

# HEAT AND THERMODYNAMICS

2

Physics Class 11

## 1.1 Principle of Measurement of Temperature

✓ তাপমাত্রা পরিমাপের নীতি

### Thermal Equilibrium

Heat is a form of energy which is related with the internal energy of the object. When two objects are brought in contact then there is a exchange of heat. Whether there will be a exchange of heat that will depend on the thermal condition of the objects.

**Watch it :** If hot tea or milk is kept in a cup it becomes cold after a while. Bringing out cold object or food from freeze kept on the table it becomes hot after sometime. Actually what is becoming cold or hot?

If a hot body is kept at an open place the body becomes cold radiating heat to the environment. This exchange of heat continues till the temperature of the body becomes equal to that of the environment. When the temperature of the body becomes equal to the environment the body can not loose any heat to the environment. We then say that the body is in thermal equilibrium with the environment. If any system is in thermal equilibrium with the environment then the system will not exchange heat with the environment. This will happen when there is no difference of temperature between the system and the environment.

**Definition :** If the different parts of a system are at same temperature with the environment and if there is no exchange of heat between them then the system is said to be in thermal equilibrium with the environment.

### Concept of Temperature

Temperature is the thermal state of a body that determines whether a body can give out heat or receive heat from another body when placed in contact with it. Sometimes we try to feel the temperature of an object by touching it with our hand. But always we do not get the correct information about temperature of the object by touching.

**Do it yourself :** Touch a piece of wood and iron keeping inside the room side by side for sometimes. What do you feel?

You will feel that the piece of iron is colder than that of wood though both of them are at same temperature.

**Experiment :** Take water in three buckets. Ice cold water in one bucket, warm water in another bucket and water of room temperature in the third bucket. Put your one hand in ice cool water and other hand in warm water for sometimes, now put both the hands in the water of room temperature. What do you feel?

To your hand from the ice cool water will give warm feeling while to the other hand from the warm water will give a colder feeling. So we cannot get the actual information of heat by sensation of touching. Again by touching the difference of temperature can be felt but the magnitude of temperature can not be determined. As for example if any body is suffering from fever we can feel by touching his forehead that fever is there. But we can not determine the quantum of fever by touching, so we need an instrument. The instrument used to measure temperature is known as thermometer.

## Thermodynamics

### Measurement of Temperature

The instrument by which temperature of a body and also the difference of temperature of different bodies can be determined is called a thermometer.

To construct a thermometer we need such substance any of whose properties changes uniformly with the change of temperature. We know that with the application of heat the volume of solid, liquid and gaseous substances increases, the resistance of a conductor increases, the colours of light radiated from a substance changes, electric current in a thermocouple changes. So temperature can be determined by observing such special properties of the substance.

The specific properties of the substances that change uniformly with temperature and observing those changes of properties temperature can be measured easily and accurately is called thermometric property. The material using whose thermometric property thermometer is constructed is known as thermometric substance.

Different thermometric substances are used conveniently to measure temperature at different ranges. Generally the thermometers are named on the basis of the thermometric substances or their thermometric properties. Such as mercury thermometer, resistance thermometer, gas thermometer etc.

### Determination of Scales of Temperature using Two Fixed Points

To measure temperature with the help of a thermometer it is necessary to select scales of temperature. To select a scale two easily reproducible temperature are chosen. Which are called fixed points.

**Lower Fixed Point :** At standard pressure the temperature at which pure ice remains in equilibrium with water that is the temperature at which pure ice begins to melt is known as lower fixed point or ice point.

**Upper Fixed Point :** At standard pressure the temperature at which pure water remains in equilibrium with water vapour that is the temperature at which pure water begins to become water vapour is known as upper fixed point or steam point.

The interval between the upper fixed point and lower fixed point is known as fundamental interval. The scale of temperature is selected by dividing the interval into several equal suitable divisions and marking each division with a temperature denoting figure.

In selecting temperature scale the thermometric property of substance is used. Let the temperatures of ice point and steam point be respectively  $\theta_{ice}$  and  $\theta_{steam}$ . The values of thermometric properties at these two temperatures be  $X_{ice}$  and  $X_{steam}$  respectively. Now if the value of that thermometric property be  $X_0$  at any other temperature  $\theta$  and if the fundamental interval is divided into  $N$  equal divisions, then the temperature  $\theta$  will be,

$$\frac{\theta - \theta_{ice}}{\theta_{steam} - \theta_{ice}} = \frac{X_0 - X_{ice}}{X_{steam} - X_{ice}}$$

$$\text{or, } \frac{\theta - \theta_{ice}}{N} = \frac{X_0 - X_{ice}}{X_{steam} - X_{ice}}$$

... ... ... (1.1)

The equation (1.1) is used to calibrate different scales of temperature. Few scales of temperature are discussed below.

### Celsius scale

In different scales different temperatures have been selected for ice point and steam point. Widely used popular scale of temperature is the Celsius scale in which the ice point is taken as  $0^{\circ}\text{C}$  and steam point is  $100^{\circ}\text{C}$ . And the fundamental interval between these two temperatures are divided into 100 equal divisions. Each division is called one degree celsius ( $1^{\circ}\text{C}$ ).

Since in Celsius scale  $\theta_{ice} = 0^{\circ}\text{C}$  and  $N = \theta_{steam} - \theta_{ice} = 100^{\circ}\text{C} - 0^{\circ}\text{C} = 100^{\circ}\text{C}$ , so for Celsius scale the equ. (1.1) becomes

$$\frac{\theta - 0^{\circ}\text{C}}{100^{\circ}\text{C}} = \frac{X_{\theta} - X_{ice}}{X_{steam} - X_{ice}}$$

$$\text{or, } \theta = \frac{X_{\theta} - X_{ice}}{X_{steam} - X_{ice}} \times 100^{\circ}\text{C} \quad \dots \quad (1.2)$$

To calibrate the thermometer in Celsius scale equ (1.2) is used.

### Farenheit Scale

This scale was introduced in 1714 by German scientist G. D. Farenheit (1686–1736). At that time the lowest temperature known to the scientists was the temperature of the mixture of equal amount of ice and ammonium chloride, whose temperature was less than melting ice. Farenheit considered this temperature as zero and steam point is the upper fixed point. He divided the fundamental interval between these two points into 212 equal division and called each division one degree farenheit or  $1^{\circ}\text{F}$ . So the upper fixed point in the Farenheit scale is  $212^{\circ}\text{F}$ . The temperature of the ice point is found to be  $32^{\circ}\text{F}$  in this thermometer. So the lower fixed point in the Farenheit scale is taken to be  $32^{\circ}\text{F}$ . According to this calculation the 100 division of Celsius or Kelvin scale is equal to 180 divisions of the Farenheit Scale.

**Definition :** The scale in which the ice point and steam point are taken to be  $32^{\circ}$  and  $212^{\circ}$  respectively and the fundamental interval is divided into 180 equal divisions is known as Farenheit scale and each division is called one degree farenheit ( $1^{\circ}\text{F}$ ).

Since in Farenheit scale  $\theta_{ice} = 32^{\circ}\text{F}$  and  $N = \theta_{steam} - \theta_{ice} = 212^{\circ}\text{F} - 32^{\circ}\text{F} = 180^{\circ}\text{F}$ , so for Farenheit scale the equation (1.1) becomes,

$$\frac{\theta - 32^{\circ}\text{F}}{180^{\circ}\text{F}} = \frac{X_{\theta} - X_{ice}}{X_{steam} - X_{ice}}$$

$$\text{or, } \theta = \frac{X_{\theta} - X_{ice}}{X_{steam} - X_{ice}} \times 180^{\circ}\text{F} + 32^{\circ}\text{F} \quad \dots \quad (1.3)$$

To Calibrate a thermometer in the Farenheit scale equation (1.4) is used.

### Mercury thermometer

In case of mercury thermometer the thermometric property,  $X$ , is the length,  $l$ , of the mercury column in a capillary tube. So in mercury thermometer if the length of the mercury column be  $l_{100}$

and  $l_o$  at upper fixed point ( $100^{\circ}\text{C}$ ) and at lower fixed point ( $0^{\circ}\text{C}$ ) respectively and if  $l_\theta$  be the length of the mercury column at  $\theta^{\circ}\text{ C}$ , then,

$$\theta = \frac{l_\theta - l_o}{l_{100} - l_o} \times 100^{\circ}\text{C} \quad \dots \quad \dots \quad \dots \quad (1.4\text{a})$$

### Resistance thermometer

In case of resistance thermometer the thermometric property,  $X$ , is the resistance,  $R$ , of the conductor. If the temperature in the resistance thermometer in Celsius scale be  $\theta$ , then

$$\theta = \frac{R_\theta - R_o}{R_{100} - R_o} \times 100^{\circ}\text{C} \quad \dots \quad \dots \quad \dots \quad (1.4\text{b})$$

Here the resistance of the conductor at  $\theta^{\circ}\text{C}$ ,  $0^{\circ}\text{C}$  and  $100^{\circ}\text{C}$  are  $R_\theta$ ,  $R_o$  and  $R_{100}$  respectively.

In a mercury thermometer if the lengths of the mercury column at upper fixed point ( $212^{\circ}\text{F}$ ) and at lower fixed point ( $32^{\circ}\text{F}$ ) are  $l_{212}$  and  $l_{32}$  respectively and the length at  $\theta^{\circ}\text{ F}$  be  $l_\theta$ , then,

$$\theta = \frac{l_\theta - l_{32}}{l_{212} - l_{32}} \times 180^{\circ}\text{F} + 32^{\circ}\text{F} \quad \dots \quad \dots \quad \dots \quad (1.5)$$

### Clinical Thermometer

It is a very sensitive maximum mercury thermometer. It is calibrated in Fahrenheit scale. Since the physicians used this thermometer to measure the fever of human body, so it is known as clinical thermometer. Since the temperature of human body varies from  $95^{\circ}\text{ F}$  to  $110^{\circ}\text{ F}$ , the thermometer is calibrated from  $95^{\circ}\text{ F}$  to  $110^{\circ}\text{ F}$ . Since this thermometer can indicate the highest temperature of human body so it is known as maximum thermometer.

### Temperature Scale based on One Fixed Point

Though the use of two fixed points in determining the temperature scales are of much practiced yet we are to face various types of difficulties. For example, it is very difficult to achieve equilibrium of pure ice and water. Again the steam point is changed remarkably with the slight change of pressure. So attempts were taken to measure temperature using one fixed point instead of two.

Let the value of thermometric property of a thermometric substance used in a thermometer be,  $X$ , which changes uniformly with temperature,  $T$ . At thermal equilibrium,

$$\begin{aligned} X &\propto T \\ \text{or, } X &= aT \\ \text{or, } T &= bX \end{aligned} \quad \dots \quad \dots \quad \dots \quad (1.6)$$

Here  $b$  is a constant whose value is to be determined. If at the temperature  $T_p$  of the fixed point of a thermometer the thermometric property of a thermometric substance be  $X_p$ , then according to equation (1.6),

$$b = \frac{T_p}{X_p}$$

Putting the value of  $b$  in equation (1.6) we get ,

$$T = T_p \frac{X}{X_p} \dots \dots \dots \quad (1.7)$$

We know, at certain temperature and pressure the three states of substance *i.e.*, solid, liquid and gaseous states of a substance co-exist in thermal equilibrium is known as the triple point of the substance.

**Triple point :** At a definite pressure the temperature at which the solid, liquid and gaseous state of a substance coexist in thermal equilibrium is called the triple point of that substance.

Since solid, liquid and gaseous form of a substance can coexist at a definite pressure and temperature so the triple point is very suitable to determine a scale of temperature. The 'International Committee of Weights and Measures' in their meeting in 1954 selected the triple point of water as the only fixed point to measure the temperature.

**Triple Point of Water :** At 4.58 mm mercury pressure and the temperature at which pure ice, water and water vapour co-exist in thermal equilibrium is known as triple point of water.

The triple point temperature is taken to be  $T_{tr} = 273.16$  K, here K means kelvin is the SI unit of temperature.

**Definition of kelvin :** The SI unit of temperature or change of temperature is kelvin.

1 K or one kelvin is  $\frac{1}{273.16}$  of triple point temperature of water.

Depending on it the absolute zero temperature is 0K, ice point is 273.15 K and steam point is 373.15 K. Taking the triple point of water as a fixed point the equation (1.7) becomes.

$$T = (273.16 \text{ K}) \frac{X}{X_{tr}} \dots \dots \dots \quad (1.8)$$

He.e,  $X_{tr}$  is the value of thermometric property of the thermometric substance at triple point of water and X is the thermometric property of that substance at temperature T. Using equation (1.8) the temperature scale for any thermometric substance can easily be determined.

The relation of Kelvin with Celsius scale is

$$K = C + 273.15 \dots \dots \dots \quad (1.9)$$

For common calculations the ice point is taken as 273K instead of 273.15K. In that case the equation (1.9) becomes

$$K = C + 273 \dots \dots \dots \quad (1.10)$$

Generally the temperature is expresed in Celsius scale by  $\theta$  and in Kelvin scale by T.

$$\therefore T = \theta + 273 \dots \dots \dots \quad (1.11)$$

### Thermodynamic or Absolute Scale of Temperature

তাপমাত্রার তাপগতীয় ক্ষেল বা পরম ক্ষেল

Temperature scales are based on the nature and thermometric properties of different thermometric properties of different thermometric substances. The use of different thermometric

substances and their properties make the scales different. The thermal expansion or contraction of a thermometric substance may not take place uniformly in all temperature regions. So a single value of temperature is different in different scales. To overcome these difficulties **Lord Kelvin** introduced thermodynamic scale to measure temperature.

**Definition :** The scale of temperature which is counted taking the triple point temperature of water equal to 273.16 kelvin and equating  $\frac{1}{273.16}$  to one kelvin is known as thermodynamic scale.

This scale does not depend on the nature and property of the substance but only on the temperature so it is also known as absolute scale. The following equation is used to determine temperature,  $T$  in ideal gas scale and thermodynamic scale.

$$T = \frac{P_T}{P_{tr}} \times 273.16 \text{ K} \quad \dots \quad \dots \quad \dots \quad \dots \quad (1.12)$$

Here,  $P_T$  = pressure of ideal gas at  $T$  kelvin temperature.

$P_{tr}$  = pressure of equal value of ideal gas at triple point of water.

Though ideal gas is not available in reality but at low temperature the real gas behaves like ideal gas.

### International Scale of Temperature

#### তাপমাত্রার আন্তর্জাতিক ক্লেল

Although the scale suggested by **Lord Kelvin** (1824–1907) is independent of properties of any substance in particular, it was not possible to construct any instrument in practice. Since there are many difficulties in its materialization the **International Committee of Weights and Measures** adopted a practical scale known as 'International Temperature Scale' in 1927. This scale is based on a number of agreed and easily reproducible fixed points, so the scale can easily be materialized in practice.

**Definition :** The scale of temperature adopted by International Committee of Weights and Measures taking the triple point temperature of water equal to 273.16 kelvin and equating  $\frac{1}{273.16}$  to one kelvin and also taking a number of agreed and easily reproducible fixed points is known as International Temperature Scale.

On adopting the scale in 1927 the International Committee of Weights and Measures depending on real situation revised the scale in 1948 and again in 1954, 1960 and 1990. A set of fixed points adopted in the 1990 session of the International Committee of Weight and Measures is given below :

### FIXED POINTS ON THE INTERNATIONAL TEMPERATURE SCALE

Substance	Designation	Temperature (K)
Neon	Triple point	24.5561
Oxygen	Triple point	54.3584
Argon	Triple point	83.8058
Mercury	Triple point	234.3156
Water	Triple point	273.16
Gallium	Melting point	302.9146
Indium	Freezing point	429.7485
Tin	Freezing point	505.078
Zinc	Freezing point	692.677
Aluminium	Freezing point	933.473
Silver	Freezing point	1234.93
Gold	Freezing point	1337.33
Copper	Freezing point	1357.77

#### Relation Among Different Scales

Since for any thermometer

$\frac{\text{temperature} - \text{lower fixed point}}{\text{upper fixed point} - \text{lower fixed point}}$  is same for all scales.

$$\therefore \frac{\text{temperature} - \text{lower fixed point}}{\text{upper fixed point} - \text{lower fixed point}} = \frac{S - M}{B - M} \quad \dots \dots \dots \dots \dots \quad (1.13)$$

Here  $S$  is any temperature,  $M$  is the ice point that is, the lower fixed point and  $B$  is the steam point that is, the upper fixed point.

So if  $C$ ,  $F$  and  $K$  be the reading of any temperature on Celsius, Fahrenheit and Kelvin scales respectively then what will be the reading of scale on other scales can be obtained using from the following equation using equation (1.13) :

$$\frac{C - 0}{100 - 0} = \frac{F - 32}{212 - 32} = \frac{K - 273}{373 - 273}$$

$$\text{or, } \frac{C}{5} = \frac{F - 32}{9} = \frac{K - 273}{5} \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (1.14)$$

#### 1.2 Concept of First Law of Thermodynamics

তাপগতিবিদ্যার প্রথম সূত্রের ধারণা

Heat is easily available. Heat is produced when a fuel is burnt. Again heat automatically comes out when a hot object is cooled. Any other energy is not so easily available as that of heat. So the main objective of the scientists is to find a method to convert large amount of heat into mechanical energy.

In nature every moment innumerable events are taking place. But all these events can not take place as per will. Every event of nature must follow certain law. In fact the world of nature is dependent on law, everything is to maintain discipline. And these laws are unchangeable. As a piece of stone rolls from uphill to down hill. It will fall from Keokradang as well as from the Himalaya. Transformation of energy is to follow certain law. These laws are called the laws of thermodynamics. We have seen that heat can be converted into mechanical energy or work. The work we get today expensing the amount of heat if we want to get that amount of work tomorrow we will have to expense the same amount of heat. There can be no exception of the amount. It has been known by number of experiments.

Scientist Joule (1818–1889) first determined the exact relation between work and heat and he expressed this relation in the form of a law. This law is known as Joule's law.

**Law :** If mechanical energy is converted into heat or heat energy is converted into mechanical energy then heat and mechanical energy will be proportional to each other. This law is also known as **first law of thermodynamics**.

According to this law,

$$W \propto H$$

$$\text{or, } W = JH \quad \dots$$

$W = \text{work}$

$H = \text{heat}$

$J = \text{Joule's constant}$

(1.15)

Here  $W$  is the amount of work done,  $H$  is the amount of heat produced and  $J$  is the Joule's constant, it is known as **mechanical equivalent of heat**. In equation (1.15) if  $H = 1$  then  $W = J$ .

\* The amount of work done to produce unit heat or the amount of work done by unit heat is known as mechanical equivalent of heat.

### 1.3 System

সিস্টেম

To perform an experiment we consider a particular portion of the material world. This particular portion of the material world is known as a system. For example, gas in a cylinder fitted with a frictionless piston or gas in a balloon etc. Everything outside the system is considered as the environment.

**Definition :** The particular portion of the material world which we consider to perform an experiment is known as a system.

In thermodynamics a system can be described with the help of pressure  $p$ , volume  $V$  and temperature  $T$  at equilibrium. These quantities are known as **thermodynamic coordinates**. Any change of the thermodynamic coordinates of the system is known as **thermodynamic process**.

Every system has a definite volume, mass and internal energy. There are various types of system namely open system, closed system and isolated system.

**Open System :** The system which can exchange mass and energy with the environment is known as open system.

**Closed System :** The system which can exchange only energy but not mass with the environment is known as closed system.

**Isolated System :** The system which is not at all influenced by the environment that is, it can not exchange neither mass nor energy with the environment is known as isolated system.

### 1.4 Internal Energy

অভ্যর্তীণ শক্তি

If we hold a metallic substance near fire then we will see that the substance has become hot. It seems to us that 'something' from the fire has come to the object to make it hot. This 'something' is heat. In fact heat is not any material substance, heat is a process that changes the **internal energy of a substance**. When a body is heated its internal energy increases and when it is cooled its internal energy decreases. Everybody has an inherent energy by which it can work. This energy can be converted into another energy. This energy is the **internal energy**. In fact the linear motion of the molecules of the substance, vibration and rotation of the atoms and the motion of the electrons, around the nucleus are the causes of production of internal energy.

**Definition :** Each body contains an inherent energy which can perform work and can be converted into other form of energy. The energy due to the linear motion, vibrational motion and rotational motion of the molecules, atoms and elementary particles of a substance is known as the **internal energy**.

The change of internal energy is more important than the magnitude of internal energy of a body. The internal energy of a body depends on pressure ( $p$ ), volume ( $V$ ) and temperature ( $T$ ) of the body. It also depends on some physical properties like specific heat, coefficient of expansion etc. The temperature of a body changes with the change of its internal energy.

It is not possible to know the internal energy of a system, we can only measure the difference of internal energy of a system.

### 1.5 First Law of thermodynamics : Relation among Heat, Internal Energy and Work (তাপগতিবিদ্যার প্রথম সূত্র : তাপ, অভ্যর্তীণ শক্তি ও কাজের মধ্যে সম্পর্ক)

The first law of thermodynamics is actually another statement of conservation of energy. Scientist **Clasius** (1822–1888) described this law in a general form. According to him, if heat energy is converted into other form of energy in a system or any other energy is converted into heat energy the total energy of the system remains same.

**Law :** When heat is supplied to any system, then a part of that heat helps to increase the internal energy of the system and the remaining part of the energy is used by the system to do external work on the environment.

**Explanation :** On supplying  $\Delta Q$  amount of heat if the change of internal energy of the system be  $\Delta U$  and the external work done by the system on the environment be  $\Delta W$  then

$$\Delta Q = \Delta U + \Delta W \quad \dots \quad (1.16)$$

In case of very small change this equation can be written as,

$$dQ = dU + dW \quad \dots \quad (1.17)$$

Here  $\Delta Q$  is taken to be positive if heat is supplied to the system. On the other hand if heat goes out from the system to the environment then  $\Delta Q$  will be negative. If work is done by the system on the environment then  $\Delta W$  will be positive and if environment does work on the system  $\Delta W$  will be negative. If the internal energy of the system increases  $\Delta U$  will be positive and  $\Delta U$  will be negative when the internal energy of the system decreases.

The convention of sign is shown in the table below :

	Positive (+)	Negative (-)
$\Delta Q$ or $dQ$	When heat is supplied to the system.	When system loses heat.
$\Delta U$ or $dU$	If the internal energy of the system increases.	If the internal energy of the system decreases.
$\Delta W$ or $dW$	If work is done by the system.	If work is done on the system.

From equation (1.16) it is observed that, the change of internal energy of any system is the difference of the amount of energy flowing to the system as heat and the amount of energy flowing from the system to the environment as work.

That is  $dU = dQ - dW$  ... ... (1.18)

### 1.6 Use of First Law of Thermodynamics : Work Done by an Expanding Gas (তাপগতিবিদ্যার প্রথম সূত্রের ব্যবহার : প্রসারণশীল গ্যাস দ্বারা কৃত কাজ)

#### Indicator Diagram (নির্দেশক চিত্র)

Generally the amount of work done in any thermodynamic process can be determined with the help of  $pV$ -diagram. This diagram is known as indicator diagram. The indicator diagram or  $pV$  diagram is drawn taking the volume  $V$  along X-axis and pressure  $p$  along Y-axis.

If the pressure of the gas changes with the volume of the gas then the indicator diagram will look like fig. 1.1. the work done due to this change of the gas will be equal to the area of  $aABb$ .

#### (a) Isobaric Process (সমচাপ প্রক্রিয়া)

**Definition :** The thermodynamic process in which the pressure of the system is not changed is known as isobaric process.

Let some gas is enclosed in a cylinder fitted with a frictionless piston (fig. 1.2). The area of cross section of the piston be  $A$ . If the pressure of the gas be  $p$  then the force on the piston due to pressure be  $pA$ . Now if an external force,  $F$  equal to this force is applied on the piston, the piston will remain in equilibrium position.

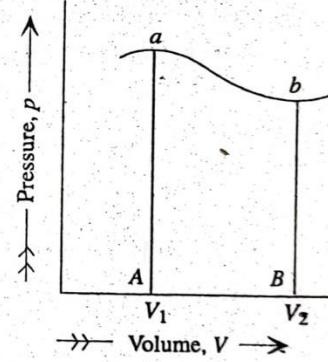


Fig 1.1

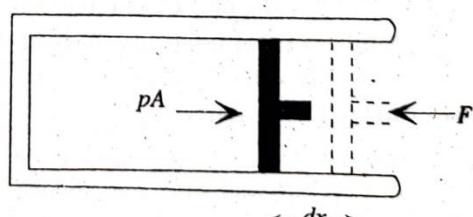


Fig 1.2

Now let us consider that the gas expands and as a result the piston has moved through a very small distance  $dx$ . Since  $dx$  is very small the pressure of the gas can be considered constant. If the external work done against the force  $F$  be  $dW$ . Then

$$dW = Fdx = pAdx \quad \dots \quad \dots \quad (1.19)$$

$$\therefore dW = pdV \quad \dots \quad \dots$$

Here,  $dV = A dx$  = small expansion of the volume of the gas.

If the volume of the gas changes from  $V_1$  to  $V_2$  at constant pressure, then the work done by the gas,

$$W = \int dW = \int_{V_1}^{V_2} pdV = p \int_{V_1}^{V_2} dV = p [V]_{V_1}^{V_2} = p \Delta V$$

That is, work done = pressure  $\times$  change of volume.

If we put the amount of work done  $pdV$  in equation (1.17) then the first law of thermodynamics can be written as

$$dQ = dU + pdV \quad \dots \quad \dots \quad (1.20)$$

The indicator diagram of isobaric process has been shown in fig (1.3). It is a straight line parallel to  $X$ -axis ( $V$ -axis)

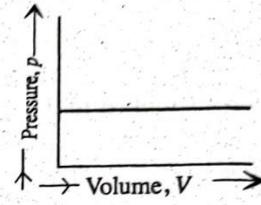


Fig 1.3

#### (b) Isochoric Process (সমআয়তন প্রক্রিয়া)

The thermodynamic process in which the volume of the system remain constant is known as **isochoric process**. If a gas is heated in a confined container then its temperature and pressure increase but volume remains constant. Such process is the isochoric process. The indicator diagram of an isochoric has been shown in fig 1.4. This is a straight line parallel to  $Y$ -axis ( $p$ -axis). In isochoric process there is no change in volume ( $dV = 0$ ), so work done.

$$dW = pdV = 0 \quad \dots \quad \dots \quad (1.21)$$

So in an isochoric process the work done is zero.

Putting the value of work in equation (1.20) the first law of thermodynamics can be written as,

$$dQ = dU \quad \dots \quad \dots \quad (1.22)$$

That is, in isochoric process whole of the applied heat is used to increase the internal energy of the system.

#### (c) Isothermal Process (সমোক্ত প্রক্রিয়া)

The thermodynamic process in which the temperature of the system remains constant is known as **isothermal process**.

In isothermal process the temperature of the system remains constant so that Boyle's Law can be applied.

Let a cylinder filled with gas and fitted with a movable piston be our system. Energy can go out or come in through

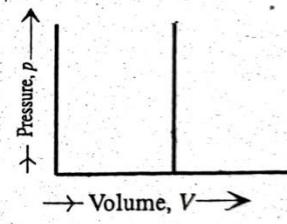


Fig 1.4

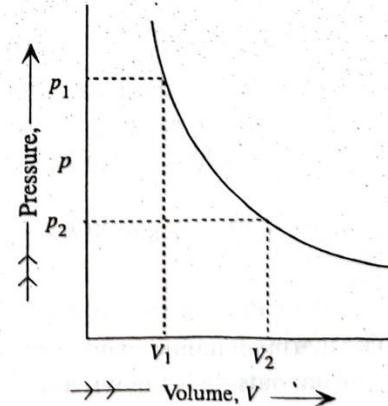


Fig : 1.5

the wall of the cylinder. If energy is supplied to system very slowly then the pressure and volume of the gas will be changed though its temperature will remain unchanged. Such change is known as isothermal change. The expansion of the gas due to this change is known as isothermal expansion.

The  $pV$ -curve for isothermal process is shown in the fig. 1.5. This curve is known as **isothermal curve**. This is a rectangular hyperbola

In isothermal process the temperature remains constant so the internal energy of the system does not change i.e.,  $dU = 0$ . So from the first law of thermodynamics we get

$$dQ = 0 + dW$$

$$\therefore dQ = dW$$

That is, in an isothermal process the work done by the system is equal to the heat energy supplied to the system.

In isothermal process

$$p_1 V_1 = p_2 V_2$$

In case of isothermal change,  $pV = nRT$

$$\text{or, } p = \frac{nRT}{V}$$

So the total amount of work will be,

$$W = \int_{V_1}^{V_2} pdV = \int_{V_1}^{V_2} nRT \frac{dV}{V} = nRT \left[ \ln V \right]_{V_1}^{V_2}$$

$$\therefore W = nRT \ln \left( \frac{V_2}{V_1} \right)$$
(1.24)

Since in the isothermal process the change of internal energy  $dU = 0$

$$\text{Therefore, } dW = dQ$$

So the heat required for isothermal expansion is,

$$Q = W = nRT \ln \left( \frac{V_2}{V_1} \right)$$

and this equal to the area  $adBA$  of the indicator diagram (1.5). So from the area of the indicator diagram we can directly determine the amount of work done by a heat engine. That is, the work done by a heat engine is,

$$W = \int_{V_1}^{V_2} pdV = \text{area of } abBA$$
(1.25)

#### (d) Adiabatic Process (রূক্ষতাপীয় প্রক্রিয়া)

The thermodynamic process in which no heat can go out of the system nor can enter the system from outside is known as **adiabatic process**.

If we can thermally insulate the system from the environment or we can expand or compress the gas very quickly then we get an adiabatic process. The change of the system during this

Since the internal energy of an ideal gas only depends on its temperature, so we can use this equation when there is a change of temperature  $dT$ . During this change of temperature it is not necessary that the volume should remain constant.

### **Relation between $C_p$ & $C_v$ for an Ideal Gas : $C_p - C_v = R$**

একটি আদর্শ গ্যাসের জন্য  $C_p$  এবং  $C_v$ -এর মধ্যে সম্পর্ক :  $C_p - C_v = R$

Let there be one mole gas in a cylinder fitted with a frictionless piston (Fig. 1.2). The pressure of this gas be  $p$ , volume  $V$ , temperature  $T$ , and internal energy  $U$ . Now keeping the pressure of this gas constant  $dQ$  amount of heat is supplied to this gas. As a result the internal energy, volume and temperature of this gas are increased respectively by  $dU$ ,  $dV$  and  $dT$ . Due to application of heat if the external work is  $dW$ , then from the first law of thermodynamics we get,

$$dQ = dU + dW$$

$$\text{or, } dQ = dU + pdV \quad \dots \quad \dots \quad \dots \quad (1.31)$$

But we know that, the increase of internal energy  $dU$  is given by the product of the molar specific heat at constant volume  $C_v$  and the increase in temperature  $dT$  i.e.,

$$dU = C_v dT$$

Putting this value of  $dU$  in equation (1.31) we get,

$$dQ = C_v dT + pdV \quad \dots \quad \dots \quad \dots \quad (1.32)$$

Again we know that the amount of heat required to raise the temperature of 1 mole of gas through 1K keeping the pressure constant, the molar specific heat of a gas at constant pressure is,

$$C_p = \frac{dQ}{dT}$$

$$\text{or, } dQ = C_p dT \quad \dots \quad \dots \quad \dots \quad (1.33)$$

Putting this value of  $dQ$  in equation (1.32) we get,

$$C_p dT = C_v dT + pdV \quad \dots \quad \dots \quad \dots \quad (1.34)$$

Again if molar gas constant be  $R$ , then for 1 mole of gas we know,

$$pV = RT$$

Differentiating it with respect to  $T$

$$\frac{d}{dT}(pV) = \frac{d}{dT}(RT)$$

$$\text{or, } p \frac{dV}{dT} = R \quad [\because p \text{ is constant}]$$

$$\text{or, } pdV = RdT \quad \dots \quad \dots \quad \dots \quad (1.35)$$

Now putting the value of  $pdV$  from equation (1.32), we get

$$C_p dT = C_v dT + RdT$$

$$\text{or, } C_p = C_v + R$$

$$\therefore C_p - C_v = R \quad \dots \quad \dots \quad \dots \quad (1.36)$$

Since the molar gas constant  $R$  is a positive quantity, so  $C_p > C_v$

$\therefore C_p$  is always greater than  $C_v$ .

The ratio of two molar specific heats,  $\gamma = \frac{C_p}{C_v}$

মোলার আপেক্ষিক তাপচয়ের অনুপাত,  $\gamma = \frac{C_p}{C_v}$

In thermodynamics the ratio of molar specific heat at constant pressure to the molar specific heat at constant volume is a very important quantity. This ratio is denoted by  $\gamma$ ; that is

$$\gamma = \frac{C_p}{C_v} \quad \dots \quad (1.37)$$

Being ratio of two same kind of quantities so  $\gamma$  has no unit.

With the help of kinetic theory of gas for monoatomic gas it is obtained that,  $C_v = \frac{3}{2} R$

$$\therefore C_p = C_v + R = \frac{3}{2} R + R = \frac{5}{2} R$$

$$\therefore \text{for monoatomic gas, } \gamma = \frac{C_p}{C_v} = \frac{\frac{5}{2}R}{\frac{3}{2}R} = \frac{5}{3} = 1.67$$

From kinetic theory of gas for diatomic gas it is obtained,

$$C_v = \frac{5}{2} R \text{ and } C_p = C_v + R = \frac{5}{2} R + R = \frac{7}{2} R$$

$$\therefore \text{For diatomic gas, } \gamma = \frac{C_p}{C_v} = \frac{\frac{7}{2}R}{\frac{5}{2}R} = \frac{7}{5} = 1.40$$

and for polyatomic gas,  $C_v = 3R$  and  $C_p = 3R + R = 4R$

$$\therefore \text{For polyatomic gas, } \gamma = \frac{C_p}{C_v} = \frac{4R}{3R} = \frac{4}{3} = 1.33$$

Dividing equation (1.36) by  $C_v$  we get,

$$\begin{aligned} \frac{C_p}{C_v} - 1 &= \frac{R}{C_v} \\ \text{or, } \gamma - 1 &= \frac{R}{C_v} \\ \therefore C_v &= \frac{R}{\gamma - 1} \quad \dots \quad (1.38) \end{aligned}$$

### Uses of $\gamma$ ( $\gamma$ -এর ব্যবহার)

The ratio of molar specific heats  $\gamma$  is very important for different reasons. Some of its uses are given below :

1. We can know from the value of  $\gamma$  that whether the gas is monoatomic or diatomic or polyatomic. If the value of  $\gamma = 1.40$  for any gas, then we can say that the gas is diatomic.

2. Velocity of sound in a gas depends on the value of  $\gamma$ .

Such as  $v = \sqrt{\frac{\gamma p}{\rho}}$ , here  $\rho$  is the density of the gas.

3. In case of adiabatic change the relation between the pressure and volume of a gas depends on  $\gamma$ . Such as  $pV^\gamma = \text{constant}$ .

## 1.8 Different Relations between Thermodynamic Variables

তাপগতীয় স্থানাঙ্কগুলোর মধ্যে বিভিন্ন সম্পর্ক

In case of Adiabatic change for an Ideal Gas  $pV^\gamma = \text{constant}$

কন্দতাপীয় পরিবর্তনের সময় আদর্শ গ্যাসের ফলে  $pV^\gamma = \text{ধ্রবক}$

Let there be one mole of ideal gas in a cylinder fitted with a frictionless piston (Fig. 13.1). The pressure of this gas be  $p$ , volume  $V$ , Temperature  $T$  and internal energy  $U$ . Now the change of pressure, volume, temperature and internal energy be respectively  $dp$ ,  $dV$ ,  $dT$  and  $dU$  due to supply of heat  $dQ$  to the gas. If the external work be  $dW$  due to supply of heat then from the first law of thermodynamics we know,

$$dQ = dU + dW$$

$$\text{or, } dQ = dU + pdV$$

But we know that the increase in internal energy  $dU$  is the product of molar specific heat at constant volume  $C_v$  and the increase in temperature  $dT$  i.e.,  $dU = C_v dT$ .

$$\therefore dQ = C_v dT + pdV$$

Now in adiabatic change,  $dQ = 0$

$$\therefore C_v dT + pdV = 0 \quad \dots \quad (1.39)$$

Again, for 1 mole of ideal gas we know

$$pV = RT$$

Differentiating this equation with respect to  $T$  we get

$$\frac{d}{dT}(pV) = \frac{d}{dT}(RT)$$

$$\text{or, } p \frac{dV}{dT} + V \frac{dp}{dT} = R \quad \text{or, } pdV + Vdp = RdT$$

$$\therefore dT = \frac{pdV + Vdp}{R}$$

Putting this value of  $dT$  in equation (1.39)

$$C_v \left( \frac{pdV + Vdp}{R} \right) + pdV = 0$$

$$\text{or, } C_v pdV + C_v Vdp + RpdV = 0$$

$$\text{or, } C_v pdV + C_v Vdp + (C_p - C_v) pdV = 0 \quad [\because R = C_p - C_v]$$

$$\text{or, } C_v pdV + C_v Vdp + C_p pdV - C_v pdV = 0$$

$$\text{or, } C_v Vdp + C_p pdV = 0 \quad \text{or, } Vdp + \frac{C_p}{C_v} pdV = 0$$

$$\text{or, } V dp + \gamma pdV = 0 \quad [\because \gamma = \frac{C_p}{C_v}]$$

Dividing both the sides by  $pV$

$$\frac{dp}{p} + \gamma \frac{dV}{V} = 0$$

Integrating this equation

$$\ln p + \gamma \ln V = \text{constant}$$

$$\text{or, } \ln(pV^\gamma) = \text{constant}$$

$$\text{or, } \ln(pV^\gamma) = \text{constant}$$

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

(1.40)

#### Extended activity

In case of adiabatic change for an ideal gas determine the relation  $TV^{\gamma-1} = \text{constant}$

If the pressure of an ideal gas be  $p$ , volume  $V$  and temperature  $T$ , then we know,

$$pV = RT \quad \text{or, } p = \frac{RT}{V}$$

Again, in an ideal gas during adiabatic change  $pV^\gamma = \text{constant}$ .

Putting the value of  $p$  in the above equation, we get

$$\frac{RT}{V} V^\gamma = \text{constant}$$

$$\text{or, } RTV^{\gamma-1} = \text{constant}$$

$$\text{or, } TV^{\gamma-1} = \text{constant}$$

[ $\because R$  is the universal gas constant]

This equation shows the relation between temperature and volume during adiabatic change.

**Extended activity : In case of adiabatic change for an ideal gas determine the relation between pressure and temperature,**

$$Tp^{\frac{1-\gamma}{\gamma}} = \text{constant.}$$

For one mole of an ideal gas if the pressure, volume and temperature be respectively  $p$ ,  $V$  and  $T$  then we know,

$$pV = RT \quad \therefore V = \frac{RT}{p}$$

Again for adiabatic change,  $pV^\gamma = \text{constant}$

Putting the value of  $V$  in the above equation we get

$$p \left( \frac{RT}{p} \right)^\gamma = \text{constant}$$

$$\text{or, } R^\gamma \times p^{1-\gamma} \times T^\gamma = \text{constant}$$

$$\text{or, } T^\gamma p^{1-\gamma} = \text{constant}$$

[ $\because R$  is the universal gas constant.]

Taking the  $\gamma$  th root on both the sides of the equation (1.42)

$$Tp^{\frac{1-\gamma}{\gamma}} = \text{constant.}$$

(1.43)

This equation is the relation between pressure and temperature.

**Extended activity : Work done due to adiabatic change**

Since in an adiabatic process no heat can enter a system or no heat can leave the system so,  $dQ = 0$ . Therefore from first law of thermodynamics we get:

$$0 = dU + dW$$

$$\therefore dW = -dU$$

If the at initial condition the pressure, volume and temperature of a gas be respectively  $p_1, V_1$  and  $T_1$  and at final condition if their values are respectively  $p_2, V_2$  and  $T_2$  then the total work done in going to final stage from the initial stage is,

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

In case of adiabatic change  $pV^\gamma = \text{constant}, K$

$$\begin{aligned} \therefore p &= \frac{K}{V^\gamma} \\ \therefore W &= \int_{V_1}^{V_2} pdV = \int_{V_1}^{V_2} \frac{KdV}{V^\gamma} = K \int_{V_1}^{V_2} V^{-\gamma} dV \\ &= K \left[ \frac{1}{-\gamma+1} V^{-\gamma} + 1 \right]_{V_1}^{V_2} \\ &= K \left[ \frac{V_1^{1-\gamma}}{1-\gamma} - V_2^{1-\gamma} \right] = \frac{K}{1-\gamma} [V_2^{1-\gamma} - V_1^{1-\gamma}] \\ &= \frac{1}{1-\gamma} [KV_2^{1-\gamma} - KV_1^{1-\gamma}] \\ &= \frac{1}{1-\gamma} [p_2 V_1^\gamma V_1^{1-\gamma} - p_1 V_1^\gamma V_1^{1-\gamma}] \quad [\because p_1 V_1^\gamma = p_2 V_1^\gamma = K] \\ &= \frac{1}{1-\gamma} [p_2 V_2 - p_1 V_1] = \frac{1}{1-\gamma} [p_1 V_1 - p_2 V_2] = \frac{1}{1-\gamma} [RT_1 - RT_2] \\ \therefore W &= \frac{R}{\gamma-1} [T_1 - T_2] \quad \dots \quad \dots \quad \dots \quad (1.44) \end{aligned}$$

and it is equal to the area  $aABb$  of the indicator diagram 1.1. That is,

$$W = \int_{V_2}^{V_1} pdV = \text{area of } abBA \quad \dots \quad \dots \quad \dots \quad (1.45)$$

## 1.10 Second Law of Thermodynamics

তাপগতিবিদ্যার দ্বিতীয় সূত্র

Out of different energies the speciality of heat is that, all other energy can be converted into heat energy very easily but heat energy cannot be converted into any other energy easily. **To convert heat energy into any other energy a device is required. This device is heat engine.** Carnot concluded after extensive research that conversion of heat energy is not possible without engine and it is impossible to convert the heat energy completely into mechanical energy.

Depending on the experimental experience of Carnot scientists like Planck, Clasius, Kelvin after various experiments formulated the second law of thermodynamics. Different scientists have stated the law in different ways.

**Carnot's statement :** No engine can be built which can extract a fixed amount of heat and will convert totally into work.

**Clasius's Statement :** It is impossible for a self acting machine, unaided by any external agency, convey heat from one body at a lower temperature to another body at a higher temperature.

**Planck's statement :** It is impossible to construct an engine which can extract heat continuously from a source of heat and completely transforms into work.

**Kelvin's statement :** Continuous flow of energy cannot be obtained from an object cooling it than the coolest part of its surroundings.

**Explanation :** From the first law of thermodynamics we came to know that transformation among different types of energy is possible. If any amount of energy is abolished then same amount of energy must evolve—that is there is no destruction of energy. The first law of thermodynamics is a special form of conservation of energy. But the first law can not tell us which system will gain heat or which system will loose it. Such as if we keep a piece of 1kg ice outside then heat will come from the environment and convert the ice into water. But if we keep this water outside then it can not be converted into ice spontaneously by giving up  $3.4 \times 10^5$  J heat to the environment though the first law of thermodynamics does to restrict it as the conservation of energy is not violated in this process.

From the first law of thermodynamics we know that the amount of heat lost by a body or a system is exactly equal to the gain of heat by other system. But the first law cannot tell us which system will gain heat or which system will loose it. To know the direction of flow of heat we are to know the temperature of the two systems. Heat always naturally flows from higher temperature to lower temperature. The reverse cannot be happened spontaneously. Even though the amount of a heat of the colder system is more than the hotter system still it will not happen. This is the law of nature. If we are to bring out heat from a colder system we are to spend mechanical energy.

Heat flows spontaneously from one system to another only when there is a difference of temperature between the two systems. The spontaneous flow of heat will continue till there is a difference of temperature. When the two systems attain at the same temperature there will be no flow of heat. When there is no flow of heat between the two systems we say that the two systems are in thermal equilibrium. So it is seen that all spontaneous processes are unidirectional and it continues till the systems have attained the thermal equilibrium. The second law of thermodynamics is evolved depending on the experience of transfer of energy in nature. The

main theme of the second law of thermodynamics is under which condition how much energy will be transferred to which direction.

### 1.11 Reversible and Irreversible Processes

#### প্রত্যাবর্তী ও অপ্রত্যাবর্তী প্রক্রিয়া

When a system changes from one state to another state, this change of state can take place in two processes namely, 1. Reversible process and 2. Irreversible process.

**Reversible Process :** It is a process which can be retraced in the opposite direction so that the system and the surroundings pass through exactly the same state at each stage as in direct process.

If heat is absorbed by a substance in a direct process to produce external work, The substance will give out an equal quantity of heat in the reverse process when the same amount of external work is done on it, then the process is considered as reversible process.

#### Examples :

1. A given mass of ice changes to water when a certain amount of heat is absorbed by it, and the same mass of water changes to ice when the same quantity of heat is removed from it.

2. Within elastic limit the linear expansion or compression of a spring very slowly is an example of reversible process. Since during expansion the amount of work done on the spring the same amount of work is done by the spring during compression.

**Irreversible Process :** It is a process which is not exactly reversed, i.e., the system does not pass through the same intermediate state as in the direct process.

All spontaneous changes in nature are irreversible. Such as heat flows from higher temperature to lower temperature. A piece of stone can go downhill spontaneously but it cannot go uphill. All spontaneous change is unidirectional and irreversible.

**Example :** The heat produce due to friction between two objects is an irreversible process. As the work done against the friction is changed into heat but this heat can not be transformed into work.

#### Distinction between reversible and irreversible processes

Reversible process	Irreversible process
1. It is a process which can be retraced in the opposite direction so that the system and the surroundings pass through exactly the same state at each stage as in direct process.	1. It is a process which is not exactly reversed, i.e., the system does not pass through the same intermediate state as in the direct process.
2. The working substance returns to its initial state.	2. The working substance cannot return to its initial state.
3. It is a very slow process.	3. It is a very fast process.
4. It is not a spontaneous process.	4. It is a spontaneous process.
5. In this process the thermodynamic equilibrium is maintained.	5. In this process the thermodynamic equilibrium is not maintained.

### 1.12 Heat Engine

তাপীয় ইঞ্জিন

To use heat energy we need a device. This device is the heat engine.

**Definition : The device which converts heat energy into mechanical energy is called heat engine.**

Engine absorbs a certain quantity of heat from a source, converts a part of it into work and rejects the remaining heat to the surroundings and again absorbs heat from the source. The temperature of the source from which the engine absorbs heat should be higher than the surroundings to which the engine rejects heat. **That is, the engine absorbs heat from a source of higher temperature and converts a part of it into work and rejects the remaining part of heat to a sink of lower temperature and the initial condition is restored.** To get continuous supply of work from an engine the cycle of operations are to be repeated. Since the cycle of operation can be repeated indefinitely therefore the heat engine gives a continuous supply of work indefinitely. Let a working substance (such as gas in a cylinder fitted with a piston) absorbs  $Q_1$  amount of heat from a source of higher temperature  $T_1$  (Fig 1.8). The engine attains the temperature of the source during converting a part of heat into work. Now to get work from this engine i.e., to convert heat energy into mechanical energy a part of heat absorbed from the source is to be rejected to the sink at lower temperature so that the temperature of the working substance is lowered to absorb heat from the source again. If  $Q_2$  be the amount of heat rejected to the sink at lower temperature  $T_2$ , the amount of heat energy converted into work by the engine is,  $W = Q_1 - Q_2$ .

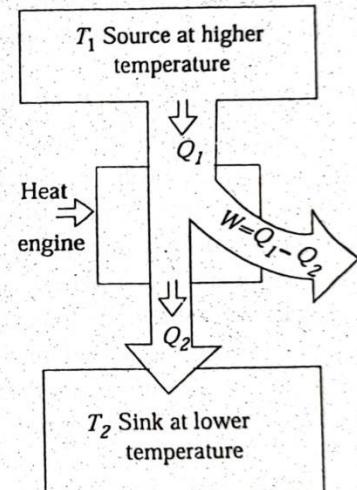


Fig : 1.8

### 1.13 Carnot's Engine

কার্নো ইঞ্জিন

Heat is converted into work with the help of a heat engine. The engine which we use in practice can not convert all the heat into work. Generally the engine can convert maximum 25% of the heat supplied. A French Engineer Nicolas Le'onard Sadi Carnot (1796–1832) conceived an ideal engine which is free from all the imperfections of an actual engine which is known as Carnot engine.

**Definition : Sadi Carnot conceived an ideal engine to convert heat energy to mechanical energy which is free from all imperfections of an actual engine is known as Carnot engine.**

The Carnot engine is only an imaginary one, it is not possible to construct such an engine in

practice. The different parts of a Carnot engine are shown in figure 1.9

1. A cylinder  $C$  with perfectly nonconducting walls and a perfectly conducting bottom. It is fitted with a perfectly nonconducting and frictionless piston  $P$ . An ideal gas is enclosed in the cylinder which acts as the working substance.

2. The heat source is a hot object with very high thermal capacity is maintained at temperature of  $T_1$ . Any amount of heat can be taken out from it without changing its temperature.

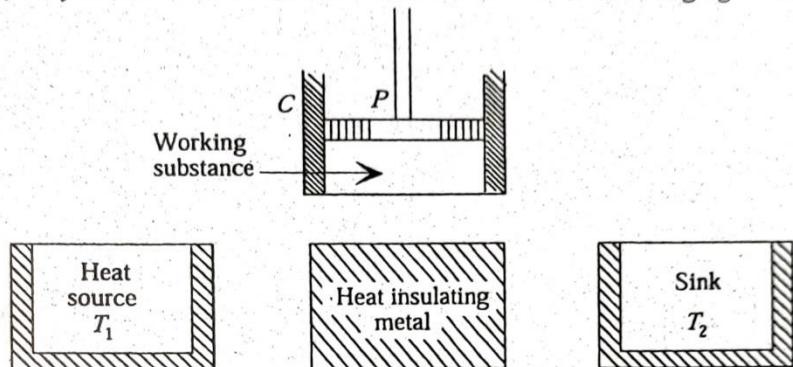


Fig : 1.9

3. The sink is a cold object with very high thermal capacity is maintained at a lower temperature of  $T_2$ . Any amount of heat can be rejected to it without changing its temperature.

4. A platform made up of completely insulating object on which the cylinder is placed.

### 1.14 Carnot's Cycle

কার্নো চক্র

**Definition :** The working substance is taken through a cycle of operations, known as Carnot cycle.

A cycle in which the working substance starting from a given condition of temperature, pressure and volume is made to undergo two successive expansions, one

isothermal and another adiabatic, and then two successive compressions one isothermal and another adiabatic and then brought back finally to its initial condition is called Carnot cycle.

In Carnot cycle the working substance is subjected to the following four successive reversible operations so as to complete one cycle. This cycle is the Carnot cycle.

**Step-1 :** The cylinder  $C$  is placed on the source and within a very short period the gas attains the temperature of the source. Let at this stage the pressure and volume are respectively  $p_1$  and  $V_1$  which is represented by the point  $A$  of the indicator diagram (Fig. 1.10). Now the ideal gas is

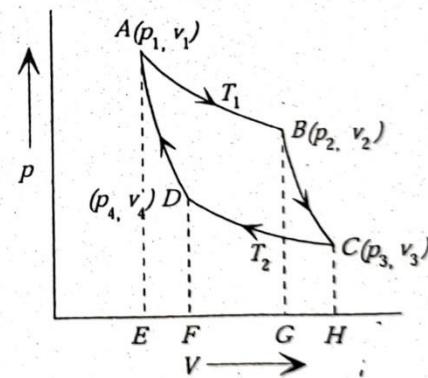


Fig : 1.10

So in one Carnot cycle the total work done by the working substance is given by the area enclosed by two isothermal and two adiabatic curves.

### 1.15 Efficiency of Heat Engine

তাপীয় ইঞ্জিনের দক্ষতা

The efficiency of an engine indicates how many part of the absorbed heat energy can the engine convert into work.

**Definition :** It is the ratio of the heat energy converted into work to the heat energy absorbed from the source by the engine.

Therefore,

$$\text{Efficiency of the Engine} = \frac{\text{Heat energy converted into work by the engine}}{\text{Heat energy absorbed by the engine}}$$

**Explanation :** If any engine absorbs  $Q_1$  amount of heat from a source at  $T_1$  temperature and rejects  $Q_2$  amount of heat at temperature  $T_2$ , then the amount of heat converted into work,

$$W = Q_1 - Q_2$$

$$\text{Therefore, the efficiency } \eta = \frac{W}{Q_1} \dots \dots \dots \quad (1.47)$$

$$\text{or, } \eta = \frac{Q_1 - Q_2}{Q_1}$$

$$\text{or, } \eta = 1 - \frac{Q_2}{Q_1} \dots \dots \dots \quad (1.48)$$

In case of Carnot engine the absorbed or rejected heat,  $Q$ , is proportional to the temperature,  $T$  of the source or sink kept in contact with the engine. That is,  $\frac{Q}{T} = \text{constant}$ .

So for a complete cycle of the Carnot engine, we get

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2} \dots \dots \dots \quad (1.49)$$

$$\text{or, } \frac{Q_1}{Q_2} = \frac{T_1}{T_2}$$

Therefore from equation (1.48) the efficiency of the Carnot engine is given by

$$\eta = 1 - \frac{T_2}{T_1} \dots \dots \dots \quad (1.50)$$

$$\text{or, } \eta = \frac{T_1 - T_2}{T_1} \dots \dots \dots \quad (1.50)$$

Efficiency is generally expressed as percentage.

$$\therefore \eta = \frac{T_1 - T_2}{T_1} \times 100\% \dots \dots \dots \quad (1.51)$$

colder more than requirement then the power supply of the compressor is to be cut off. For this there is a thermostat inside the refrigerator. When the temperature becomes lower than requirement the thermostat automatically starts functioning.

#### The efficiency of a Refrigerator (Coefficient of Performance or COP) K :

In fig 1.13 the direction of flow of heat of a refrigerator and the  $p$ - $V$  diagram has been shown. Refrigerator performs work in the opposite direction of Carnot cycle. Refrigerator performs work along  $ADCBA$ . That is, if a Carnot engine is operated oppositely then it will work as a refrigerator.

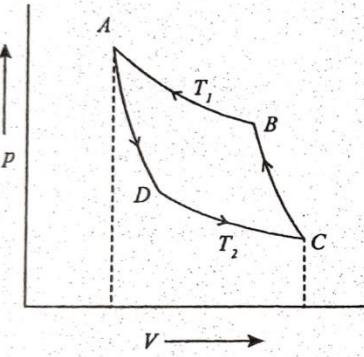


Fig 1.13

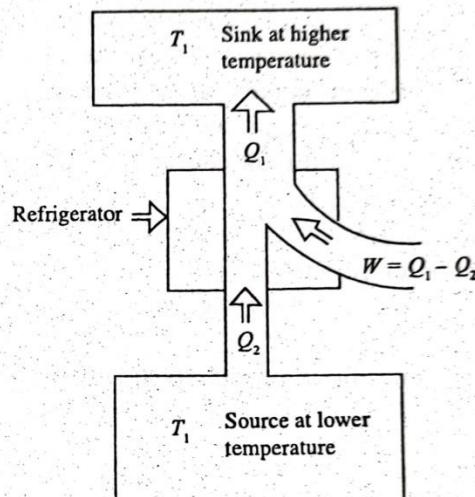


Fig 1.14

Refrigerator absorbs  $Q_2$  quantity of heat from the source of lower temperature and for rejecting  $Q_1$  quantity of heat performs  $W = Q_1 - Q_2$  amount of work on the working substance by a compressor from outside (fig 1.14).

So the efficiency or the coefficient of performance of a refrigerator is the ratio of the heat removed from the source of lower temperature to the work performed by the external agent that is, by the compressor.

$$\therefore \text{COP or } K = \frac{\text{Heat absorbed by the system}}{\text{Work done on the system}} = \frac{Q_2}{W} = \frac{Q_2}{Q_1 - Q_2} = \frac{T_2}{T_1 - T_2} \dots \quad (1.52)$$

### 1.17 Entropy

ଏନ୍ଟ୍ରୋପି

Now we are going to introduce a new concept which is known as entropy and which is a quantity of prime importance in the discussion of science. To have energy in a system is not enough to get work from it. It depends on the condition of the system of that time. The following example will explain the situation. Let two water filled vessels constitute a system. One vessel contains 500 kg water at 90°C and the other vessel has 500 kg water at 10°C. Considering the water at 90°C as source and the water at 10°C as sink we can start an engine. We can get work

from the system till the water of both the vessel attain the same temperature. Now if we mix the water of the two vessels we will get 1000 kg water at 50°C temperature. But from this water no engine can get any work since there is no difference of temperature, the flow of heat ceases. According to first law of thermodynamics though the energy of water before and after mixing remains the same yet it is unable to convert heat energy into mechanical energy since the system has attained the thermal equilibrium. The disability of a system to convert energy is known as **entropy**. We know that due to the work done on a gas when it is compressed there is an increase of internal energy and the temperature of the gas. Again when a gas is allowed to expand adiabatically some work is to be done by the gas. Therefore it is observed that in an adiabatic process both the internal energy and temperature change. A quantity remains constant in an adiabatic process like temperature in the isothermal process. Clasius named this quantity entropy. Entropy is a physical quantity. It is represented by  $S$ .

**Definition :** The disability of converting energy of a system or unavailability of energy to convert into work is **entropy**.

**Explanation :** It has not yet been possible to measure the absolute magnitude of entropy. If any body absorbs or rejects heat then its entropy is changed. **The change of entropy is measured by the rate of absorption or rejection of heat by the system with respect to temperature.**

If any system absorbs or rejects  $dQ$  amount of heat at temperature  $T$ , then the change of entropy,

$$dS = \frac{dQ}{T} \quad \dots \quad (1.53)$$

From equation 1.53 it is seen that, since the working substance do not exchange heat with the surroundings in an adiabatic process, so  $dQ = 0$

$$\text{Therefore the change of entropy, } dS = \frac{dQ}{T} = 0 \quad \dots \quad (1.54)$$

That is, in an adiabatic process there is no change of entropy.

Therefore, **by entropy of a system we mean a physical quantity which always remains constant in an adiabatic reversible process.**

The unit of change of entropy is joule/kelvin or  $\text{JK}^{-1}$ .

If the temperature does not remain constant or in case of any large change that is, if the temperature of an object of mass  $m$  and specific heat  $s$  changes from  $T_1$  to  $T_2$  then the change of entropy will be,

$$\Delta S = \int_{T_1}^{T_2} \frac{dQ}{T} = \int_{T_1}^{T_2} \frac{msdT}{T} = ms \int_{T_1}^{T_2} \frac{dT}{T}$$

$$\text{or, } \Delta S = ms \left[ \ln T \right]_{T_1}^{T_2} = ms \left[ \ln \frac{T_2}{T_1} \right]$$

$$\therefore \Delta S = ms \left[ \ln T_2 - \ln T_1 \right] \quad \dots \quad (1.55)$$

### Change of Entropy in Reversible and Irreversible processes

#### (a) Change of Entropy in Reversible Process

Carnot cycle is a reversible cycle. In fig 1.15 ABCD is a Carnot cycle. From the Carnot cycle it is seen that AB is an isothermal expansion curve and CD is an isothermal compression curve. Again BC is an adiabatic expansion curve and DA is an adiabatic compression curve. Since BC and DA are adiabatic curves so there will be no change of heat along them as a result there is no change of entropy of the working substance.

$$\text{The change of entropy along the isotherm } AB = \frac{Q_1}{T_1}$$

$$\text{The change of entropy along the isotherm } CD = -\frac{Q_2}{T_2}$$

∴ The total change of entropy of the working substance,

$$\Delta S = \frac{Q_1}{T_1} - \frac{Q_2}{T_2} \quad \dots \quad (1.56)$$

$$\text{But in Carnot cycle, } \frac{Q_1}{T_1} = \frac{Q_2}{T_2}$$

$$\therefore \text{The total change of entropy, } \Delta S = \frac{Q_1}{T_1} - \frac{Q_2}{T_2} = 0 \quad \dots \quad (1.57)$$

That is, in a reversible cycle the entropy remains constant.

#### (b) Change of Entropy in Irreversible Process

Again in an irreversible process the entropy does not remain constant. Let two objects completely isolated from the environment are in contact with each other. The temperature of the two objects are respectively  $T_1$  and  $T_2$ . If  $T_1 > T_2$  then heat will flow from the warm object to the cold object. Let within a very short period of time  $dQ$  amount of heat is transferred from the warm one to the cold one. That is, the warm object loses  $dQ$  amount of heat and the cold object gains  $dQ$  amount of heat.

$$\text{Therefore, } -\frac{dQ}{T_1} = \text{Decrease of entropy of the warm object.}$$

$$\text{and } \frac{dQ}{T_2} = \text{Increase of entropy of the cold object}$$

$$\text{Therefore the change of entropy of the system, } dS = -\frac{dQ}{T_1} + \frac{dQ}{T_2} \quad \dots \quad (1.58)$$

It is observed from the equation (1.58) since  $T_1 > T_2$

∴  $dS > 0$  that is, the change of entropy is always positive.

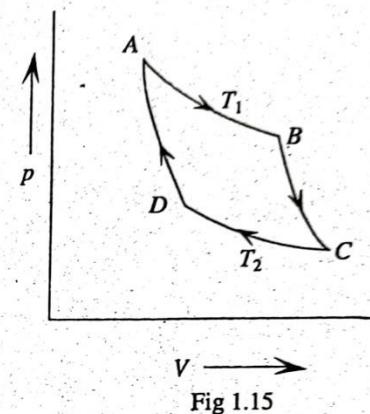


Fig 1.15

Everything in nature tries to acquire the state of equilibrium. As a system goes towards equilibrium the possibility of getting work from the system reduces and when it attains the equilibrium no work is found from it. This disability of converting the energy is known as entropy. As the systems proceed towards the equilibrium their entropy also increase. The entropy of a system becomes maximum when we do not get any work from it. All spontaneous changes are directed towards the equilibrium. Therefore in case of all spontaneous change the entropy is increased. Since everything in nature wants to attain equilibrium so the entropy of nature is gradually increasing. When the entropy of the universe will reach at the highest point then everything will attain the same temperature. As a result heat energy will not be possible to convert into mechanical energy. This state of the universe is the so called **heat death of the universe**.

#### Change of Entropy at Every Step of Carnot Cycle

In fig 1.15  $ABCD$  is a Carnot cycle. From the Carnot cycle it is seen that,  $AB$  the first step of the cycle is an isothermal expansion curve and the second step of the cycle  $BC$  is an adiabatic expansion curve. The third step of the cycle  $CD$  is an isothermal compression curve and the fourth step  $DA$  is an adiabatic compression curve.

At the first step that is, along the isotherm  $AB$  the change of entropy =  $\frac{Q_1}{T_1}$

At the second step that is along the adiabat  $BC$  there is no change of heat so this step change of entropy is zero.

At the third step that is along the isotherm  $CD$  the decrease in entropy =  $-\frac{Q_2}{T_2}$

At the fourth step that is along the adiabatic  $DA$  there is no change of heat so like the second step here also the change of entropy is zero.

#### Entropy and Disorder

Entropy and disorder are inseparable. With the increase of entropy of a system as the possibility of getting work from the system is reduced as well as the disorderliness of the system increases. We can explain it with an example. Keeping some salt in a glass if we pour water into the glass the salt will go on dissolving and the molecular ions of salt will spread out all around in the solution randomly. In the solid state the ions of salt are arranged in a regular fashion. Though salt is heavier than water instead of depositing at the bottom of the glass it spreads out all around. When salt spreads out all around in the solution we say that the solution has achieved the equilibrium state. When the solution achieves the equilibrium state the molecules are most disordered. That is why entropy is called the measure of disorderliness.

If we try to bring orderness of a system by applying force on the system then the entropy of the system will be reduced. When a substance is in a crystalline state then its molecules are arranged in a regular orderly fashion. For this reason the entropy of solid substance is less. It can be compared with the parading soldiers or the students listening lecture in a class. Here entropy is low. But when the parade is over or the teacher leaves the class as the bell rings the students become indisciplined—the entropy increases:

(5) Kelvin and Planck stated the law as follows : "It is impossible to construct an engine which operating in a cycle will produce no effect other than extraction of heat from a reservoir and performance of an equivalent amount of work."

(6) Maxwell stated the law as follows; "It is impossible to produce any difference in temperature and pressure in any isolated mass originally at uniform temperature and pressure without some expenditure of energy."

Arguments can be advanced to show that these various statements of the second law are essentially equivalent to one another.

It is not possible to prove the law by direct experiment but its validity is fully substantiated by the experimental verification of a great number of predictions based upon it.

The law explains our failure to utilize the immense quantity of heat energy in our surroundings. For example, we cannot run an engine on the heat content of the oceans because we have no large sink at a lower temperature into which the engine could discharge heat.

It is possible to deduce from the second law of thermodynamics that the reversible engine is the most efficient and that its efficiency depends on the operating temperatures and not on the substance used.

To be more fruitful in application the second law may be stated in a precise mathematical way. This requires the introduction of a new physical quantity called entropy which will be discussed in page 504.

### 11.21 Impossibility of perpetual motion machine of the second kind

A cyclic device which would continuously abstract heat from a single reservoir and convert the heat completely to mechanical work is called a *perpetual motion machine of the second kind*. Such a machine would not violate the first law (the principle of conservation of energy) since it would not create energy, but economically it would be just as valuable as if it did so, because of the existence of heat reservoirs, such as the oceans or the earth's

atmosphere, from which heat could be abstracted continuously at no cost. Hence the second law is sometimes stated: "A perpetual motion machine of the second kind is impossible."

### ~~II~~ 22 Carnot's theorem

Assuming the truth of the second law of thermodynamics, we may deduce two important results which are usually taken together to constitute **Carnot's theorem**.

- (a) *Working between the same initial and final temperatures, no engine can be more efficient than a reversible engine.*
- (b) *The efficiency of all reversible engines working between the same limits of temperature is the same.*

Let us start with two engines R and S, of which R is a reversible engine and S an irreversible engine. Let us see if it is possible for the engine S to be more efficient than the engine R.

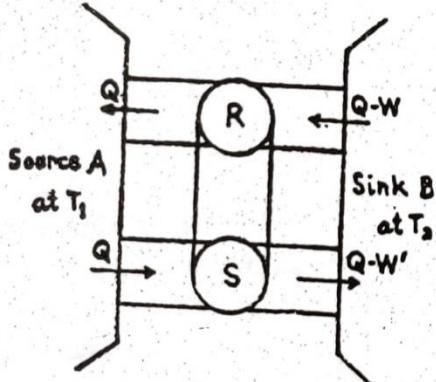


Fig. 184. Coupling a reversible and irreversible engine

To start with, let us assume that S is more efficient than R. We couple these engines together such that the irreversible engine drives the reversible one backwards. That means R is working as a refrigerator conveying heat from the sink to the source. Let these two engines act between the same temperature limits  $T_1$  and  $T_2$ . Let S

absorbs an amount of heat  $Q$  from the source A, convert a part of it (say  $W'$ ) into work and convey the rest  $Q-W'$  to the sink B. R in its turn is made to abstract a certain amount of heat from the sink, work  $W$  is performed on it and it is again made to return the same heat  $Q$  to the source. (This may be arranged by adjusting the quantity of working substance). The amount of heat that R abstracts from the sink B must then be equal to  $Q-W$ .

Now since S is assumed to be more efficient than R,

$$\frac{W'}{Q} > \frac{W}{Q},$$

or,  $W' > W$ , and hence  $Q-W > Q-W'$ ,

i.e., R abstracts more heat from the sink B than S restores to it. Thus the net result is that the compound engine R-S abstracts a certain quantity of heat  $Q-W-(Q-W')-(W'-W)$  per cycle from the sink B and converts the whole of it into work, while the source remains unaffected. It can be easily seen that the net loss of heat of the source is nil; the heat taken out by S is balanced by rejection of heat by R and hence the source is unnecessary. This in effect gives rise to a situation in which, the machines R-S, acting as a self-acting machine are able to perform external work, unaided by any external agency, without the use of a separately maintained source of heat. This is contrary to experience and is impossible and hence we have to discard our basic assumption that S is more efficient than R. In other words, no engine can be more efficient than a reversible engine working between the same temperature limits.

Now suppose we have two reversible engines as in fig. 184. (in place of R and S). Let them be denoted by  $R_1$  and  $R_2$ . We are as above led to see that two reversible engines acting as a self-acting machine are in a position to extract heat and convert the whole of it into work without the necessity of a separately maintained source. This as stated earlier is contrary to experience and is impossible and hence  $R_1$  cannot be more efficient than  $R_2$  and similarly  $R_2$  cannot be more efficient than  $R_1$ . In other words, the efficiency of all reversible engines working between the same temperature limits is the same and this is the highest limit for the efficiency of any engine that can be imagined or constructed. This is Carnot's theorem.

### **11.23 Absolute scale of temperature**

The efficiency of a perfectly reversible engine such as a Carnot engine is independent of the properties of the working substance employed and depends only on the temperatures of the source and the sink. Thus, here we have got a quantity which depends on temperature and temperature alone and is, therefore, ideally

suites for defining a scale of temperature. Such a scale of temperature was defined by Lord Kelvin in 1848 and it goes by the name of Kelvin or the thermodynamic scale of temperature. Such a scale will have the advantage over all others that it does not depend on the nature of any particular substance, and will in fact based on the fundamental principles of thermodynamics only.

Let the temperatures of the source and the sink be  $T_1$  and  $T_2$  respectively on any arbitrary scale between which a Carnot engine works. A Carnot engine absorbing  $Q_1$  amount of heat at a temperature  $T_1$  and rejecting  $Q_2$  amount of heat at a temperature  $T_2$  has an efficiency given by

$$\eta = \frac{\text{output energy}}{\text{input energy}} = \frac{\text{work done}}{\text{heat taken in}} \\ = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1} = f(T_1, T_2),$$

where  $f$  is an unknown function of  $T_1$  and  $T_2$ . Rearranging the above equation, we get

$$\frac{Q_1}{Q_2} = \frac{1}{1-f(T_1, T_2)} = F(T_1, T_2),$$

where  $F$  denotes some other function of  $T_1$  and  $T_2$ .

Now suppose we have two reversible engines, the first taking in heat  $Q_1$  at  $T_1$  and rejecting heat  $Q_2$  at  $T_2$ , and the second taking in heat  $Q_2$  at  $T_2$  and rejecting heat  $Q_3$  at  $T_3$ . Then,

$$\begin{aligned} \frac{Q_1}{Q_2} &= F(T_1, T_2), \\ \frac{Q_2}{Q_3} &= F(T_2, T_3). \end{aligned} \quad \dots \quad \dots \quad \dots \quad \dots \quad (1)$$

Since the heat rejected by the first Carnot engine,  $Q_2$ , is absorbed by the second Carnot engine, both the engines working together constitute a third Carnot engine which absorbs heat  $Q_1$  at  $T_1$  and rejects heat  $Q_3$  at  $T_3$ . We have therefore

$$\frac{Q_1}{Q_3} = F(T_1, T_3).$$

Since  $\frac{Q_1}{Q_3} = \frac{Q_1}{Q_2} \times \frac{Q_2}{Q_3}$

we take the quantity  $z$  through a cycle, such as ABCDA, the value of the "cyclic integral"  $\oint dz$  will be 0.

Let us choose infinitesimal changes  $dx$  and  $dy$  in the variables  $x$  and  $y$ . Draw the elementary rectangle ABCD (Fig. 176), the coordinates of A being  $x, y$  and the sides of the rectangle  $dx$  or  $dy$ .

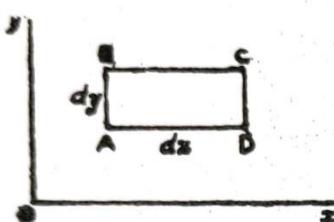


Fig. 176.

In the diagram, AB is  $dy$ , AD is  $dx$ , the coordinates of D will be  $x+dx, y$ ; the coordinates of B will be  $x, y+dy$ ; and the coordinates of C will be  $x+dx, y+dy$ .

Suppose we choose the path ABC from A to C. Then if the value of the quantity is  $z$  at A its value at B will be  $z + \frac{\partial z}{\partial y} dy$ .

The value of  $z$  at C will be

$$\left( z + \frac{\partial z}{\partial y} dy \right) + \frac{\partial}{\partial x} \left( z + \frac{\partial z}{\partial y} dy \right) \times dx.$$

Secondly, let us choose the path ADC from A to C. The value of  $z$  at D will be  $z + \frac{\partial z}{\partial x} dx$ . The value of  $z$  at C will be

$$\left( z + \frac{\partial z}{\partial x} dx \right) + \frac{\partial}{\partial y} \left( z + \frac{\partial z}{\partial x} dx \right) \times dy.$$

Now, if  $dz$  is a complete differential, this result must be the same as the previous one, that is,

$$z + \frac{\partial z}{\partial x} dx + \frac{\partial z}{\partial y} dy + \frac{\partial^2 z}{\partial y \partial x} dx dy = z + \frac{\partial z}{\partial y} dy + \frac{\partial z}{\partial x} dx + \frac{\partial^2 z}{\partial x \partial y} dy dx,$$

and therefore,  $\frac{\partial^2 z}{\partial y \partial x} = \frac{\partial^2 z}{\partial x \partial y}$ .

This relation holds good only when  $dz$  is a perfect differential. The meaning of this mathematical expression is that we can carry out the two processes of differentiation in either order without affecting the final result.

#### 11.4 Thermodynamic equilibrium

A body or system is said to be in thermodynamic equilibrium when it is in equilibrium from the mechanical, thermal and chemical

points of view. Mechanical equilibrium means that there is no unbalanced force either in the interior of the system or between the system and its surroundings. Thermal equilibrium means that all the parts of the body or system are at the same temperature as that of the surroundings. When a body or system does not undergo any change of chemical composition it is said to be in chemical equilibrium.

### **11.5 Thermodynamic state of a body and equation of state**

The thermodynamic condition or state of a simple homogeneous body like a gas or a solid is specified by its temperature  $T$ , pressure  $P$  and volume  $V$ . The quantities are, therefore, referred to as thermodynamic variables or coordinates. Among the three quantities, only two are independent variables and the third is automatically fixed by the values of the other two. The volume of a block of copper is completely determined when the temperature of the block and the pressure on it are specified. Thus for every homogeneous substance there exists an equation of equilibrium which connects the thermodynamic coordinates and which robs one of them of its independence. Such an equation is called an *equation of state*. Every thermodynamic system has its own equation of state. The general form of the equation of state is

$$F(P, V, T)=0,$$

or, if it is solved for each of the thermodynamic variables,

$$P=f_1(V, T),$$

$$V=f_2(P, T),$$

$$T=f_3(P, V).$$

In some cases of thermodynamic systems, the mathematical relation for the equation of state is so complicated that they cannot be expressed in terms of simple mathematical functions.

### **FIRST LAW OF THERMODYNAMICS**

#### **11.6 The conservation of energy**

The conversion of work into heat was first established by the experiments of Rumford and Joule. We have already described those experiments in details in the previous chapter. During the

times of Rumford and Joule, the steam engine was in wide use for industrial purposes. The steam engine is simply a mechanical contrivance for the conversion of heat into work. That heat and work are interconvertible was thus established. When a given amount of work  $W$  is done, an equivalent amount of heat  $Q$  is produced or when a certain quantity of heat  $Q$  disappears, an equivalent amount of work  $W$  is always obtained, or mathematically,

$W=JQ$ , the equivalence being given by the constant  $J$  known as *mechanical equivalent of heat or Joule's equivalent*, given by  $4.18 \times 10^7$  ergs/calorie. This equivalence between heat and work has been called *the first law of thermodynamics* which may be regarded simply as a special case of the general law of the conservation of energy.

The first law of thermodynamics, therefore, defines what heat actually is. It states that heat is a form of energy and is subjected to the principle of conservation of energy.

There are, of course, about seven forms of energy other than heat energy and the two forms of mechanical energy, i.e., kinetic and potential. They are strain, sound, radiant, electrical, magnetic, chemical and nuclear. All these are interconvertible, and in 1905 Einstein showed that even mass  $m$  and energy  $E$  are interconvertible by the equation  $E=m c^2$ , where  $c$  is the velocity of light, i.e.,  $3 \times 10^{10}$  cm./sec.

**Statement :** (1) **Negative stand point (Planck) :** It is impossible to design a machine which will create energy out of nothing and produce perpetual motion.

(2) **Positive stand point (Joule) :** When work is transformed into heat or heat into work, the quantity of work is mechanically equivalent to the quantity of heat, i.e.,  $W=JQ$ .

### II.7 Thermodynamic cycles

A change from one state to another is called a *thermodynamic process*, or *transformation*. Such a change can be represented in a number of ways, of which the  $P$ - $V$  plot is the most common. Fig. 177 represents a process in which a gas is taken from a state  $P_1$ ,  $V_1$ , to another whose variables have the values  $P_2$ ,  $V_2$ .

The temperature  $T$  will in general have different values at different points of the path.

The work done by the gas during the passage from A to B is, according to art. 3·20, page 171,

$$W_{AB} = \int_{V_1}^{V_2} P dV$$

and this is equal to the shaded area in fig. 177.

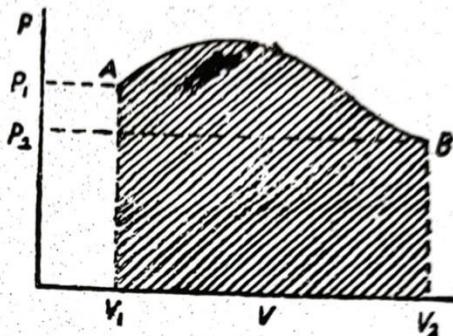


Fig. 177. P-V diagram

A transformation that returns the gas to its original state is called a *cycle*. Fig. 178 represents a cycle, the gas being taken from A to B and back to A. During the passage from A to B the gas expands and does an amount of work equal to the area under the upper curve.

In passing from B to A the gas is compressed to a smaller volume. Here work is done on the gas and is given by the area under the lower curve. The net work done by the gas during the cycle is the area on the P-V plot that is enclosed by the cycle. In a cycle, although

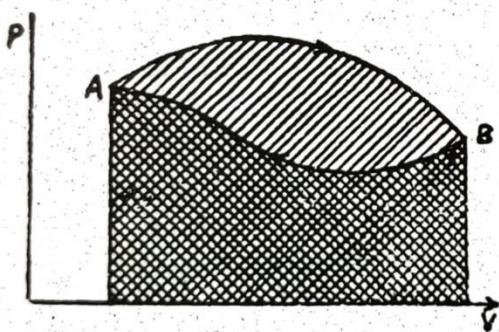


Fig. 178. Diagram of a cycle

the substance returns to its initial state, the net work done is not zero. The reason is that the gas has received heat while performing the cycle and this heat has been transformed into work.

If the cycle in fig. 178 had been traversed in the opposite sense, so that what was previously an expansion has now become a compression and vice versa, the work done by the gas is the area under the lower curve, and the work done on the gas is the area under the upper curve, and the work enclosed by the cycle is no longer the work done by the gas but that done on the gas during