of work done in each intermediate process and is equal to the area inside the loop on P-V diagram.

For example, work done in cyclic process of first figure = W_1

= work done in isobaric expansion AB + work done in isochoric process BC + work done in isobaric compression CD + work done in isochoric process DA

$$W_1 = \text{area ABFE} + 0 - \text{area CFED} + 0 \quad (\text{compression work is negative})$$

or, $W_1 = \text{area ABCD} = \text{area inside the loop}$

The net work done W is positive

Similarly, work done in cyclic process of the second figure = W_2

= work done in expansion MYN + work done in compression MZN

$$W_2 = \text{area MYNST} - \text{area MZNST}$$

= - area MZNYM = - area inside the loop

The net work done W is negative

Application of first law:

For an ideal gas, in a cyclic process, $\Delta U = 0$

From first law, $\Delta U = Q - W = 0$

Or, $W = Q$

It implies:

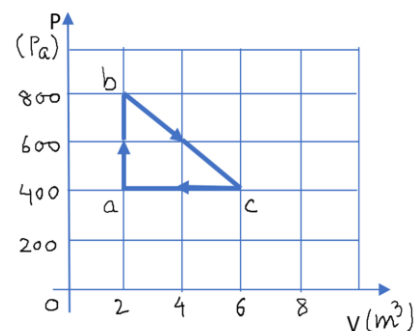
1. total heat absorbed by the system equals the work done by the system.
2. Net work is done by the system only during clockwise cyclic process.

CHECK YOUR UNDERSTANDING

EXAMPLE

One mole of an ideal gas is taken through a closed cycle $a \rightarrow b \rightarrow c \rightarrow a$. Use the given graph to find the following:

- (i) Temperature at point a.
- (ii) Sign and amount of work done in $c \rightarrow a$
- (iii) Sign and amount of work done in entire cycle.
- (iv) Change in internal energy for the entire cycle
- (v) Sign and amount of heat transferred.
- (vi) Part of cycle with no work.



SOLUTION:

- (i) 96.4 K (Hint: $PV = nRT$)
- (ii) $W = -800 \text{ J}$
- (iii) $W = +800 \text{ J}$ (Hint: $W = \text{area inside the loop, expansion curve above compression}$)
- (iv) $\Delta U = 0$
- (v) $Q = +800 \text{ J}$ (Hint: $\Delta U = Q - W$)

(vi)a \rightarrow b

12. REVERSIBLE & IRREVERSIBLE PROCESSES:

Reversible process

A reversible process is defined as a process in which the system remains close to equilibrium at all times and an infinitesimal change of conditions in the surroundings restores the system as well as the surroundings to their original state.

It is a process that can be reversed without leaving any change in the surroundings and at the end of the reverse process, both system and surroundings are returned to their initial states.

A process is reversible if the system can be made to retrace its path such that any change occurring in any part of the direct process is exactly reversed in the corresponding part of the reverse process. If some heat is absorbed by the system in direct process, the same amount must be released to the surroundings in the reverse process at each step. If some work is done by the system in the direct process, an equal amount must be done by the surroundings on the system in the reverse process. At the end of the reversible process, both the system and the surroundings must be back to their initial state.

For a reversible process, two conditions are necessary:

1. **The process must be quasi-static.**
2. **Dissipative factors should be absent.**

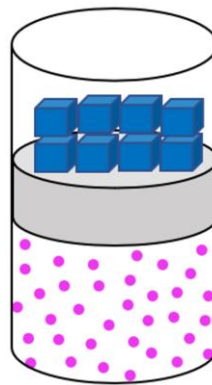
Some dissipative factors are: Friction, heat transfer across finite temperature difference, free expansion.

Why reversible process must be quasi-static?

A quasi-static process can extract maximum work from the system in going from one state to another. Also, it requires minimum work by the surroundings to create a

change in state. This is because the system is always very close to equilibrium and the desired change is infinitesimal.

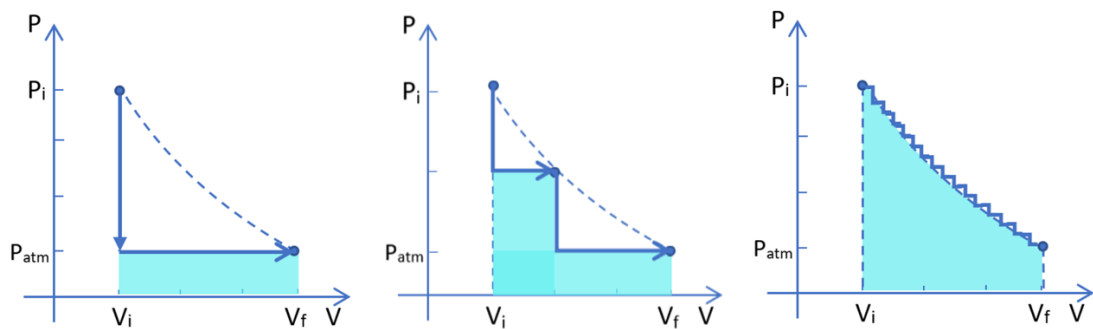
Consider an ideal gas in a thermally insulated container. The gas is contained by a thermally insulated massless frictionless piston with a stack of many small weights on top of it. Initially the system is in mechanical and thermal equilibrium with the surroundings.



Let us compare some processes that do work between two states and understand how the quasi-static produces maximum work.

Consider the following three processes:

- **All the weights are removed from the piston suddenly and the gas is allowed to expand until its volume is increased four times. (a free expansion).**
- **Half the weights are removed from the piston instantaneously; the system is allowed to double in volume. Then, the remaining halves of the weights are instantaneously removed from the piston and the gas is again allowed to expand till its volume doubles again.**
- **One small weight is removed from the piston at one time and enough time is given before removal of the next small weight. This way the reduction in external pressure on piston is small and gas needs to expand only by small amount to equalize the pressure on the piston. The gas is very close to being in equilibrium with the surrounding. When the last weight is removed, the volume has increased by a factor of four.**



Maximum area under the curve obtained in quasi-static process

From the corresponding P-V diagrams of the three processes, shown above, it is quite clear that maximum area under the curve is obtained for quasi-static process. Hence quasi-static process extracts maximum work from a system.

How dissipative factors affect reversibility of a process?

Friction & viscous forces

Suppose in the previous example of ideal gas in a container, the piston is not frictionless. When the piston is allowed to move up by removing weights, a certain amount of work is done by the gas. Some of the work is required to overcome friction between the piston and the container walls and the rest is utilised to push the piston.

The piston can be restored to its initial position by adding the weights back on the piston. The gas is restored to its initial volume, but its temperature has risen due to heat generated by friction. To restore the gas to its initial temperature, some heat must be released to the surroundings.

Since the temperature of the surroundings is now more, surroundings are not restored to their initial state at the conclusion of the reverse process. No heat is supplied by the surroundings in the forward process, but heat is being given to surroundings in the reverse process. Hence, we conclude that friction has rendered the process irreversible.

Heat Transfer through a finite temperature difference

Consider a system of two bodies – one at high temperature and another at low temperature. Let heat be transferred from the high-temperature body to the low-

temperature body. The only way in which the system can be restored to its initial state is through refrigeration, which requires work from the surroundings, and in the process some heat transfer to the surroundings will also take place. Because of the heat transfer and the work, the surroundings are not restored to their original state. Hence the heat transfer through a finite temperature difference is irreversible.

Interestingly, heat-transfer process approaches a reversible process as the temperature difference between the two bodies approaches zero. Therefore, a reversible heat transfer process is one in which the heat is transferred through an infinitesimal temperature difference. It should be noted that if the difference between the temperatures of two bodies is infinitely small, the rate of heat transfer between them will also be infinitely small. Hence, transfer of a finite amount of heat through an infinitesimal temperature difference would require an infinite amount of time or an infinite area.

Reversible processes do not occur; they are only idealizations of actual processes. We use reversible process concept because, a) they are easy to analyse (since system passes through a series of equilibrium states) b) they serve as limits (idealized models) to which the actual processes can be compared.

Irreversible process:

- An irreversible process is one that is carried out in such a way that the system and surrounding cannot be exactly restored to their respective initial state at the end of the reverse process.
- The change takes place without the system being in equilibrium with its surroundings at any stage during the change.
- In an irreversible the surrounding would always be affected by loss of work and gain of low temperature heat, which is unusable heat for the surrounding.
- The irreversibility of a process may be due to either lack of equilibrium or due to involvement of dissipative factors or both.

LIMITATION OF THE FIRST LAW

- A. First law of thermodynamics does not differentiate between heat and work. In theory, it allows full convertibility of one into other. But in practice, even
- B. **Though work can be completely converted into heat but full conversion of heat into work is not possible.**
- C. First law of thermodynamics is silent about the direction or spontaneity of a process. For example, heat transfer from low temperature body to high temperature body is not forbidden by first law if the heat lost by cold body is equal to the heat gained by hot body. But in nature this reverse process does not occur. Spontaneity of the process is not taken care of by the first law of thermodynamics.

13. SUMMARY

- For a closed system, the change in internal energy is equal to the difference between the heat added to the system and the work done by the system, i.e. $\Delta U = Q - W$.
- For an ideal gas, $C_p - C_v = R$
- A thermodynamic process is any operation that changes the equilibrium state of a thermodynamic system.
- Pressure Volume diagram (P-V diagrams) is a graphical representation of the state of a thermodynamic system using variables pressure and volume.
- Every point on a P-V diagram represents a specific state of the system. As a system under goes a thermodynamics process, the state of the gas shifts around, tracing out a path on the PV diagram.
- On P-V diagram, rightwards shifting path indicates positive work. Area under the curve gives the magnitude of work.
- On P-V diagram, path shifting right and up indicates positive change in internal energy ΔU .
- Quasi-static process is a process so slow that the system is always in (or very close to) an equilibrium state. All processes in thermodynamics must be quasi-static.
- Isochoric process: process at constant volume.
- Isobaric process: process at constant pressure.

- Isothermal process: process at constant temperature.
- Adiabatic Process: process with no heat exchange.
- Cyclic Process: process in which system returns to initial state after series of intermediate processes.
- A system does no work during free expansion.
- Reversible process: process in which the system remains close to equilibrium at all times and an infinitesimal change of conditions in the surroundings restores the system as well as the surroundings to their original state.
- Maximum possible work between two states is extracted in reversible process. Reversibility possible only with quasi-static processes and absence of dissipative factors.
- First law of thermodynamics is silent about the direction or spontaneity of a process.