12

THERMODYNAMICS

12.1 INTRODUCTION

You are familiar with the sensation of hot and cold in your daily life. When you rub your hands together you get the feeling of warmth. Have you ever thought about the cause of heating in such cases? In fact it occurs as a result of mechanical work done in both the above mentioned examples. Here, it is obvious that there is a relationship between mechanical work and thermal effect. The subject of thermal effects deals with pehnomena involving energy transfer between bodies at different temperature. A quantitative description of thermal phenomena requires a definition of temperature, heat and internal energy. The laws of thermodynamics provide a relationship between heat flow, work and the internal energy of a system.

In this lesson you will study about the principles of thermodynamics which provide a relationship between heat flow, work and the internal energy of a system. In this lesson you will also study the principles of thermodynamics in the form of three laws. These are the zeroth, first and second laws of thermodynamics. In this lesson you will also study about the Carnot's engine and its efficiency, concept of entropy and its physical significance.

12.2 OBJECTIVES

After studying this lesson, you should be able to:

- *differentiate between heat and temperature and describe different types of thermometeres stating the three common temperature scales;*
- *explain the meaning of the thermodynamic terms and the indicator diagram and show that area under the indicator diagram represents work;*
- *state thermodynamic equilibrium and Zeroth law of thermodynamics and discuss the principle of calorimetry;*
- *explain the concept of internal energy of a system and state first law of thermodynamics and its limitations;*
- *explain pressure-temperature phase diagram and evolve the concept of triple point;*
- *state second law of thermodynamics in different forms;*
- *describe Carnot cycle for a perfect gas and derive expression for work done and efficiency; and discuss the concept of entropy.*

12.3 CONCEPT OF HEAT AND TEMPERATURE

12.3.1 Heat

You are familiar with the sensation of hot and cold. Some bodies are found hotter and other colder as compared to a given body. For example, a piece of burning charcoal is very hot, while a chip of ice is very cold. This sensation of hot and cold can be understood in terms of heat of the body. Now you may ask : What is heat? ***Heat is a form of energy which produces in us the sensation of warmth.***

Heat is a form of energy. It is due to the kinetic energy of the molecules constituting the body. Heat energy can change into mechanical energy, electrical energy etc.

Flow of heat : You can understand this concept from the following example:

Take two containers having water up to different levels. Join these containers through a rubber tube. Water will flow from the container having water up to the higher level to the container in which level of water is low. Similarly, when two bodies at different temperatures are placed in contact, heat also flows from a body at higher temperature to the body at lower temperature.

The energy which flows from a body at higher temperature to a body at lower temperature, because of temperature difference is called heat-energy.

The unit of heat is *calorie*, one calorie is defined as; ***The quantity of heat energy required to heat 1 gram of water from 14.5 °C to 15.5°C is called one calorie. It is denoted as: 1 Cal.***

Calorie is the smallest unit of heat energy. Kilocalorie (k Cal) is the larger unit of heat energy, and

$$1 \text{ kCal} = 10^{-3} \text{ Cal}$$

Also $\boxed{1 \text{ Cal} = 4.18 \text{J}}$

12.3.2. Concept of temperature

When we talk of the temperature of a body we often think the degree of hotness or coldeness of the body. Thus, ***the degree of hotness of a body is its temperature.***

When we touch a body our senses provide us with a qualitative idea of temperature. Our senses are usually un-reliable and misleading. For example: If we remove an ice tray and a package of frozen vegetables from the freezer, the ice tray feels colder to the hand even though both are at the same temperature. Thus we need a reliable method to observe the relative hotness or coldness i.e. temperature of bodies. Scientists have developed various types of thermometers. A device used to measure temperature is a thermometer. You know that the property of a substance changes with temperature. This property can be used for the measurement of temperature by various thermometers. On the basis of the physical properties of a substance used in thermometers, we can divide them in the following ways:

(i) Mercury Thermometer

In such thermometers we use the volume of a fixed mass of mercury to indicate the temperature. A fine glass tube is attached to a larger tube. The bulb and a part of the

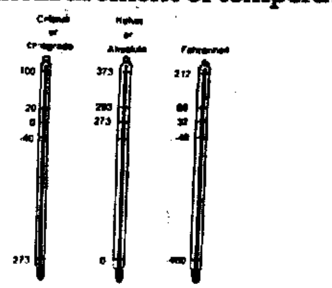

Fig.12.1: *Mercury Thermometer*

tube are filled with mercury. The tube is evacuated and sealed (Fig.12.1). As the bulb is heated, the mercury expands and rises in the tube. Hence the height of the mercury in the tube can be used as a measure of the temperature of the bulb.

To fix up a temperature scale, we choose two reference temperature and divide the interval between them into some equal numbers, parts. The scale is calibrated in terms of celsius or Kelvin.

Considering the temperatures of melting ice and boiling water at normal atmospheric pressure as the lowest and highest points for a mercury thermometer, Celsius and Kelvin Scale temperatures were defined.

(a) Centigrade or Celsius Scale: In this thermometer zero is the lower fixed point and 100 is the upper fixed point. The interval between the two fixed points is divided into 100 equal parts. Each part is equal to 1°C or 1°Celsius.

(b) Fahrenheit Scale: In this thermometer the lowest fixed point is marked as 32 and the upper fixed point is marked as 212. The interval is divided into 180 equal parts. Each part is equal to 1°F.

(c) Kelvin Temperature Scale: In this scale the lowest fixed point is marked as 273 K and the upper point is marked as 373 K. The interval is divided into 100 equal parts. Each part is equal to 1 K.

Relation between Kelvin and Celsius Scale:

Following is the relation between Kelvin and Celsius scale.

$$T = (T_c + 273)\ K \qquad \text{...... (12.1)}$$

where T_c is the temperature in Celsius and T in Kelvin.

For scientific measurement the standard temperature scale adopted is the Kelvin Scale. The Kelvin is the SI unit of temperature.

Following is the general relation between Celsius (C), Kelvin (K) and Fahranheit (F) Scales.

$$\frac{C-0}{100} = \frac{F-32}{180} = \frac{K-273}{100} \qquad \text{..... (12.2)}$$

We will also mention about two more types of thermometers.

(ii) The Constant Volume Gas Thermometer:

It is based on the principle that, when volume of a given mass of a gas is kept constant, its pressue increases or decreases by a constant amount for every °C rise or fall in temperature.

(iii) The Electrical Resistance Thermometer:

It is based on the principle that the resistance of a conductor increases with increase in temperature. The resistance of a conductor at θ°C is given by

$$R = R_0\,(1 + \alpha\theta) \qquad \text{...... (12.3)}$$

Where R_0 is resistance of conductor at 0°C and α is a temperature coefficient of resistance for the material of given conductor.

Before we discuss about thermodynamics, let us first define a few basic terms.

12.3.3 Thermodynamic Terms

(i) Thermodynamic system: A thermodynamic system refers to a definite quantity of matter bounded by some closed surface. This closed surface is called the boundary of the system. The boundary may enclose a solid, liquid or gas.

Here we will discuss three types of systems as:

(a) Open System: It is a system which can exchange mass, heat and work with the surroundings.

(b) Closed system: It is a system which can exchange heat and work but not mass with the surroundings.

(c) Isolated system: It is a system which has no exchange with the surrounding; not even heat exchange.

(ii) Thermodynamic Variables or Coordinates: In the first book, we have studied the motion of a body (or a system) in terms of its mass, position and velocity. To describe a thermodynamic system, we need its temperature (T), pressure (P), volume (V), density (ρ) etc.These are called *thermodynamic variables* or coordinates of a thermodynamic system.

Those variables in terms of which a thermodynamic system can be described, are called thermodynamic variables or thermodynamic coordinates.

(iii) Indicator diagram: You have studied about different types of graphs in your mechanics lessons. Generally we use graphs to study the variation of a physical quantity with respect to the another one. To study a thermodynamic system we use a pressure-volume graph. This graph indicates how the pressure (P) of a system varies with its volume (V), during a process. This graph which indicates how the pressure (P) of a system varies with its volume during a thermodynamic process, is known as an indicator diagram.

We can get the work done in any particular case using the indicator diagram.

Now we will show that the area under the P - V diagram is equal to the work done by the system. Fig. (12.2) shows an indicator diagram of a thermodynamic system. Suppose the pressure P at the start of a very small expansion ΔV hence work done by the system (ΔW)

$$\Delta W = P\Delta V \qquad \text{...... (12.4)}$$

Approximately,

$$\Delta W = \text{Area of shaded strip ABCD}$$

Now total work done by the system from V_1 to V_2 = Area $P_1P_2V_2V_1P_1$. The value of the area depends upon the shape of the indicator diagram.

The indicator diagram is widely useful in calculating the work done in the process of expansion or compression.

Really, it is found more useful in the process where relationship between P and V is not known. Indicator diagram plays very important role to explain the theory of heat engine.

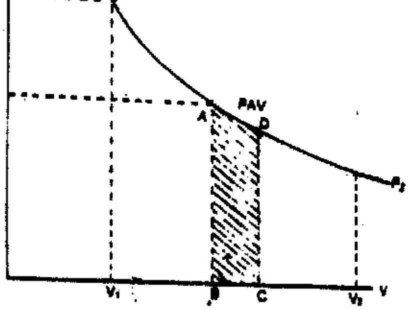

Fig. 12.2: Indicator Diagram

12.4 THERMAL EQUALIBRIUM

To understand the phenomenon of thermal equilibrium, let us consider two metal blocks (of the same material) A and B. Suppose A is warmer than B. Bring A and B into contact and surround them by a thick layer glass wool. After sometime you will find both the blocks equally warm. This is called as the thermal equilibrium of this system.

It is a state of thermodynamic system in which temperature of the system is uniform. And also there is no temperature difference between the system and its surrounding.

12.4.1 Zeroth Law of Thermodynamics

In order to state Zeroth law of Thermodynamics, let us consider three metal blocks A,B and C. Suppose block A is in thermal equilibrium with block B. It means the temperature of block A is equal to the temperature of block B. Further, suppose that block A is also in thermal equilibrium with block C. It means that the temperature of block A is equal to the temperature of block C. It follows that the temperatures of blocks B and C are equal. We can summarize these results in a statements known as Zeroth Law of Thermodynamics:

If two bodies or systems A and B are separately in thermal equilibrium with a third body C, then A and B are in thermal equilibrium with each other. This statement is known as the Zeroth law of thermodynamics.

12.4.2 Principle of Calorimetery

You take some cold water in a glass and some hot water in another glass. Now mix water of both the glasses. You will see now, the temperature of hot water is less than the hot water and more than the cold water. You may say that the temperature of the mixture of hot and cold water lies between the temperature of hot and cold water. Have you ever thought about the cause of such a problem? You will learn this change of temperature with the help of calorimetery.

To study the principle of calorimetery let us first discuss a few terms given as;

Calorimeter: It is a cylindrical vessel made of copper and provided with a stirrer and a lid.

Specific heat: *The specific heat of a material (solid or liquid) is the amount of heat required to raise the temperature of unit mass of the material through 1 K. It is denoted by C.*

If heat ΔQ is required to raise the temperature of mass M of the solid through ΔT, then,

$$C = \frac{\Delta Q}{M \times \Delta T} \qquad \text{..... (12.5)}$$

SI unit of C is J/kg K.

In SI, the specific heat of a solid mass is equal to the amount of heat required to raise the temperature of 1 kg of the solid through 1K.

Heat Capacity: *The heat capacity of a body is equal to the amount of heat required to raise its temperature through one degree.* It is also called as thermal capacity of the body.

Mathematically we can express it as,

$$\Delta Q = MC$$

Where ΔQ = heat capacity of the body, M = mass of the body, and C = specific heat of the body

The unit of ΔQ is J/K in S.I. system.

Water equivalent: *The water equivalent of a body is defines as the mass of water, which absorbs or emits the same amount of heat as is done by the given body for the same rise or fall in temperature.*

Mathematically we can express it as:

$W = MC$

where W = Water equivalent of the body, M = Mass of the body, and C = Specific heat of the body

Its SI unit is kg.

Now you will study about the *Principle of Calorimetery.*

When bodies at different temperatures are mixed together in the Calorimeter, they exchange heat with each other. Bodies at higher temperature lose heat, while those at lower temperature gain heat. The contents of the calorimeter are stirred constantly so as to keep the temperature of the contents uniform.

If no heat is lost to surroundings the heat lost by hot body must be euqal to the heat gained by cold body. *It in called the principle of calrometery* or principle of mixture. We can express this statement as:

Heat lost = Heat gain

This principle can be used to find the specific heat of one content if specific heat of another is given, in case of mixture.

Suppose a calorimeter whose water equivalent is W containing mass M_1 of water at temperature T. A hot solid at temperature T_2 and having mass M_2 is dropped into the calorimeter. The contents are stirred constantly and the mixture acquires a final temperature$T$.

Suppose C is the specific heat of solid to be determined and C' is the specific heat of water then

$$C = \frac{(M_1 + W)C'(T - T_1)}{M_2(T_2 - T)} \quad \text{.... (12.6)}$$

Specific heat of solids can be calculated using above relation.

Now it is time to check you understanding. Solve the following questions.

INTEXT QUESTION 12.1

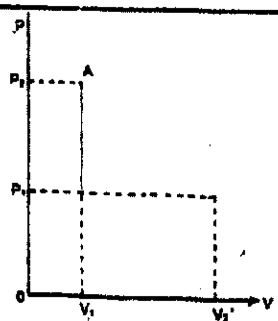

Fig. 12.3:

1. *At what temperature do the Kelvin and Fahreinheit scale coincide?*

   ....

2. *Fill in the blanks*

   (i) *Zeroth law of thermodynamics provides basis for the concept of*.............................

   (ii) *If a system A is in thermal equilibrium with a system B while B is in thermal equilibrium with another system C then, system A will also be in thermal equilibrium with system*

   ....

   (iii) *The unit of heat is*..

3. *State the principle of mixture.*

   ....

4. *In the figure 12.3 is shown, how much work is done by the system in the process*
   (a) *along the path ABC from A to C*
   (b) *If the system is returned from C to A along the same path, how much work is done by the system.*

....

12.5 INTERNAL ENERGY OF A SYSTEM

Have you ever thought about the energy which is released when water freezes into ice? Don't you think that there is some kind of energy stored in the water. This energy is released when water changes to ice. This stored energy is called *the internal energy*. We can discuss the concept of internal energy on the basis of kinetic theory of matter. First we will discuss about the internal kinetic energy then internal potential energy.

(a) Internal Kinetic energy: As you have studied earlier according to kinetic theory of matter, matter is made up of large number of molecules. These molecules are in a state of constant rapid motion and hence possess kinetic energy. The total kinetic energy of the molecules is called the ***internal kinetic energy.***

(b) Internal Potential energy: The energy arising due to the inter-molecular attraction is called the ***internal potential energy.***

The energy of the system may be increased by causing its molecules to move faster (a gain in kinetic energy). It can also be increased by causing the molecules to move against inter-molecular force or both. The sum of the kinetic and potential energies of the molecules of a body is called its internal energy. Generally it is denoted by the letter U

Internal energy of a system = Kinetic energy of molecules + Potential energy of molecules of the system

Let us consider an isolated thermodynamic system subjected to external force. Suppose W amount of work is done on the system in going from initial state i to final state f, adiabatically. Let U_i and U_f be internal energies of the system in its initial and final state respectively. Since work is done on the system, internal energy of final state will be higher than that of initial state.

According to the law of consesrvation of energy

$$U_i - U_f = -W$$

Negative sign indicates that work is done on the system.

12.5.1 First law of thermodynamics

We have discussed Zenoth law of thermodynamics, which tells us about the equilibrium among different systems in contact. It also introduces concept of temperature. However, Zeroth law does not tell us anything about the non-equilibrium state.

Let us consider two examples: (i) two systems at different temperature in contact with each other and (ii) mechanical rubbing between two systems causing change in their temperatures. These facts cannot be explained merely with the help of Zeroth law. However, physicists have been working for the explanation of these facts since very early ages, long before the evolution of Zeroth law. These facts were explained by the first law of thermodynamics.

The first law of thermodynamics is, infact, the law of conservation of energy, and it states that the amount of heat given to a system is equal to the sum of change in internal energy of the system and the external work done.

Suppose

ΔQ = amount of heat given to the system,

ΔU = increase in internal energy of the system, and

ΔW = external work done by the system

then according to the statement of first law of thermodynamics, we can write:

$$\Delta Q = \Delta U + \Delta W \quad \text{... (12.7)}$$

This is the mathematical form of the first law of thermodynamics. Here ΔQ, ΔU and ΔW all are in the same units.

The signs of ΔQ, ΔU and ΔW are known from the following sign conventions:

Sign conventions:

(i) *Work done (ΔW) by a system is taken as positive whereas work done on a system is taken as negative.*

(ii) *Heat gained (added) by a system is taken as positive whereas heat lost (extracted) by a system is taken as negative.*

(iii) *The increase in internal energy (ΔU) is taken as positive and the decrease in internal energy is taken as negative.*

12.5.2 Limitations of First Law of Thermodynamics

First law of thermodynamics also asserts the equivalence between heat and work. This law tells us that how much work is obtained by transferring a certain amount of heat. However, it fails to explain the following points.

(i) You know that heat always flows from a hot body to a cold body. But first law of thermodynamics fails to explain why heat cannot flow from a cold body to a hot body. It means that this law does not indicate the direction of heat flow.

(ii) This law does not indicate as to what extent heat can be converted into work.

(iii) You know that when a bullet strikes on a target, the kinetic energy of the bullet is converted into heat. This law does not indicate as to why heat developed in the target cannot be changed into the kinetic energy of bullet to make it fly. It means that this law fails to provide the condition under which heat can be changed into work.

Now take a pause and try to solve the following questions.

INTEXT QUESTION 12.2

1. *Fill in the blanks*

   (i) *The total kinetic energy of the molecule is called* ....

   (ii) *Work done = –W, it indicates that work is done* .... *the system.*

2. *State first law of thermodynamics.*

   ....

12.6 THERMODYNAMIC PROCESS

If the thermodynamic variables of a system change while going from one equilibrium state to another, the system is said to execute a thermodynamic process. For example the expansion of a gas in a cylinder at constant pressure due to heating in a thermodynamic process.

Now we will define number of thermodynamic processes.

(i) Reversible process: A process which can be returned in the opposite diretion from its final state to its initial state is called reversible process. For example

(a) Take a piece of ice in a beaker and heat it. You will see that it changes to water. If you remove the same quantity of heat of water by keeping it inside a refrigerator, it again changes to ice. It means you have returned back to the initial state (ice).

(b) Consider a spring supported at one end. Put some mass at its free end. Spring will elongate (increase in length). Now remove the mass, you will see that spring retraces to its initial position. Hence it is a reversible process.

(ii) Irreversible process: A process which cannot be retraced along the same equilibrium state from final to the initial state is called irreversible process. For example,

(i) Heat produced during friction,

(ii) Sugar dissolved in water, and

(iii) Rusting of iron in the environment.

(iii) Isothermal process: Any thermodynamic process that occurs at constant temperature is an isothermal process. For example, the expansion and compression of a perfect gas in a cylinder made of perfectly conducting walls.

(iv) Adiabatic process: Any thermodynamic process that occurs at constant heat is an adiabatic process. For, example the expansion and compression of a perfect gas in a cylinder made of perfectly insulating walls.

(v) Isobaric process: A thermodynamic process that occurs at constant pressure is an isobaric process. For example, heating of water under atmospheric pressure is an isobaric process.

(vi) Isochoric process: A thermodynamic process that occurs at constant volume of the system is an isochoric process.For example heating of a gas in a vessel of constant volume is an isochoric process.

12.6.1 Phase Diagram

You have learnt that solid, liquid and gas are three states of matter. ***The different states of matter are called its phases.*** For example, ice (solid), water (liquid) and steam (gas) are three states of water. We can discuss that three phases using a three dimensional diagram drawn in pressure (P), temperature (T) and volume (V). To draw and discuss three dimensional and diagram may be difficult for you. Thus, we shall discuss the three phases of matter by drawing a pressure-temperature diagram. This is called ***phase diagram.***

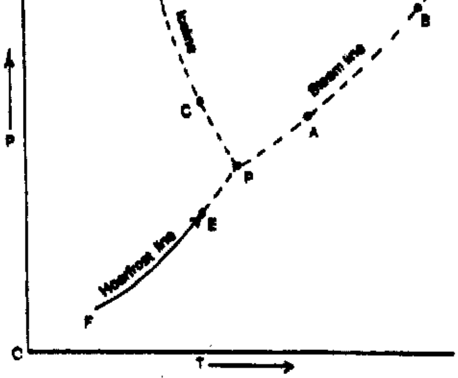

Fig. 12.4 *Phase diagram of water*

Pressure-temperature phase diagram:

Fig.12.4 shows phase diagram of water. In Fig.12.1 you can see three curves: CD, PB and EF.

Curve CD shows the variation of melting point of ice with pressure. It is known as a ***fusion curve.***

Curve PB, shows variation of boiling point of water with pressure. It is known as ***vaporization*** curve.

Curve EF, shows change of ice directly to steam. It is known as a ***sublimation curve.*** This curve is also known as ***Hoarfrost Line.***

If you extend the curve AB, CD and EF (as shown in the Figure with dotted lines) they meet at point P. This point is called ***triple point.***

Triple point: It is a point on the phase diagram which represents a particular ***temperature*** and pressure of matter. At this point solid, liquid and vapour states of matter can co-exist.

Stop and try to solve the following questions.

INTEXT QUESTION 12.3

1. *Fill in the blanks.*
   (i) *A reversible process is that which can be ....in the opposite direction from its final state to its initial state.*
   (ii) *A ....is that which cannot retrace along the same equilibrium state from final state to the initial state.*
2. *Distinguish between isothermal and adiabatic processes.*

   ....
3. *State one characteristic of triple point.*

   ....

12.7 SECOND LAW OF THERMODYNAMICS

According to the first law of thermodynamics you have learnt that heat can be converted into work. Here one question may arise in your mind whether heat can be wholly converted into work or not. Also you would be keen to know the conditions under which this conversion occurs. You will get the answers of these questions by a new principle known as *Second law of thermodynamics*. There are number of ways to state second law of thermodynamics. However, you will study Kelvin-Planck and Clausius statements of second law of thermodynamics.

(i) Kelvin-Planck's statement is based upon his experience about the performance of a heat engine (heat engine is discussed in next section). In a heat engine, the working susbstance extracts heat from the source (hot body), converts a part of it into work then it rejects the rest of heat to the sink (cold body). There is no engine which converts whole heat into work, without rejecting to the sink. These observations led Kelvin-Planck state second law of thermodynamics as : ***It is not possible to obtain a continuous supply of work from a single source of heat.***

Infact idea of second body (cold body or sink) is the basis of Kevin-Planck's statement of second law of thermodynamics.

(ii) Clausisus statement of second law of thermodynamics is based upon the performance of a refrigerator. A refrigerator is a heat engine working in the opposite direction. It transfers heat from a colder body to a hotter body when external work is done on it. Here concept of external work done on the system is important. To do this external work, supply of energy from some external source is a must. These observations led Clausius to state second law of thermodynamics in the following form.

Heat cannot flow from a colder body to a hotter body without doing external work on the working substance.

Thus, second law of thermodynamics plays an unique role for practical devices like, heat engine and refrigerator.

12.7.1 Carnot's Engine and Carnot's Cycle

You must have noticed that when water is boiled in vessel closed by a lid, the steam generated inside throws off the lid. This shows that high pressure steam can be made to do work. It shows that transfer of heat results in a situation where work can be done. ***A device which can continuously convert heat into work is called heat engine.***

Modern engines which we use in our daily life are based on the principle of heat engine. These may be categorised in three types namely, steam engine, internal combunstion engine and gas turbines.

Sadi Carnot in 1824 conceived a theoretical engine which is free from all the defects of practical engine. There are essential components of a heat engine as given below:

(i) **Source:** A hot body at very high temperature T_1 which supplies heat to the engine. After supplying any amount of heat its temperature remains constant.

(ii) **Sink:** A cold body at very low temperature T_2 to which any amount of heat can be rejected.After receiving any amount of heat its temperature remains constant.

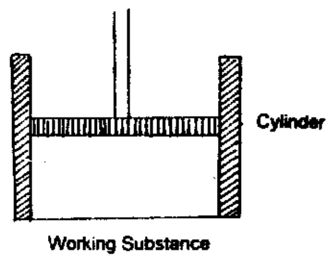

Fig. 12.5:

(iii) **Working substance:** Perfect gas filled in a cylinder fitted with a frictionless piston (Fig. 12.5) The sides of the cylinder are perfecting insulating.

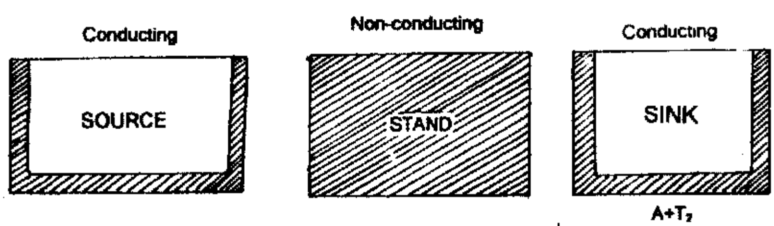

Fig. 12.6: *Carnot Engine*

(iv) **Non-conducting stand:** A perfectly non-conducting platform used as a stand for the cylinder.

The working substance is subjected to a cycle of four operations: (a) isothermal expansion (b) adiabatic expansion (c) isothermal compression and (d) adiabatic compression. Such a cycle is known as Carnot's cycle and is represented on the P-V diagram (Fig.12 7). To describe four operations of Carnot's cycle, let us fill one gm. mol. of the working substance in the cylinder (Fig.12.5). Original conditions of the substance is represented by point A on the indicator diagram. At point A, substance

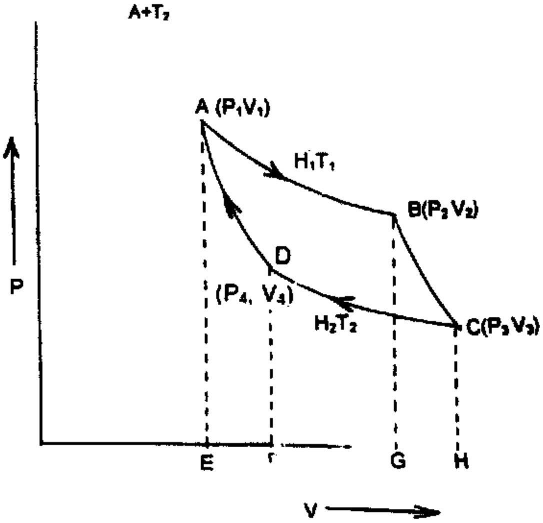

Fig. 12.7: *Indicator Diagram*

has temperature T_1, pressure P_1 and volume V_1.

(a) **Isothermal expan-sion:** Place the cylinder on the source. Decrease load slowly on the piston to P_2. The volume of the working substance increase to V_2. Thus working substance expands and does external work in raising the piston. In this way the temperature of the working substance tends to fall. As it is kept in thermal contact with the source, it will absorb a quantity of heat, H_1 from the source at temperature T_1. This way we get point B. At B the values of pressure and volume are P_2 and V_2 respectively. On the indicator diagram (Fig. 12.7), you see that going from A to B temperature of the system remains constant and working substance expands. We call it isothermal ***expansion process.*** H_1 is the amount of heat absorbed in the isothermal expansion process. Then, in accordance with the first law of thermodynamics H_1 will be equal to the external work done by the gas during isothermal expansion from A to B at temperature T_1. Suppose W_1 is the external work done by the gas during isothermal expansion AB, then it will be equal to the area ABGEA. Hence

$$W_1 = \text{Area ABGEA}$$

(b) **Adiabatic expansion:** Now remove the cylinder from the source and place it on the perfectly non-conducting stand. Further decrease the load on the piston to P_3. The expansion is completely adiabatic because no heat can enter or leave the working substance. Therefore working substance performs external work in raising the piston at the expense of its internal energy. Hence its temperature falls. This gas is thus allowed to expand adiabatically until its temperature falls to T_2, the temperature of the sink. It has been represented by the adiabatic curve BC on the indicator diagram. We call it ***adiabatic expansion.*** If P_3, V_3 be the pressure and volume of the substance at C, and W_2 be the work done by the substance from B to C then

$$W_2 = \text{Area BCHGB.}$$

(c) **Isothermal compression:** Remove the cylinder from the non-conducting stand and place it on the sink at temperature T_2. In order to compress the gas slowly, increase the load (pressure) on the piston until its pressure and volume become P_4 and V_4 respectively. It is represented by the point D on the indicator diagram (Fig. 12.7). The heat developed (H_2) due to compression will pass to the sink. Thus, there is no change in the temperture of the system. Therefore, it is called as an *isothermal compression process.* It is shown by the curve CD (Fig. 12.7). The quantity of heat rejected (H_2) to the sink during this process is equal to the work done (say W_3) on the working substance. Hence

$$W_3 = \text{Area CHFDC}$$

(d) **Adiabatic compression:** Once again place the system on the non-conducting stand. Increase the load on the piston slowly. The substance will go under an *adiabatic compression.* This compression continues until the temperature rises to T_1 and the substance comes back to its original pressure P_1 and volume V_1. This is an adiabatic compression process and represented by the curve DA on the indicator diagram (Fig. 12.7). Suppose W_4 is the work done during this adiabatic compression from D to A then

$$W_4 = \text{Area DFEAD}$$

During the above cycle of operation, the working substance takes H_1 amount of heat from the source and rejects H_2 amount of heat to the sink. Hence the net amount of heat absorbed by the working substance.

$= H_1 - H_2$

Also the net work done (say W) by the engine in one complete cycle

$W =$ *Area ABGEA* + *Area BCHGB* − *Area CHFDC* − *Area DFEAD*

(As you have studied earlier in this lesson that work done by the system is positive and on the system is negative)

W = Area ABCHEA − Area CHEADC (see Fig.12.7)

= Area ABCD

Thus, the work done in one cycle is represented on a P-V indicator diagram by the area of the cycle.

You have studied that the initial and the final states of the substance are the same. It means its internal energy remains unchanged and hence according to the first law of thermodynamics, we know

$$W = H_1 - H_2$$

Therefore, heat has been converted into work done by the system. And any amount of work can be obtained by merely repeating the cycle.

12.7.2 Efficiency of Carnot's Engine

It is defined as ratio of heat converted into work in a cycle to heat taken from the source by working substance. It is denoted η as :

$$\eta = \frac{\text{Heat converted in to work}}{\text{Heat taken from source}}$$

or $$\eta = \frac{H_1 - H_2}{H_1} = \frac{H_2}{H_1} \qquad \ldots (12.8)$$

It can be shown that for Carnot's engine,

$$\frac{H_2}{H_1} = \frac{T_2}{T_1}$$

Hence, $$\boxed{\eta = 1 - \frac{T_2}{T_1}} \qquad \ldots (12.9)$$

If $H_2 = 0$ (i.e., no heat is rejected to the sink)

then $\eta = 1$ or $\eta = 100\%$

It means total heat is converted into work. But in practice there is no such engine. Hence efficiency of an engine is always below 100%. In practice the efficiency of a heat engine is about 12% to 16%.

12.7.3 Limitation of Carnot's Engine

You have studied about the Carnot's cycle in terms of isothermal and adiabatic processes. Here it is important to note that the isothermal process will only take place when piston moves very slowly. It means there should be sufficient time for the heat transfer from working substance to source. On the other hand, during the adiabatic process the piston moves extremely fast to avoid heat transfer. In practice it is not possible to fulfill these vital conditions. Due to these very reasons all practical engines have an efficiency less than the Carnot's engine.

12.7.4 Entropy

Till now you have studied about the various thermodynamic variables namely, pressure (P), temperature (T), volume (V) and internal energy (U). You have also seen that all these variables depend upon each other. Now, you will study about a new variable known as *entropy*. It is denoted by the letter S and defined as: ***entropy is a measure of the unavailability of a system's energy to do work.***

Mathematically, we can express the change in entropy (ΔS) during a reversible process, as

to $$\Delta S = \frac{\text{Energy absorbed by the system (DQ) at temperature } T}{T}$$

or $$\Delta S = \frac{\Delta Q}{T} \qquad .....(12.10)$$

Thus, we can say that when heat is absorbed during a process entropy increases. And when heat is rejected during a process, entropy decreases. Entropy increases during a reversible process and decreases during a irreversible process.

Physical significance of entropy — *Molecular disorder approach:* Till now we have studied entropy in terms of mathematical relation. But we have not analysed what it physically mean. In a wider sense entropy can be discussed as a measure of a system's disorder. If disorder is greater, entropy of the system will be higher. To understand this, let us discuss the following example:

Take some quantity of ice in a beaker. Convert it into water by heating. Here you find that going from ice to water, disorder of the molecules increases. It means entropy of water is more than the ice. Convert water into steam by further heating. You will see that disorder of the molecules further increases. It shows that the entropy of steam is more than water. Hence we can conclude that entropy is a measure of the disorder of the molecules of the system.

After studing the carnot's engine and its efficiency and the entropy take a break.

INTEXT QUESTION 12.4

1. *State whether the following statements are true or false.*
   (i) *In a Carnot engine, when heat is taken by a perfect gas, from a hot source, the temperature of the source decreases.*

   ....

   (ii) *In a Carnot engine, if the temperture of sink is decreased the efficiency of engine also decreases.*

   ....

2. (i) *A Carnot engine has the same efficiency between 1000K and 500K and beteween T K and 1000K calculate T.*

   ....

   (ii) *A Carnot engine working between an unknown temperature T and ice point given an efficiency of 0.68. Deduce the value of T.*

   ....

3. *Draw a typical P-V diagram for a Carnot cycle and show on it the area which would represent (i) heat taken from the source (ii) heat rejected to the sink (iii) heat converted into work.*

   ....

4. *Compute the change in entropy when 5 kg of water at 100°C is converted into steam at the same temperture.*

   ....

12.8 WHAT YOU HAVE LEARNT

- Heat is a form of energy which produces in us the sensation of warmth.
- The energy which flows from a body at higher temperature to a body at lower temperature, because of temperature difference is called heat energy.
- The most commonly known unit of heat energy is calorie. 1 Cal = 4.18J and 1 kCal = 10^3 Cal.
- The degree of hotness of a body is its temperature and the device used to measure temperature is a thermometer.
- The three scales of temperature widely used are the Celsius, Kelvin and Fahrenheit.
- A graph which indicates how the pressure (P) of a system varies with its volume during a thermodynamic process, is known as an indicator diagram.
- Work done during expansion or compression of a gas is = $P\Delta V = P(V_f - V_i)$
- Zeroth law of thermodynamics states that if two systems are in thermal equilibrium with a third system, then they must be in thermal equilibrium with each other.
- Heat lost = heat gain, in the principle of mixture.
- The total kinetic energy of the molecules of a body is called the internal energy and the relation between internal energy and work $U_i - U_f = -W$.
- The first law of thermodynamics states that the amount of heat given to a system is equal to the sum of change in internal energy of the system and the external work done.
- First Law of thermodynamics tells nothing about the direction of the process.
- A process which can be retraced in the opposite direction from its final state to initial state is called reversible process.
- A process which can not be retraced along the same equilibrium state from final to the initial state is called irreversible process but the process that occurs at constant temperature is an isothermal process
- Any thermodynamic process that occurs constant heat is an adiabetic process.
- The different states of matter are called its phase and the pressure and temperature diagram showing three phases of matter is called a phase diagram.
- Triple point on the phase diagram which represents a particular temperature and pressure of matter. At this point solid, liquid and vapour state of matter can co-exist.
- According to Kelvin-Planck's statement of second law it is not possible to obtain a continuous supply of work from a single source of heat.
- According to Clausius statement of second law: Heat can not flow from a colder body to a hotter body without doing external work on the working substance.
- The three essential requirements of any heat engine are:

  (i) source from which heat can be drawn

  (ii) a sink into which heat can be rejected

  (iii) working substance which performs mechanical work after being supplied with heat.
- Carnot's engine is an ideal engine in which the working substance is subjected to four operations (i) Isothermal expansion (ii) adiabatic expansion (iii) isothermal compression and (iv) adiabatic compression. Such a cycle is called Carnot-cycle.
- Net work-done by the Carnot's engine in a cycle = area of the curve indicating the cycle in P-V diagram.
- Efficiency of a Carnot engine is

  $\eta = 1 - \frac{H_2}{H_1}$, H_1 = Amount of heat absorbed and H_2 = Amount of heat rejected

  $= 1 - \frac{T_2}{T_1}$, T_1 = Temperature of the source, and T_2 = Temperature of the sink
- Efficiency does not depend upon the nature of the working substance

- Entropy is a measure of the unavailability of system's energy to do work and mathematically

  $\Delta S = \frac{\Delta Q}{T}$. ΔS = change in entropy and ΔQ = energy absorbed by the system at temperature T.

12.9 TERMINAL QUESTIONS

1. Distinguish between the terms internal energy and heat energy.
2. At what temperature do the Celsius and the Fahrenheit scales coincide?
3. What do you mean by an indicator diagram. Derive an expression for the work done during expansion of an ideal gas.
4. Define temperature using the Zeroth law of thermodynamics.
5. State the principle of mixture.
6. State the first law of thermodynamics and its limitations.
7. What is the difference between isothermal, adiabetic, isobaric and isochoric processes?
8. State the Second law of thermodynamics.
9. Discuss reversible and irreversible process with examples.
10. Explain Carnot's cycle Use the indicator diagram to find out the efficiency of Carnot Engine.
11. Find the change in internal energy of the system when (a) a system absorbs 2000J of heat and produces 500J of work (b) a system absorbs 1100J of heat and 400J of work is done on it.
12. A Carnot's engine whose temperature of the source is 400K takes 200 calories of heat at this temperature and rejects 150 calories of heat to the sink. (i) what is the temperature of the sink. (ii) Calculate the efficiency of the engine.
13. A Carnot's engine working as refrigerator between 260 K and 300K receives 500 calories of heat from the reservoir at the lower temperature. Calculate (i) the amount of heat rejected to the reservoir at the higher temperature and (ii) the amount of work done in each cycle to operate the refrigerator.
14. What do you mean by entropy of a system. Discuss its physical significance.
15. Calculate the change in entropy when 10 grams of ice at 0°C is converted into water at the same temperature.

ANSWERS TO INTEXT QUESTIONS

Intext Questions 12.1

1. 574.25
2. (i) Temperature (ii) C (iii) Calorie
3. See section 12.4.2
4. (a) $P\ (V_2 - V_1)$; (b) $-P_1\ (V_2 - V_1)$

Intext Questions 12.2

1. (i) Internal energy (ii) on
2. It states that the amount of heat given to a system is equal to the sum of change in internal energy of the system and the external energy.

Intext Questions 12.3

1. (i) retrace (ii) irreversible
2. An isothermal process occurs at constant temperature whereas an adiobatic process occurs at constant heat.
3. At triple point all three states of matter i.e. solid, liquid and vapour co-exist.

Intext Questions 12.4

1. (i) False (ii) True

2. (i) 2000K (ii) 853.1K.
3. See section 12.6.2
4. 7240 Cal/K.

TERMINAL QUESTIONS

11. (a) 1500 Joules, (b) 700 Joules
12. (i) 300 K, (ii) 25%
13. (i) 576.92 cal., (ii) 323.08 Joules
15. $\Delta S = 2.93$ cal/K.