## 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 2, Internal Energy Chapter 12, Thermodynamics |
| Module Id | keph_201202_eContent |
| Pre-requisites | Work, kinetic energy, potential energy, thermodynamic system, open, closed and isolated systems, adiabatic and diathermic walls, macroscopic variables, equilibrium state, thermal equilibrium, heat, temperature, |
| Objectives | After going through this module, the learner will be able to <br> - Differentiate between path function \& state function. <br> - Classify thermodynamic variables as extensive or intensive variables <br> - Understand the conceptual difference between internal energy and total mechanical energy of a thermodynamic system <br> - Distinguish between work and heat as tools of changing equilibrium state. <br> - Understand the relationship of work and heat with internal energy qualitatively <br> - Compare the molecular nature of heat and work |
| Keywords | Thermodynamic variables, internal energy, |

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## 1. UNIT SYLLABUS

## UNIT 8: THERMODYNAMICS

## SYLLABUS

## Chapter 12: Thermodynamics

Thermal equilibrium and 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 <br> 6 Modules

| Module 1 | • Thermal equilibrium <br> $\bullet \bullet$ <br> • Heat exchange <br> • Zeroth law of thermodynamics |
| :--- | :--- |
|  | Daily life observations |


|  | or released by a body <br> - Relevance of first law to gases <br> - P-V indicator diagram <br> - Thermo-dynamical processes Isothermal, adiabatic, isobaric, isochoric, reversible and irreversible |
| :---: | :---: |
| Module 4 | - Second law of thermodynamics <br> - Heat engines <br> - Carnot cycle <br> - Efficiency of engines |
| Module 5 | - Refrigerator <br> - Heat machines -devices that produce heat geyser, toaster, stove - devices that operate on using internal energy |
| Module 6 | - Understanding the thermal effect of heat and thermodynamics <br> - Problem solving in thermodynamics |

## 3. WORDS YOU MUST KNOW

Work: measure of energy transfer that occurs when a force displaces an object in its own direction, given by $W=\int \mathbf{F} . \mathbf{d r}$

Work-kinetic energy theorem: work done by all the forces acting simultaneously on an object equals the change in kinetic energy of the object.

Potential energy: energy stored in a system by virtue of change in its configuration when work is done against a conservative force.

Specific heat capacity: heat required to raise the temperature of unit mass of a substance by unity.

Molar specific heat capacity: heat required to raise the temperature of one mole of a substance by unity.

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

Latent heat: heat required to change the state of unit mass of a substance at constant temperature.

Thermodynamic system: Part of the universe that is under consideration.

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

Boundary: surface separating the system from surroundings

Open system: system that can exchange matter and energy with the surroundings

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

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

Adiabatic wall: boundary that prevents heat exchange

Diathermic wall: boundary that allows heat exchange

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.

Temperature: the fundamental property of every system which directs heat flow between any two systems.

## 4. INTRODUCTION

Internal energy, work and heat are three concepts critical for manipulating the state of a thermodynamic system to our advantage. In this module, we first look at some definitions and then explore internal energy, work and heat in detail.

## 5. PATH FUNCTIONS \& STATE FUNCTIONS

Macroscopic variables of thermodynamics can be either path functions or state functions. Path functions are those quantities whose magnitudes depend on the path followed during a process as well as the initial and final points/ states. State functions are those quantities whose magnitudes depend only on the initial and final points/states and not on the path/process followed.

Consider the case of a football player running from position 1 to position 2 in a football field. His final position with respect to the initial position is a state function because it will remain the same irrespective of the path he chooses to reach it. On the other hand, the distance moved by him from the position 1 to position 2 will depend on the
 route followed by him to reach his position; hence the distance is a path function.

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## 6. STATE VARIABLES IN THERMODYNAMICS

The variables used to describe the equilibrium states of a thermodynamic system are called the state variables because they are state functions.

For example: the volume of a gas.
The Volume $\mathbf{V}_{\mathbf{f}}$ of the gas in figure below

does not depend upon whether it was brought to this state via Process A or via Process B. Hence volume is a state variable.

State (describing condition) variables are of two kinds: Extensive and intensive.
Extensive: state variables whose value depends on the size of the system. For example, volume, mass. They get doubled if we double the quantity of matter.
Intensive: state variables whose value does not depend on the size of the system. For example, density, pressure, temperature. Density of mercury is always $13.6 \mathrm{~g} / \mathrm{cm}^{3}$ whether we take 100 ml portion or 200 ml portion.

The various state variables are not necessarily independent. The mathematical relation between state variables is called the equation of state.

For example, for an ideal gas, the equation of state is the ideal gas relation $\mathbf{P V}=\mathbf{n R T}$.
The state of a given ideal gas, i.e. for given $\mathbf{n}$ moles, can be completely described if only two variables $P$ and $V$ are known- the third variable $T$ gets fixed automatically.

The relationship between variables can be also expressed through graphs.

A graphical representation of the state of a system using pressure and volume is called an indicator diagram.

For example, the indicator diagram
(a) Describes various states of a system undergoing expansion. Each point on the curve represents a state of the system characterised by coordinate values ( $\mathrm{P}, \mathrm{V}$ ). Graphical representation of the state of a system using pressure and temperature is called a phase diagram.
(b) Indicates pressure and temperature relationship for various states of a thermodynamic system.

(a) Indicator diagram

(b) Phase diagram

## 7. INTERNAL ENERGY

Internal energy is the thermodynamic property of a system which arises from the potential and kinetic energies of molecules of the system. Potential energy of molecules here is the result of work done against intermolecular forces only. Kinetic energy of molecules here is the energy associated with internal vibrations, translation, tumbling, twisting of molecules of the system.

In internal energy, we are not referring to the total potential energy and kinetic energy of the molecules. Instead, we are focusing on that part of the energies which arise from dynamics of internal forces alone.

The total potential energy ( $\mathrm{U}_{\text {total }}$ ) of the molecules comes from two sources -
(a) Their collective, potential energy $\left(\mathbf{U}_{\mathbf{C M}}\right)$ as part of a system.

This is acquired due to external work done on center of mass of the system against some conservative force e.g. is gravitational potential energy of an object when center of mass is raised to a height ' $h$ '.
(b) Their individual potential energies due to intermolecular forces.

These are continuously changing because of changing intermolecular distances as molecules vibrate/translate/rotate randomly. Internal potential energy ( $\mathrm{U}_{\text {internal }}$ ) refers to contribution from source (b) only.

We can say

$$
\mathbf{U}_{\text {total }}=\mathbf{U}_{\mathbf{C M}}+\mathbf{U}_{\text {internal }}
$$

See figures below.


Similarly, the total kinetic energy $\mathbf{K}_{\text {total }}$ of the molecules comes from two sources -
(a) Their collective kinetic energy $\left(\mathrm{K}_{\mathrm{CM}}\right)$ of organized motion due to motion of center of mass
(b) Their individual kinetic energies of

- random
- vibratory
- translatory
- tumbling
- twisting


## motions under intermolecular forces.

Internal kinetic energy ( $\mathrm{K}_{\text {internal }}$ ) refers to contribution from source (b) only.

We can say

$$
\mathbf{K}_{\text {total }}=\mathbf{K}_{\mathbf{C M}}+\mathbf{K}_{\text {internal }}
$$

See figure below.


Internal Kinetic Energy $=K_{\text {internal }}$
molecules $\longleftrightarrow$ random oscillations $\longrightarrow$ translation due to motion of center of mass
$K_{\text {internal }}=$ Kinetic energy of disorganized motion of molecules under intermolecular forces
$\mathrm{K}_{\mathrm{CM}}=$ Kinetic energy of organized motion of molecules due to motion of center of mass

The total mechanical energy of molecules of the system is
$\mathbf{E}_{\text {total }}=\mathbf{U}_{\text {total }}+\mathbf{K}_{\text {total }}$
$=\left(\mathbf{U}_{\mathbf{C M}}+\mathbf{U}_{\text {internal }}\right)+\left(\mathbf{K}_{\mathrm{CM}}+\mathbf{K}_{\text {internal }}\right)=\left(\mathbf{U}_{\mathrm{CM}}+\mathbf{K}_{\mathrm{CM}}\right)+\left(\mathbf{U}_{\text {internal }}+\mathbf{K}_{\text {internal }}\right)=\mathbf{E}_{\mathrm{CM}}+$

## $\mathbf{E}_{\text {internal }}$.

Internal energy of the system is $\mathrm{E}_{\text {internal }}$ which is the energy of disorganized motion of molecules when center of mass is assumed to be at rest.

We will henceforth represent it by $U$.

Internal energy (U) is a state variable.
It depends only on the state of the system and not on how that state was achieved. For a given mass of a gas, its internal energy depends only on the state of gas described by specific values of pressure, volume and temperature.

The concept of internal energy is an accounting tool. It saves us the tyranny of keeping track of potential and kinetic energy of each single molecule of the system. Measuring absolute internal energy is virtually impossible but if we keep account of the changes in internal energy, the accounting of individual energies of molecules gets done automatically.

How can we change the internal energy of a thermodynamic system? Heat and work are the only methods available for this. For example, how do we warm our numb hands on a cold winter night? Either rub them together or warm them over fire. Rubbing relates to 'work' and warming over fire refers to 'Heat'.

## CHECK YOUR UNDERSTANDING

EXAMPLE:

Internal energy of an object is the total of
a. Its gravitational potential energy and energy of its motion
b. Net potential energy and net kinetic energy of its molecules
c. Net potential and net kinetic energy related to jiggling of its molecules
d. None of these

## SOLUTION:

c. Net potential and net kinetic energy related to jiggling of its molecules

EXAMPLE:
Is Internal energy an extensive variable or intensive?

## SOLUTION:

Extensive

## 8. WORK

Work is a key player in energy dynamics of thermodynamic systems.
Work can be done by the surroundings on a thermodynamic system or by the system on the surroundings. When surroundings apply a force on the system and displace the whole system or a part of the system, work is done on the system. If the system applies force on the surroundings and produces displacement in the surroundings, the work is done by the system.

By convention, the work done by the system on the surroundings is taken as positive and the work done on the system by the surroundings is taken to be negative.

Work is not a state variable. It is meaningless to say, 'a gas in a given state has a certain amount of work'. It does not characterise the state of a system. A more meaningful statement is 'a certain amount of work was done by the system'.

Work changes the energy of a thermodynamic system. When work is done by surroundings on a thermodynamic system, it gains energy but when work is done by the system on the surroundings, the system loses energy. For example, when a hot iron piece in a stationary cylinder pushes the piston outward, the gas loses energy. If the piston is pushed inwards, the gas molecules gain energy.

Thermodynamic work refers to that work only which can change the internal energy of a thermodynamic system. Every work may not change the internal energy of a thermodynamic system, even though it will certainly change its total energy.

## Consider a gas in a cylinder,

fitted with a movable piston, lying on a table.
If the gas cylinder is pushed, it moves along the table.
All the gas molecules also move along with the cylinder.
The work done by the external force increases the kinetic energy of forward motion of gas molecules.

As a result, their total mechanical energy increases, but not their internal energy.

Internal energy does not include the kinetic energy arising out of collective organised motion!

So, the work which brings a change in organised motion of the molecules of a thermodynamic system does not change its internal energy.

Next, the cylinder is kept stationary and the piston is moved inward. It pushes the gas molecules which collide with it and imparts them acceleration in forward direction. But since the molecules were already moving in haphazard directions before colliding, the velocities after collision are still in random directions. So, the work done by the piston affects the random motion of the molecules and hence the internal energy of the system.

We conclude, only the work that brings a change in the random motion of the molecules of a thermodynamic system, can change its internal energy. Now onwards, the word 'work' will refer to this type of thermodynamic work only.

(a)

(b)
(a)Forward motion of the whole cylinder increases kinetic energy of organized motion (b) Inward motion of the piston increases the kinetic energy of random motion.

## DIFFERENT MODES OF DOING WORK ON THERMODYNAMIC SYSTEMS

Work can be performed on a thermodynamic system to change its state via many modes - compression/expansion work, electrical work etc.

Let us get a feel of some of them and learn to calculate the work done in each case.
WORK ON A GAS

Work done on a gas or by a gas is often called compression-expansion work or pressure -volume work and is calculated as

$$
\mathbf{W}=\int \mathbf{P} \mathbf{d V}
$$

where $P$ is the external pressure and $V$ is the volume of the gas.
Consider a gas in a cylinder fitted with a frictionless piston of cross-sectional area A.
Let the external pressure on the piston at a given instant be P .
The gas must exert a force $\mathrm{F}=\mathrm{PA}$ on the piston to move it. In moving the piston outward an infinitesimally small distance dx , small work done on the piston by the gas is $d W=F d x=P A d x=P d V$ where $d V$ is the infinitesimal change in the volume of the gas when piston is moved by dx .

The volume of the gas changes from $\mathbf{V}_{\mathbf{i}}$ to $\mathbf{V}_{\mathbf{f}}$ as the piston moves from its initial position to final position inside the cylinder. The net work done in expansion of the gas is

$$
\mathbf{W}=\int \mathbf{d W}=\int_{\mathbf{v}_{\mathbf{i}}}^{\mathbf{v}_{\mathbf{f}}} \mathbf{P d V}
$$

The work done is also equal to the area under P-V graph.


WORK ON A LIQUID

The state of a liquid may be changed by making it fall through a height, or by stirring or by using an electric immersion rod in it.

Work done in each case can be calculated by realizing that all work is equivalent to work done in lowering/raising of an object through a certain height.

## When a block of mass $\mathbf{m}$ falls or rises through height $h$,

## Work done is $\mathbf{W}=\mathbf{m g h}$

where mg is the force and h is the height through which the block moves.
Churning can be carried out using a falling weight as shown in figure.

As the weight falls, the paddles in the liquid rotate and churn it. Work done on liquid is equivalent to the work done by falling weight i.e. $\mathrm{W}=\mathrm{mgh}$.


## WORK ON SOLID

Thermodynamic work is done on a solid when motion of a moving object is suddenly stopped and the kinetic energy of motion is converted into internal energy of the solid.

For example, when a falling stone hits the ground, its external kinetic energy is transformed into the internal kinetic energy of molecules and its temperature rises. Another example is that of a bullet striking a solid wooden block. As the moving bullet is stopped by the friction, some of the external kinetic energy of the moving bullet gets converted into internal energy of the block and some gets converted to internal energy of the bullet itself - this is evident from the rise in temperatures of the wooden block and the bullet. In mechanics, we have already learnt how to calculate the work done by friction on a bullet when it pierces a solid.

## WORK, CHANGE OF EQUILIBRIUM STATE AND INTERNAL ENERGY

Same amount of work, regardless of the method, brings about the same change in equilibrium state of a thermodynamic system. Let us understand this through an experiment on an adiabatic system. Suppose we take some amount of water in a long, insulated glass jar sealed at both ends. We measure the temperature of water, invert the jar repeatedly (Fig a) and note the change temperature that this activity brings about. Work done is calculated as $\mathrm{W}_{1}=\mathrm{n}$ mgh, where n is the of times the jar is inverted, mg the

(a)

(b)

(c) weight of water and $l$ is the length of the jar through which the water falls. Then we remove the insulation and allow the water to return to its original state. Next, we place paddles in the water in insulated jar and churn it, by making the connected weights fall (Fig b) through a distance which results in work $\mathrm{W}_{2}=\mathrm{W}_{1}$. The work $\mathrm{W}_{2}$ is calculated as $\mathrm{W}_{2}=\mathrm{Mgh}$ where Mg is the weight and h is the distance through which it falls. The temperature of the water is noted. Again, we remove the insulation and allow the water to return to original temperature. Next, we replace the insulation and insert a heating rod into the system (fig c) and pass current for a time duration that results in work done $\mathrm{W}_{3}=\mathrm{W}_{2}=\mathrm{W}_{1}$. The work $\mathrm{W}_{3}$ can be calculated using the method described in previous paragraph. Again, the final temperature of the system is noted. The experimental observations show that the temperature of the system changes by the same amount in all the three cases.

This situation is like climbing a mountain via different paths.
Suppose three friends A, B and C are at the base of a mountain.
They must reach a camp located higher on the mountain.
A decides to climb up the stairs leading straight to the camp

## $B$ rides a bike up a meandering trail and

$C$ takes the bus on the road around the mountain.
Each of them opts for a different mode of travel but in all three cases there exists a quantity which changes by the same amount - altitude.

Clearly, altitude is a state function.
Hence, it is possible to assign a number to altitude associated with each level on the mountain and calculate the height moved, regardless of the path taken, by finding the difference of altitude between the initial and final positions.


The same applies to our experiments with water.
Adiabatic work is done via three different modes but the change in state of water is the same in each case i.e. the change in state is path independent. This means there exist a quantity which changes by same amount in all three cases and must depend on the state. This quantity must be internal energy (U). Hence, it is possible to assign a number to internal energy associated with each state of the system and calculate the adiabatic work required to go from one state to another by
$\mathbf{W}=\mathbf{U}_{\text {final }}-\mathbf{U}_{\text {initial }}$.

## CHECK YOUR UNDERSTANDING

## EXAMPLE:

An ideal gas is taken from state $S_{1}$ to $S_{2}$ via two different methods $M_{1}$ and $M_{2}$. In which one is the work done more and why?


## SOLUTION:

In $\mathrm{M}_{1}$, since the area under the graph is greater in this case.

## 9. HEAT

Heat is energy in transit which is transferred by virtue of temperature difference, without the need for any bulk movement of the system or its parts. We have already learnt about conduction, convection and radiation -the three modes of heating a system.

By convention, heat gained by a system from the surroundings is taken as positive and heat lost by the system to the surroundings is negative.

Heat is not a state variable.
It is meaningless to say that 'a gas, in a given state, has a certain amount of heat' because the state of a gas is characterised by its internal energy, not heat.

What is contained in a system is internal energy, not heat. It is more meaningful to say, 'a certain amount of heat is supplied to a gas'. 'Heat' exists only during the transfer process.

Heat changes the equilibrium state of a system characterized by specific values of temperature, volume, pressure, length, phase etc.

In absence of any work, if the temperature of a system increases, heat is gained by the system. If the temperature of the system goes down, heat is lost by the system. We have already learnt the amount of heat required to raise the temperature of a substance by unity is a characteristic property of a substance and is called specific heat capacity. We can think of specific heat capacity as a measure of the ability of a material to store energy transferred in form of heat. This ability varies with the method of bringing about the temperature change. For example, specific heat capacities of gases at constant pressure and at constant volume differ in their values.

We are also aware if the phase of a material changes from solid to liquid or from liquid to gas or from solid to gas, then the heat is gained by the system and vice-versa. The heat required to change unit mass of substance from one state to another without change in temperature is called Latent heat. Latent heat is also a measure of the
ability of a material to store energy transferred in form of heat during a phase change $\qquad$ Again, we note this ability varies with specific type of process of phase change as evident from different values of latent heat of melting, latent heat of vaporization and latent heat of sublimation for the same substance.


## Heat Storage \& release at phase transition

## HEAT, CHANGE OF EQUILIBRIUM STATE AND INTERNAL ENERGY

When no work is done, same amount of heat, regardless of the mode, brings about the same change in state of a thermodynamic system. For example, to heat a water sample from $25^{\circ} \mathrm{C}$ to $40^{\circ} \mathrm{C}$, we may use conduction and convection mode by putting the container of water over a gas burner. Alternately, we can use radiation mode by keeping it in a microwave oven.

In these cases, no work is done to raise the temperature of water. Water is only heated in two different ways but the change in state of water is the same i.e. the change in state is path independent. This, like in case of work, leads us to conclusion that there exists a property in the system which changes by same amount in both the cases and
must depend on the state. Clearly, this quantity is the internal energy ( $\mathbf{U}$ ) and if no work is done, the heat required to take the system from one state to another must be

$$
\mathrm{Q}=\mathrm{U}_{\text {final }}-\mathrm{U}_{\text {initial }} .
$$

The constancy of temperature during phase change indicates internal energy of a substance is not measured entirely by temperature.

Temperature must be a measure of only the kinetic energy part of internal energy of the molecule.

During the melting and vaporisation phase changes, the energy goes into breaking down of the solid or liquid bonds and not in changing of average kinetic energy of the molecules, hence no temperature change occurs. At phase change, the heat supplied results only in increase of intermolecular potential energies. Large values of latent heats indicate a large amount of contribution to internal energy comes from the potential energy associated with the intermolecular forces.

## CHECK YOUR UNDERSTANDING

## EXAMPLE:

Heat is transferred across a boundary by virtue of a temperature difference. The heat is transferred, that means
A. force transfer takes place
B. energy transfer takes place
C. temperature transfer takes place
D. transfer of calorific fluid takes place

## SOLUTION

B. energy transfer takes place

## 10. COMBINING HEAT \& WORK TO CHANGE EQUILIBRIUM STATE

When a thermodynamic system is in state $A$, it has a certain internal energy $U_{A}$. $U_{A}$ can be determined by knowing only the state since internal energy is a state variable. If the system undergoes some unknown process that leaves it in state B, again its internal
energy $U_{B}$ can be determined by knowing only the state. Clearly, to get from state $A$ to state $B$, the system requires a net amount of energy $\Delta U=U_{B}-U_{A}$, no matter what the process is.

How this energy $\Delta \mathrm{U}$ is given to the system depends on the type of process. Either it can be given as work only or as heat only or as a combination of heat and work.

Does the system make a distinction between work and heat? The distinction between heat and work is made only in the surroundings. Once the energy is inside the system, there is no record of how the energy was given to the system - whether through work or through heat. Inside the system, all energy received is stored as internal energy. When withdrawn from the system, the energy can be given to the surroundings either as heat or as work. Again, the system is not concerned as to how its store of internal energy will be utilized in the surroundings or by what process.

## Work and heat as path functions

Different processes can use different combinations of heat and work and in different modes. Depending upon the process by which the system gets to state A from state B, the amount of energy transferred by work and the amount transferred by heat can vary. That is why work and heat are path functions and not state functions.

As an example, consider $n$ moles of an ideal gas at temperature $T_{1}$ in a cylinder made of adiabatic walls and diathermic base. The cylinder is fitted with a frictionless movable piston. The temperature of the gas is to be raised from $T_{1}$ to $T_{2}$. One process could be to first insulate the base and then move the piston quickly down keeping pressure constant at say, P. (Fig a) till the temperature rises to $\mathrm{T}_{2}$. This is adiabatic compression.


If the volume changes from $V_{1}$ to $V_{2}$, the work done $W_{1}$ is

$$
W_{1}=-\int_{V_{1}}^{V_{2}} P d v=-P\left(V_{2}-V_{1}\right)=P\left(V_{1}-V_{2}\right)
$$

The work is done on the system (gas) by the surroundings (piston), hence the negative sign before the integral. There is no heat exchange, hence heat transferred $\mathbf{Q}_{1}=$ 0 in this process.

A second process can be to just heat the gas cylinder by keeping its diathermic base over fire and keep the piston at a fixed position (Fig b). In this case the volume remains fixed at say, V hence work done in this process $\mathrm{W}_{2}=0$. The heat gained by the system is $\mathrm{Q}_{2}=\mathrm{n} \mathrm{C}_{\mathrm{V}}\left(\mathrm{T}_{2}-\mathrm{T}_{1}\right)$ where $\mathrm{C}_{\mathrm{V}}$ is the molar specific heat capacity of the gas at constant volume.

A third process could be to first insulate the base and then move the piston down keeping pressure constant at say, $\mathbf{P}$. (Fig c) till the temperature rises to $\mathbf{T}_{1}$ and the volume reduces to $\mathbf{V}_{1}$. Then remove the insulation from the base and heat the cylinder by keeping over fire till the temperature rises from $\mathrm{T}_{1}{ }^{\prime}$ to $\mathrm{T}_{1}$. In this process the work done $\mathbf{W}_{3}=-\mathbf{P}\left(\mathbf{V}_{1}-\mathbf{V}_{1}\right)=\mathbf{P}\left(\mathbf{V}_{1}-\mathbf{V}_{1}\right)$ and the heat gained is $\mathbf{Q}_{3}=\mathbf{=} \mathbf{C l}_{\mathbf{V}}\left(\mathbf{T}_{\mathbf{1}}-\mathbf{T}_{1}\right)$.

Clearly, $W_{1} \neq W_{2} \neq W_{3}$ and $Q_{1} \neq Q_{2} \neq Q_{3}$. Hence, work and heat are path functions which depend upon process.

## CHECK YOUR UNDERSTANDING

## EXAMPLE

Which of the following is NOT a path function?
A. Internal energy only
B. Heat energy only
C. Work energy only
D. Both Heat and Work

SOLUTION
A. Internal energy

## 11. MOLECULAR NATURE OF WORK AND HEAT

At observational level, work is done when an object moves on application of a force. At molecular level, it corresponds to all the molecules of the object moving in same direction. When we move a piston inward in a cylinder of gas, all the molecules of the piston move together in same direction and change the internal energy of the gas. So, work is the transfer of energy which makes use of the orderly motion of the molecules in the
 surroundings.

Heat, at observational level, is the energy given out by a hot object to a cold object because of
 temperature difference. At molecular level, it corresponds to more vigorous oscillations of molecules of hot object in random directions as compared to cold object. In case of a hot plate, the molecules of hot plate are oscillating vigorously in all possible directions. When a cold metal vessel is kept over it, the more vigorously vibrating molecules of hot plate jostle against the less vigorously vibrating molecules at the edge of the vessel and pass on some of their kinetic energy to the jostling neighbours. Neither the hot plate nor the metal vessel moves yet the energy gets transferred through the random jiggling and jostling. So, Heat is the transfer of energy which makes use of the random motion of the molecules in the surroundings.

Why is the system blind to the mode of energy transfer? Because at molecular level, the effect of both within the system is same. If a gas in an adiabatic cylinder is compressed by a piston, the incoming piston acts like a bat. When a molecule strikes the piston, piston sends it
flying back into the gas with some acceleration. As it goes back, it collides with other molecules. The gain in kinetic energy is quickly dispersed among other molecules in successive collisions and direction of its motion is randomized. If the same gas sample is heated in a cylinder with a metallic base, the vigorous jostling of molecules of hot surroundings stimulates more vigorous random motion in the gas molecules. The gain in kinetic energy of the molecules near conducting base is again dispersed quickly to the entire gas through collisions.

## CHECK YOUR UNDERSTANDING

## EXAMPLE:

A resistor is heating a volume of water as shown below. Is the state of system being changed by heat transfer or by work?


## A resistor heating the water

## SOLUTION:

If water is the system, its state is changed by heat transfer from the resistor. If the system is water and the resistor combined, the state is changed by work.

Check whether the energy transfer makes use of random motion (work) or the organized motion of molecules in the surroundings (heat).

## 12. SUMMARY

- Quantities whose magnitudes depend on the path between the initial and final points/ states are path functions whereas quantities whose magnitudes depend
only on the initial and final points/states and not on the path/process followed are state functions.
- Internal energy is the thermodynamic property of a system which arises from the potential and kinetic energies of molecules of the system, assuming center of mass of the system to be at rest.
- Heat and work are the only tools in the surroundings, available for changing the internal energy of a thermodynamic system i.e. its equilibrium states.
- Thermodynamic work refers to that work only which brings a change in the random motion of the molecules of a thermodynamic system and hence can change its internal energy. Every work changes the total energy of molecules but not necessarily their internal energy.
- Same amount of adiabatic work, regardless of mode, brings about the same change in equilibrium state of a thermodynamic system. This points to existence of internal energy and its nature as a state variable.
- Heat is energy in transit which is transferred by virtue of temperature difference, without the need for any bulk movement of the system or its parts.
- When no work is done, same amount of heat, regardless of the mode, brings about the same change in state of a thermodynamic system. This points to existence of internal energy and its nature as a state variable.
- Sign convention:

1. Work done by the system is positive and the work done on the system is negative.
2. Heat gained by a system positive and heat lost is negative.

- Work and heat are path functions, not state functions. The amount of energy transferred by work and the amount transferred by heat vary from process to process.
- At molecular level, work is the transfer of energy which makes use of the orderly motion of the molecules in the surroundings. Heat is the transfer of energy which makes use of the random motion of the molecules in the surroundings
- Thermodynamic system does not differentiate between work and heat. All energy that enters the system via these tools is stored as internal energy.

