

BASIC CONCEPTS OF THERMODYNAMICS

1.1 Introduction

Thermodynamics is a branch of science that deals with energy in all its forms and the laws governing the transformation of energy from one form to another. Since, there are many forms of energy such as mechanical, thermal or heat, chemical, electrical, etc., this science covers a very broad field of application and is a base to many branches of natural science and engineering and technology. That part of the subject which applies to engineering, is generally referred to as *Engineering Thermodynamics* or *Applied Thermodynamics*.

Thermodynamics deals with the behaviour of gases and vapours (working substance) when subjected to variations of temperature and pressure and the relationship between heat energy and mechanical energy, commonly referred to as work. When a substance undergoes a change from one condition to another in a process, energy transformation may occur. Common processes are those of heating or cooling and expansion or compression in the cylinder or passages with or without production or supply of mechanical work. Chemical reaction and/or change of phase may occur in some processes involving liberation of heat.

Engineers concerned with power generating machinery should have a working knowledge of all matters dealing with the conversion of heat energy into work or power. The laws based on experimental results obtained from the study of gases and vapours are useful in the design of boilers, steam engines, steam turbines, internal combustion engines, gas turbines, refrigerating machines and air compressors. In the present days of industrialisation, demand for energy is increasing rapidly. It is, therefore, necessary to design and operate thermal plants and machines at their highest level of performance for efficient utilization of fuels and natural resources available.

1.2 Working Substance or Medium

Any thermodynamic process or change involves the use of *working substance* or *thermodynamic medium*, which has the ability to receive, store and give out (or reject) energy as required by the particular process. The medium may be in any one of the four physical states or phases, namely—solid, liquid, vapour and gaseous. The vapours and gaseous substances are sometimes termed together as gases.

The power generating machines (plants) which operate according to thermodynamic laws, require the use of some working medium. For example, steam power generating plants use water vapour and refrigerator or ice plant uses ammonia or freon as the working substance. Steam is a very suitable medium for steam power plants because it readily absorbs heat, flows easily, exerts pressure on the piston or blade while it moves and allows considerable expansion of its volume. Ammonia or Freon is a suitable medium for an ice plant because it boils at a temperature below 0°C and at a moderate pressure and absorbs heat from water, making it to freeze into ice. A mixture of air and fuel forms a working medium in the initial processes and product of combustion in remaining processes of internal combustion engines and gas turbines.

1.3 System

A thermodynamic *system* is a specific portion of matter, with definite boundary, on which our attention is focussed. The *system boundary* may be real or imaginary, fixed or deformable. Everything outside the system which has direct bearing on its behaviour is known as *surroundings* as shown in fig. 1-1. Thermodynamic problems are concerned with the transfer of energy and mass across the boundary of a system. There are three types of systems :

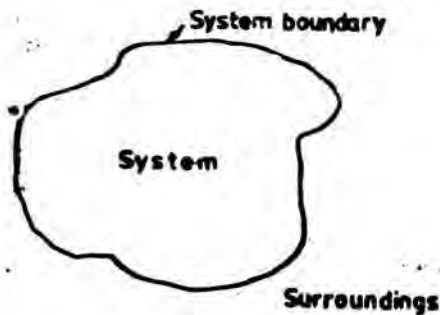
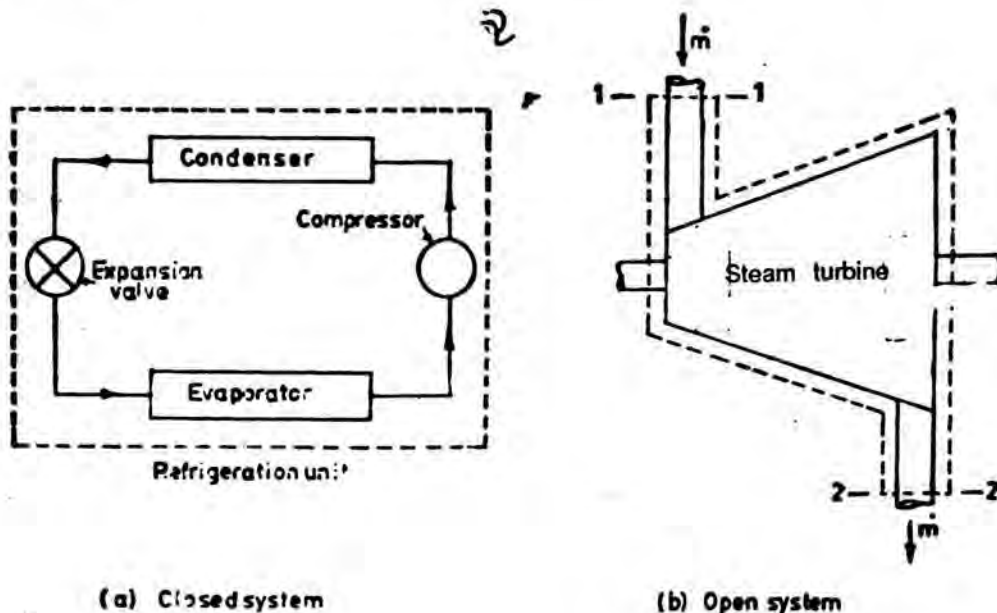


Fig. 1-1. System and surroundings.

- Isolated systems,
- Closed system, and
- Open system.

An *isolated system* cannot exchange both energy and mass with its surroundings. System and surroundings together form a Universe. Universe is, thus, considered as an isolated system.



(a) Closed system

(b) Open system

Fig. 1-2. Closed and open systems.

Across the boundary of *closed system*, transfer of energy (work and or heat) takes place but transfer of mass does not take place. Compression of a gas in a piston cylinder assembly, refrigerator, heating of water in a closed vessel, are examples of closed system. Figure 1-2(a) shows a refrigeration unit as an example of closed system.

In an *open system*, mass and energy both may be transferred between the system and surroundings. Gas turbine, axial flow and centrifugal air compressors, boiler delivering steam, etc. are some examples of open system. Steam turbine is also an example of open system which is shown in fig. 1-2(b).

1.4 State and Properties of a Substance

The exact condition of a substance is called its *state* and variables which determine the state are spoken of as its *properties* or *parameters*. The principal properties are pressure, volume, temperature, internal energy, enthalpy and entropy. The fundamental properties are pressure, volume and temperature. The other properties listed above are

dependent in some manner on one or more of these fundamental properties. Any two of the properties such as pressure, volume, temperature, internal energy, enthalpy, entropy, much be known to determine the '*thermodynamic state*' of the working medium. Thus, if the thermodynamic state is fixed, all these properties are fixed with it.

1.5 Process and Cycle

A change of state occurs when one or more of the properties of a system changes. When a system undergoes changes on its state, it is said to have undergone a *process*. Thus, a process is the path joining succession of states passed through by a system. Process is named according to its specification, i.e., constant pressure process, constant volume process, etc.

A *cycle* is a process or a combination of processes so conducted that the initial and final states of the system are the same. A thermodynamic cycle is also known as a *cyclic operation of processes*.

1.6 Basic Properties

Pressure, volume and temperature are named as basic properties or parameters as they may be determined by direct observations or simple measurements.

1.6.1 Pressure : Pressure is a force applied over a unit area.

In SI (international system) units, the unit for pressure is the force of one newton (N) acting on a square metre area, which is called the *pascal* (Pa), i.e. $1 \text{ Pa} = 1 \text{ N/m}^2$.

As this unit is rather small for practical use, engineers measure pressure in kilopascals and megapascals. We note that,

$$1 \text{ kilopascal} = 1,000 \text{ pascals} = 1 \text{ kPa}$$

$$1 \text{ megapascal} = 10,00,000 \text{ pascals} = 1 \text{ MPa}$$

Other units for pressure, not included in the SI units, commonly used are :
bar and standard atmosphere (atm).

$$1 \text{ bar} = 10^5 \text{ Pa} = 100 \text{ kPa (kilopascal)} = 0.1 \text{ MPa (megapascal), and}$$

$$1 \text{ standard atmosphere (atm)} = 1,01,325 \text{ Pa, which is somewhat larger than a bar.}$$

The atmosphere surrounding the earth, exerts a pressure on its surface equivalent to the weight of air over a unit area of the earth's surface. The pressure of the atmosphere is recorded by a barometer. The height of the mercury column also varies with the altitude above or below sea level. At sea level, 760 mm of mercury column at 0°C is taken as the standard barometric pressure. This is known as a *physical atmosphere* or *barometric atmosphere (atm)*.

To express this physical atmosphere in kilogram per square centimetre (technical or metric atmosphere), we must first determine the weight of a column of mercury with a cross-section of one square centimetre and a height of 760 mm. The density of mercury is 13, 595 kilograms per cubic metre at 0°C; hence the standard height of 760 mm at 0°C of a mercury column corresponds to a pressure of

$$pgh = 13,595 \times 9.80665 \times \frac{760}{1,000} = 1,01,325 \text{ N/m}^2 \text{ or } = 1,01,325 \text{ Pa}$$

Thus, one physical or standard atmosphere (1 atm) = 760 mm of Hg

$$= 1,01,325 \text{ Pa} = 101.325 \text{ kPa} = 0.101325 \text{ MPa} = 1.01325 \text{ bar.}$$

From this, it can be shown that 1 mm of Hg = 0.13332 kPa, = 0.0013332 bar, and
750 mm of Hg = 100 kPa = 1 bar.

Vacuum may be defined as the absence of pressure. Quite often the pressure of a confined fluid is less than that of the surrounding atmosphere. The confined fluid is then said to be under a partial vacuum. In such a case, the instrument used to measure the pressure is vacuum gauge. It records the difference between the surrounding atmospheric pressure and that within the vessel in millimetres of mercury. A vessel having no pressure within it is said to have a perfect vacuum.

In practice, pressure of a fluid is measured by means of instruments known as gauges. Gauges which measure pressure greater than atmospheric pressure are called

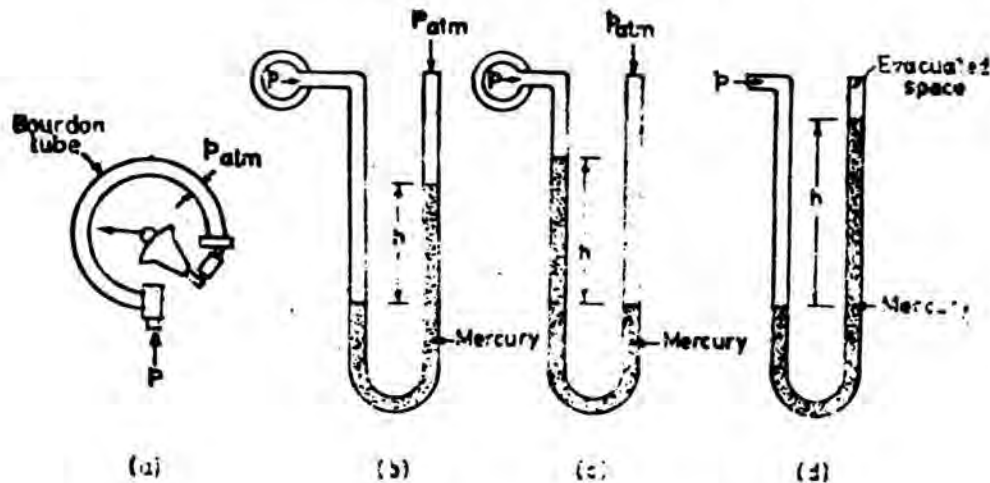


Fig. 1-3. Measurements of pressure.

pressure gauges. A pressure gauge attached to a vessel indicates the difference between the pressure inside the vessel and the pressure of the atmosphere.

Figure 1-3(a) illustrates a *Bourdon pressure gauge*. This pressure gauge is commonly used to measure the pressure of steam in a boiler. The reading of the pressure gauge is called *gauge pressure*. The absolute pressure of steam within the boiler is, therefore, equal to the observed gauge pressure plus the atmospheric pressure.

Gauges measuring pressure less than atmospheric pressure are called *vacuum gauges*. The principle of working of pressure gauges is the same. The pressure in a steam condenser is usually less than atmospheric pressure. A vacuum gauge attached to the condenser, measures the difference between the atmospheric pressure and the pressure inside the condenser. This difference is called the *vacuum* and is expressed in millimetres of mercury. The absolute pressure within the condenser is, therefore, equal to atmospheric pressure minus the vacuum.

A manometer is employed to measure slight variation in the pressure above or below atmospheric pressure. Manometers read the pressure in millimetres of mercury or water, or in terms of height of the column of any fluid that may be used in the manometer tube.

Figure 1-3(b) shows the principle of working of a U-tube manometer, measuring pressure above atmospheric pressure. One limb of the U-tube is open to atmosphere and the other end is connected to a vessel having pressure more than that of atmosphere. Suppose the manometer indicates a reading of h millimeters as difference between the mercury levels in the two limbs of the U-tube. Then, the pressure of the gas p is being

balanced by the atmospheric pressure, P_{atm} plus the pressure due to the column of mercury, h . Hence,

$$p = p_{atm} + h \quad \dots(1.1)$$

i.e. absolute pressure of gas (p) in the vessel or pipe line is the sum of atmospheric pressure and the manometer reading.

Figure 1-3(c) shows a U-tube manometer measuring pressure less than atmospheric pressure (vacuum). One limb of the U-tube is open to atmosphere and the other end is connected to a vessel having pressure less than that of the atmosphere. Here,

$$p = p_{atm} - h \quad \dots(1.2)$$

i.e. absolute pressure in the vessel is the difference of atmospheric pressure and the manometer reading.

Figure 1-3(d) shows a closed U-tube indicating absolute pressure. If p is the atmospheric pressure, then this gauge is known as a *barometer*.

Practically in all thermodynamic analysis and calculations, absolute pressures are used.

Problem - 1 : Convert the following readings of pressure to kilopascal (kPa) : (i) 8 bar, (ii) 10 atm, (iii) 2 MPa, (iv) 1,12,000 N/m², (v) 200 kN/m², (vi) 0.05 N/mm², and (vii) 1,500 mm of Hg.

(i) 8 bar = 8×10^5 Pa = 8,00,000 Pa or 800 kPa.

(ii) 10 atm = $10 \times 1,01,325$ Pa = 10,13,250 Pa or 1,013.25 kPa.

(iii) 2MPa = 2×10^6 Pa = 20,00,000 Pa or 2,000 kPa.

(iv) 1,12,000 N/m² = 1,12,000 Pa = 112 kPa.

(v) 200 kN/m² = 2,00,000 N/m² = 2,00,000 Pa = 200 kPa.

(vi) 0.05 N/mm² = 0.05×10^6 N/m² = 50,000 N/m² = 50,000 Pa = 50 kPa.

(vii) 1500 mm of Hg = $1,500 \times 0.13332$ kPa = 200 kPa.

Problem - 2 : A pressure gauge reads 2.3 MPa, and the barometer reads 98 kPa. Calculate the absolute pressure in MPa.

$$\begin{aligned} \text{Absolute pressure} &= \text{atmospheric pressure} + \text{gauge pressure} \\ &= 0.098 \text{ MPa} + 2.3 \text{ MPa} = 2.398 \text{ MPa} \end{aligned}$$

Note : In this text, the pressure stated in Pascals will indicate the absolute pressure. Gauge pressure will be indicated as gauge pressure or pressure gauge reading.

Problem - 3 : A vacuum gauge on the condenser reads 620 mm of mercury and at the same time barometer reads 740 mm of mercury. What is the absolute pressure in the condenser in kPa ?

$$\begin{aligned} \text{Using eqn. (1.2), Absolute pressure in the condenser} \\ &= \text{atmospheric pressure in mm of Hg} - \text{vacuum gauge reading in mm of Hg} \\ &= 740 - 620 = 120 \text{ mm of Hg.} \end{aligned}$$

$$\therefore \text{Absolute pressure in the condenser} = 120 \times 0.13332 = 16 \text{ kPa.}$$

Problem - 4 : The pressure of the gas supplied to an engine is measured as 76.2 mm of water gauge. If the barometer reads 730 mm of mercury, what is the absolute pressure of gas in mm of mercury and in bar ?

Very low pressures are generally measured by the height of water column; this is convenient because the height of water column is 13.6 times greater than that mercury column for any given pressure, i.e. 1 mm of Hg = 13.6 mm of H₂O.

Gauge pressure of gas = 76.2 mm of water

$$\text{or} = \frac{76.2}{13.6} = 5.6 \text{ mm of mercury.}$$

Absolute pressure of gas = gauge pressure + barometric pressure

$$= 5.6 \text{ mm of Hg} + 730 \text{ mm of Hg} = 735.6 \text{ mm Hg}$$

Absolute pressure of gas in bar = $735.6 \times 0.13332 = 98.07 \text{ kPa} = 0.9807 \text{ bar}$.

1.6.2 Volume : Volume of gas is defined as the space which the gas occupies and it is measured in cubic metres. A widely used unit of volume is the litre which is 1,000th part of a cubic metre,

$$\text{i.e. } 1 \text{ litre} = 10^{-3} \text{ m}^3$$

The *specific volume* of a substance is its volume per unit mass. It is generally in cubic metres per kilogram. One kilogram of air at 0°C and under a pressure of 101.325 kPa (760 mm of Hg) has a volume of 0.7734 cubic metre. Therefore, the specific volume of air under these conditions is 0.7734 m³/kg.

The *density* of a substance is its mass per unit volume is generally stated in kilogram per cubic metre.

From definitions of density and specific volume, it is clear that density of any substance is the reciprocal of its specific volume and vice-versa. Thus, if specific volume of air is 0.7734 m³/kg, its density is $1/0.7734 = 1.293 \text{ kg/m}^3$ under the same conditions of pressure and temperature. Density is denoted by the symbol ρ (roh).

Problem - 5 : Three kilograms of dry hydrogen occupy 33 cubic metres. What is the specific weight (density) of hydrogen ?

$$\text{Specific volume} = \frac{33}{3} = 11 \text{ m}^3/\text{kg. Density} = \frac{1}{\text{Specific volume}} = \frac{1}{11} = 0.09 \text{ kg/m}^3.$$

1.6.3 Temperature : The temperature of a substance may be defined as measure of hotness or degree of coldness of a body. A body is said to be hot when it has a relatively high temperature; it is said to be cold when it has a relatively low temperature. It is known fact that heat energy has a tendency to flow from a hot body to one that is cooler. Thus, temperature determines which way (direction) the heat flow will take place. It is not a measure of quantity of energy possessed by the body but it indicates level of internal energy possessed by the body as explained in art 1.7.5.

Ordinarily temperatures are *measured* by instruments called *thermometers*. Very high temperatures are measured by instruments known as *pyrometers*. Small and precise changes of temperature can be measured by resistant thermometers and thermocouples.

Engineers measure temperature by Centigrade thermometer. In the Centigrade thermometer the freezing point of water is marked as zero and the boiling point as 100. The freezing point and the boiling point of water at atmospheric pressure (101.325 kPa or 760 mm of Hg) are called fixed points of the thermometer; other temperatures are measured by reference to these points. The Centigrade scale of temperature is constructed by dividing the thermometer stem between the fixed points in 100 equal parts or degrees.

Centigrade scale may be extended above the boiling point and below the freezing point. Temperatures lower than zero are denoted by negative sign. Thus, -15°C means 15 Centigrade degrees below the freezing point.

The centigrade scale in SI units is now named after Mr. Celsius, the Swedish astronomer, who invented this scale in 1953. Therefore, this scale is called *Celsius scale*.

The *absolute scale of temperature* is based on so called absolute zero of the temperature.

Absolute zero is the temperature at which all vibratory, translatory and rotational motions of molecules of a substance is supposed to have ceased, i.e., internal energy becomes zero. A gas on cooling will contract in volume as the temperature falls. Charles found that with perfect gases, the decrease in volume per degree centigrade decrease in temperature is $1/273^{\text{rd}}$ of its initial volume at 0°C , pressure remaining constant. Thus, the volume of gas will be zero at temperature -273°C . This temperature 273°C below 0°C (or -273°C) is called the *absolute zero of temperature*.

The absolute temperature is the temperature measured above the point of absolute zero. Absolute temperatures are expressed by the capital letter T . Absolute temperature is expressed in degrees of the Kelvin scale or K.

$$\text{Temperature K} = \text{Temperature}^{\circ}\text{C} + 273$$

$$\text{i.e. } T = t + 273 \text{ K} \quad \dots(1.3)$$

$$\text{or } t = T - 273^{\circ}\text{C}$$

The exact relationship between Kelvin scale and Celsius scale is

$$\text{Temperature K} = \text{Temperature}^{\circ}\text{C} + 273.15$$

Problem - 6 : (i) The temperature of steam in a boiler on absolute scale (Kelvin scale) is 343. What will be its temperature on Celsius scale ?

(ii) The temperature of steam in a boiler is 200°C . What will be its temperature on the absolute or Kelvin scale ?

$$(i) \text{ Temperature K} = \text{Temperature}^{\circ}\text{C} + 273$$

$$\text{i.e. } 343 = \text{Temperature}^{\circ}\text{C} + 273$$

$$\therefore \text{Temperature}^{\circ}\text{C} = 343 - 273 = 70^{\circ}\text{C}$$

$$(ii) \text{ Temperature K} = \text{Temperature}^{\circ}\text{C} + 273 = 200 + 273 = 473 \text{ K}$$

1.7 Energy

Energy may be defined as the capacity, a body possesses for doing work. Energy appears in many forms, i.e. mechanical (potential and kinetic), internal, electrical, chemical, nuclear, work, heat, etc. Energy cannot be seen and does not have mass.

All forms of energy mainly can be classified as *stored energy* and *energy in transition*.

Energy residing in a system is called *stored energy*. Energy is found stored in many forms, such as mechanical, internal (or thermal), electrical, chemical and nuclear energy. *Mechanical energy* is concerned with the system as a whole. It may be in the form of kinetic and or potential energy of a body as a whole. *Internal energy* is associated with the molecules of a system (kinetic and potential energy of molecules of a system). The system has the ability to receive, to store and to emit energy and undergo a *thermodynamic process* that results as the change in properties of the system. The change in stored

energy of a system must derive completely from energy which has transferred across its boundary (in the form of work and heat), since energy can be neither created nor destroyed.

Energy in transition is the energy that is transferred to or from a system. Transient form of energy has significance only while energy is being transferred. Work and heat are forms of energy in transition which can only cross the boundaries of a system. Work and heat are not stored by system hence there is nothing like work of a body or heat of a body. *Work and heat are not properties or state parameter.* They are not state functions. They are only path functions. They exist only in transition or transfer.

1.7.1 Work : Work is a transient form of energy. When a force acts upon a body, causing the body to move and to overcome continually a resistance, work is said to be done. This work is equal to the force multiplied by the distance through which it acts. The time element is of no consideration. The unit of work done is *newton-metre (N-m)*, which is the product of a unit force (one newton) and a unit distance (one metre) moved in the direction the force. This unit of work is also known as *joule (J)*,

that is $1 \text{ joule} = 1 \text{ newton-metre (N}\cdot\text{m)}$

$1 \text{ kilojoule (kJ)} = 1,000 \text{ joules}$

When work is done by a system, it is arbitrarily taken to be positive. and when work is done on a system it is taken to be negative. Work of compression or expansion of a gas, shaft work and flow work are different forms of work.

We have seen that unit of work done is independent of time. Suppose one machine does the same amount of work as another, but in one-fourth the time, it is evident that the first machine can do four times the work of the second in the same time and hence to compare or to rate the machine, time must be considered. The rate at which work is done by or upon the system is known as *power*.

The unit for power is a rate of one joule per second (J/s) which is a watt (W), i.e. $1 \text{ watt} = 1 \text{ joule per second}$.

A common unit for power is kilowatt (kW).

$1 \text{ kW} = 1,000 \text{ W}$ or $1,000 \text{ J/s}$ or $1,000 \text{ N}\cdot\text{m/s}$.

kWh (kilowatt hour) is work done by a source of 1 kW in one hour. Electrical energy consumption is measured in terms of kWh.

$1 \text{ kWh} = 1,000 \times 3,600 \text{ joules}$ or $3,600 \text{ kJ}$

The unit for time in SI units is the second (s). Other units for time often used are the hour (hr.) and the day, although neither one is a basic SI unit.

1.7.2 Heat : Heat is that form of energy which is transferred from one body to another on account of temperature difference. Heat energy, therefore, is not a stored form of energy but occurs only in transition and when present, energy of some other form is being transferred from one body to another. Heat energy may be transferred in three ways, by conduction, convection and radiation. In all the three modes of heat transfer there must be temperature difference and the direction of heat transfer is in the direction of decreasing temperature. It may be noted that conduction and convection require some definite medium while radiation can occur in vacuum also.

If one end of metal rod, insulated against heat transfer to the air, is heated to a higher temperature, heat energy will flow from the hot end to the cold end and the temperature of the cold end will rise. The heat is transferred from one cross-section to

the next by molecular activity. The molecular activity at the hot end causes the molecules in an adjacent section to increase their molecular activity. Thus, energy is carried along the entire length of the bar, and the temperature of cold end rises. If the two ends of the bar are at same temperature, the molecules of the two ends have the same level of molecular activity and there is no tendency of energy to be transferred from one cross-section to the next, i.e., there is no heat transfer. This mode of heat transfer is called *conduction* and is predominant in solid form of matter. Over and above molecular communication, free electrons present in the material also help to conduct heat from hot end to cold end. For details refer chapter-I of vol. III.

In *convection*, heat is transmitted from one place to another by fluid currents. As gases or liquids are heated by conduction through the wall of containing vessel, they tend to expand and rise, and their place is taken by the upper colder layers which being heavier than the heated liquid or gas tend to flow downwards. In this way convection currents are set up and the whole volume of gas or liquid is gradually heated to uniform temperature. Water in a steam boiler is heated uniformly throughout by the convective currents set up by upward flow of the lighter heated water in contact with the heated surface and by the downward flow of heavier colder water from above.

Radiant heat is in the form of temperature excited electromagnetic waves which passes from one body to another without much raising the temperature of the medium through which it passes. Substances which are transparent to light usually allow radiant heat to pass freely through them even when they are poor conductors of heat. This is one reason why radiant heat is so important in boilers, since it will pass through a thin film of gas clinging to the tube or plate which offers considerable resistance to the passage of heat by conduction.

In a steam boiler, the heat from the surface of the burning coal in a furnace is transferred to the crown and sides of furnace by radiation; it passes through the furnace plate by conduction, and the water is heated by convection.

As discussed earlier, heat like work is a form of energy which is transferred to and from a system. Therefore, the unit for heat, and for any other form of energy, is the same as the unit for work in the International System of Units viz. joule (J).

1.7.3 Potential Energy : Potential energy is the energy of a body due to its position or elevation relative to some datum plane. Therefore, the term potential energy is exclusively used for gravitational energy. The potential energy of a substance is equal to the work that can be done by allowing a substance to fall from the given position to the surface of the earth or other datum. The maximum possible work done is the product of gravitational force (or weight) of a falling body and the distance through which this body falls. The unit of potential energy is newton-metre (N.m) and the symbol used to represent this energy is *P.E.* If a body of m kg mass is allowed to fall from an elevation L_2 to an elevation L_1 , the change in potential energy,

$$\begin{aligned}\Delta PE &= PE_2 - PE_1 \\ &= mg (L_2 - L_1) \quad \dots(1.4)\end{aligned}$$

1.7.4 Kinetic Energy : The kinetic energy (*KE*) possessed by a body is due to its motion. The unit of (*KE*) is also N.m. Water held behind a dam has potential energy and if released, the water in its flow has its potential energy changed into kinetic energy. The energy, therefore, could be utilized or work could be done equal to the energy possessed by the water, by permitting it to flow through blades of a water wheel or a water turbine.

A body of mass m kg moving with a velocity V possesses a certain amount of kinetic energy (KE) with reference to earth. Kinetic energy,

$$KE = m \cdot \frac{V^2}{2} \quad \dots(1.5)$$

Potential energy and kinetic energy are extensive properties, since they depend upon the mass of the system.

1.7.5 Internal Energy : Matter is composed of an aggregation or collection of molecules which are moving continuously. The movement of molecules is more pronounced in gases than in liquids. When the gas is stored in closed vessel it is stagnant, that is, not moving as a whole. However, it possesses a considerable amount of *internal kinetic energy* due to the motion of its molecules within the limits of its containing vessel. In addition to the internal kinetic energy, substance have *internal potential energy* due to the relative position of their molecules with respect to one another.

A change in mechanical potential energy of a body occurs when the elevation of the body relative to the earth as a datum is changed. The force acting in this case is the force of gravity. Now, since there is a cohesive force between the molecules of a substance there will be a change in the internal potential energy, if anything happens which increases or decreases the average distance between the molecules. It may be noted that distance between the molecules can be more widely increased or decreased in a gas than in a liquid, say water. During the formation of steam, the molecules of water are separated against their attractive force which require a large amount of energy. The energy used to overcome the attractive force is stored in the steam as internal potential energy.

The *internal energy*, u of a substance may be defined as the algebraic sum of internal kinetic energy and the internal potential energy of its molecules. Internal energy is an extensive property, since it depends upon the mass of the system.

Thus, the internal energy of a substance is the energy stored within the substance and it is due to the motion and configuration (relative position) of its molecules. If the temperature of a gas is increased, the molecular activity increases. Therefore, the internal energy is a function of temperature and its value can be increased or decreased by adding or subtracting heat to or from the substance. The absolute value of internal energy of a body cannot be determined, but, it is possible to estimate changes of internal energy from changes of state of the body. The internal energy value of a substance in any event is measured above an arbitrary datum condition, at which the substance or medium is said to possess zero internal energy. Value of internal energy is expressed in joules. The change of internal energy when the substance passes from state 1 to state 2 can be expressed in a general way,

$$\Delta u = u_2 - u_1 \quad \dots(1.6)$$

1.7.6 Enthalpy : The other terms in use for enthalpy are *total heat* and *heat content*. It is said that the term enthalpy is more convenient than the term heat content and total heat. Enthalpy is an energy term and is defined as follows :

$$H = u + pv$$

where u is the internal energy, p is the absolute pressure, and v is the volume.

Since, we cannot measure the absolute quantity of internal energy, it is impossible to measure the absolute enthalpy of a substance. What we wish to know in actual practice is the change in internal energy and the change in enthalpy. Wherever the change of

internal energy can be calculated and whenever the product pv is known for any two states of any fluid, the change in enthalpy, ΔH can be evaluated as

$$\Delta H = H_2 - H_1 = (u_2 - u_1) + p_2v_2 - p_1v_1 \quad \dots(1.7)$$

To find the simpler expression for change in enthalpy of a perfect gas, we know that

$$u_2 - u_1 = mk_v (T_2 - T_1), p_2v_2 = mRT_2 \text{ and } p_1v_1 = mRT_1.$$

Substituting these values in eqn. (1.7), we have

$$\begin{aligned} \Delta H = H_2 - H_1 &= mk_v (T_2 - T_1) + mRT_2 - mRT_1 \\ &= mk_v (T_2 - T_1) + mR (T_2 - T_1) \end{aligned}$$

But from eqn. (1.27), $k_p - k_v = R$ or $k_v = k_p - R$

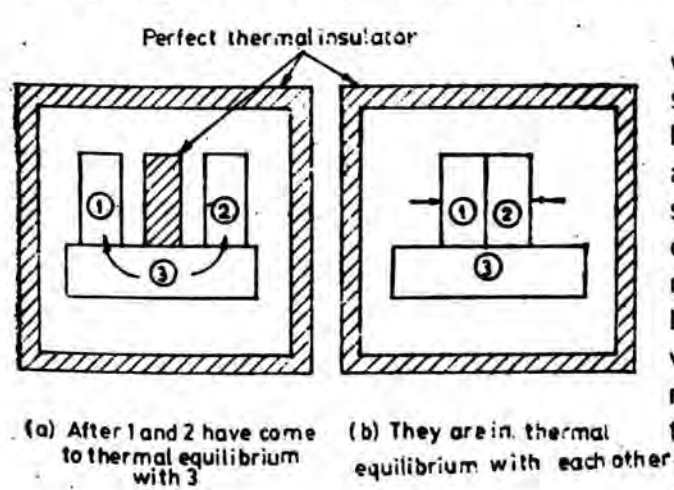
$$\therefore \text{Change of enthalpy, } \Delta H = H_2 - H_1 = mk_p (T_2 - T_1) \quad \dots (1.8)$$

1.8 Laws of Thermodynamics

Laws of thermodynamics lie at the centre of the classical thermodynamics. These laws (zeroth, first, second and third) are natural or fundamental laws formulated on the basis of natural observations. They are not derived from any mathematics.

1.8.1 Zeroth Law of Thermodynamics : If we take two bodies, one hotter than the other and bring them into contact, we shall find after some time that both the bodies are equally hot. When this state is attained we say that two bodies are in thermal equilibrium. The bodies in *thermal equilibrium* will have some property in common and this property is called *temperature*. In other words, bodies in thermal equilibrium will be at the same temperature. As stated above, temperature indicates the intensity of molecular activities (kinetic fraction of internal energy). The higher the temperature, the greater is the level of activities. When two bodies whose temperature are different, are brought in contact, an increase will take place in the molecular activities of one body (which is at lower temperature) and a decrease in the other body (which is at higher temperature). These changes in molecular activities will continue till the time the temperature of the bodies become the same. After this, the bodies will be in thermal equilibrium with each other.

The association of temperature with the quantitative evaluation of internal kinetic energy may be extended to the formulation of the *Zeroth law of thermodynamics*.



As a basis for describing when bodies will be in thermal equilibrium, we consider systems 1 and 2 insulated from each other but in good thermal contact with a third or a common system. As indicated in fig. 1-4(a), systems 1 and 2 will come to thermal equilibrium with system 3. If the insulator is now removed and systems 1 and 2 are brought into contact as shown in fig. 1-4(b), we find that there is no further change. This means that the combined system has come to thermal equilibrium; consequently systems 1 and 2 are in thermal equilibrium. This experimental observations lead to the conclusion that *two systems in thermal equi-*

Fig. 1-4. Schematic illustration of the Zeroth law.

librium with a third are in equilibrium with each other. This statements is known as the Zeroth law.

The above law suggests the existance of a system property. The fact that two systems can be said to be in thermal equilibrium with each other before they are placed in contact implies that there must be some characteristic of the systems indicative of this. We recognize this characteristic as temperature, which can be defined as that property of a system which determines whether or not it is in thermal equilibrium with other systems. In the logical development of the science of thermodynamics, the Zeroth law preceeds the First and Second laws but chronologically, the First and Second laws were established prior to the presentation of this statement and hence it is designated as the Zeroth law.

If the properties of a system are uniform throughout, then, so long as the external conditions are unaltered, the system is said to be in *thermodynamic equilibrium*. A system in thermodynamic equilibrium satisfies all the three mechanical, thermal and chemical equilibriums, i.e., a system is in thermodynamic equilibrium if it in mechanical, thermal and chemical equilibrium.

Mechanical equilibrium exists if there are no net forces between the system and surroundings and if there are none within the system.

Thermal equilibrium exists if the temperature of the system is uniform throughout and equal to that of the surroundings with which it is in thermal contact.

Chemical equilibrium exists if the composition of each compound present is constant and if diffusion and solution do not occur.

1.8.2 First Law of Thermodynamics : This law is the same as the law of the conservation of energy, which states that *energy can neither be created nor destroyed if mass is conserved. The sum total of the energy in the universe is constant. Energy, however, can be converted from one form into another form.* This is the thermodynamic aspect of first law. A machine cannot create work from nothing nor it can deliver more work than it receives. In a steam generating plant, the chemical energy of the fuel is converted into heat energy in the boiler, which in turn is converted into mechanical work in the steam engine or steam turbine. If the turbine is coupled to an electric dynamo, the mechanical energy is converted into electrical energy. If the dynamo is supplying the electrical energy produced by it to drive an electric motor, the electrical energy is again converted into mechanical energy.

It was established by Joule that heat and mechanical energies are mutually convertible. Heat requires for its production, a definite number of units work for each unit of heat produced. Similarly, heat produces by its disappearance, a definite number of units of work for each unit of heat converted. This is known as the first law of thermodynamics.

Joules experiments showed that for a closed system during a cyclic process, the sum of the work transferred is equal to the sum of the heat transferred. Mathematically, it is written as

$$\oint dW = \oint dQ \quad \dots (1.9)$$

The circle on integral sign represents a cyclic process.

This means during any cycle, a closed system executes, the cyclic integral of work is equal to cyclic integral of heat. Work and heat both being measured in joules (J) or kilojoules (kJ).

For a non-cyclic process, a closed system (in absence of KE and PE) executes, the work transferred and heat transferred may not be equal, and the difference between the two is accounted for by a change in internal energy, u of the system. This can be stated mathematically as

$$Q - W = \Delta u$$

$$\text{or } Q = \Delta u + W$$

$$\text{or } Q_{1-2} = u_2 - u_1 + W_{1-2} \quad \dots (1.10)$$

In differential form this can be written as

$$dQ = du + dW \quad \dots (1.11)$$

Equation (1.11) is the mathematical form of the first law of thermodynamics. It may be noted that heat and work are not state functions, but internal energy is a state function or property.

1.8.3 Second Law of Thermodynamics : This law states that "*It is impossible for self-acting machine, unaided by any external agency, to convey heat from a body at low temperature to a body at higher temperature*", i.e., *heat cannot itself pass from a cold body to a warmer body*. This statement, known as second law of thermodynamics, was given by Clausius.

The second law states that heat will not pass automatically from a colder to a hotter body. Heat can be forced to pass to a higher temperature, as in the action of a refrigerating machine, but only by applying an 'external agency' to drive the machine, i.e., by doing work on the system.

Number of other statements have been put forth to formulate the second law of thermodynamics; all these can be shown logically equivalent and any one statement can be derived from the other. The second law like the first law is the statement of the net result of common experience. The following are the statements of the second law formulated by different authors at different times. However, they all are more or less indicative of one and the same meaning.

- .. No apparatus can operate in such a way that its only effect (in system and surroundings) is to convert the heat taken in completely into work.
- .. It is impossible to convert the heat taken in completely into work in a cyclic process.
- .. For heat to be converted into work there must be, in addition to the source of heat, a cooling agent possessing a lower temperature, i.e., there must be a drop in temperature.
- .. The heat of the cooler body in the given system cannot serve as a source of work.
- .. It is impossible to construct an engine that operating in a cycle, will produce an effect other than the extraction of heat from a single reservoir and the performance of an equivalent amount of work, – Kelvin-Planck.
- .. It is impossible to take heat from a reservoir and convert it into work by cyclic process, without transferring it to a colder reservoir.
- .. All natural or spontaneous processes take place in one direction only and cannot be reversed.
- .. All natural or spontaneous processes can be made to do work but the maximum work can only result from a reversible process.
- .. Any process which consists solely in the transfer of heat from one at a lower temperature to another at a higher temperature is impossible.

- .. Heat passes spontaneously only from a system at higher temperature to another at lower temperature. The passage of heat in the reverse direction requires the expenditure of work from an external source.
- .. It is impossible to construct a device that, operating in a cycle, will produce no effect other than the transfer of heat from one body to a second body at higher temperature-Clausius.
- .. All natural or spontaneous processes are in transition from a less probable to a more probable state.

A little thought would reveal that all these statements essentially convey the same meaning but each one has definite aspect of thermodynamics to cover.

First statement does not imply that heat cannot be converted into work, but does mean that changes other than those resulting directly the conversion of heat into work must occur in either the system or surroundings. Consider the case of an ideal gas in a vertical cylinder-piston assembly, expanding reversibly at constant temperature. Work is produced in the surroundings (consider the gas as the system) equal to the integral of the pressure times the change in volume. Since the gas is ideal, $\Delta u = 0$. Then, according to the First law the heat absorbed by the gas from the surroundings is equal to the work produced in the surroundings because of the reversible expansion of the gas. At first this might seem to be a contradiction of first statement since in the surroundings the only result has been the complete conversion of heat into work. However, the second law statement requires that there also be no change in the system, a requirement which has not been met in this example. Since the pressure of the gas has decreased, this process could not be continued indefinitely. The pressure of the gas would soon reach that of the surroundings, and further expansion would be impossible. Therefore, a method of continuously producing work from heat by this method fails. If the original state of the system were restored in order to meet the requirements of first statement, it would be necessary to take energy from the surroundings in the form of work in order to compress the gas back to its original pressure. At the same time energy as heat would be transferred to the surroundings in order to maintain constant temperature. This reverse process would require just the amount of work gained from the expansion; hence the net work produced would be zero.

In the second statement viz it is impossible to convert the heat taken in completely into work in a cyclic process which is an alternative way of expressing the Second law, the term cyclic requires that the system be restored periodically to its original state. In the previous example, the expansion and compression back to the original state constituted a complete cycle. If the process is repeated, it becomes a cyclic process. The restriction of cyclic process in statement 2 amounts to the same limitation as that introduced by the words *only effect* in first statement. The second law does not prohibit the production of work from heat, but it does place a limitation upon the efficiency of any cyclic process. Thus, partial conversion of heat into work forms the basis for mechanisms, called heat engines, without which the conversion is impossible.

A process of a system in which reverse or back movement of system restoring the system as well as surroundings along the same path is possible, is called a *reversible process*. In a reversible process all means of energy dissipation (due to friction, viscosity, electric resistance, magnetic hysteresis, plastic deformation, etc.) are absent. Reversible processes are hypothetical and are useful for comparison purposes. In a reversible process, a system must be in thermodynamic equilibrium at all states.

Any process that is not reversible is known as an *irreversible process*. All naturally occurring (i.e. spontaneous) processes are irreversible i.e. heat transfer, frictional losses and mass transfer.

Entropy is an important derived thermodynamic property introduced by Clausius. The property entropy is consequence of the Second law of thermodynamics. Entropy is defined as the ratio of heat supplied or rejected during a reversible process and the absolute temperature at which the heat is supplied or rejected.

It is the change of entropy for the system which is of interest, since absolute values cannot be determined. The change of entropy for the same thermodynamic states would have the same value regardless of the process between the states.

Entropy is discussed in detail in chapter-4.

Problem - 7 : 500 kg of coal per hour are burned in the furnace of a boiler. Supposing each kg of coal produces 33.5 MJ of heat, find how much work in MJ could be done per hour, if 20 per cent of heat developed were converted into work.

1 kg of coal gives out 33.5 MJ of heat.

∴ 500 kg of coal per hour will give out $33.5 \times 500 = 16,750$ MJ per hour.

Heat converted into work is 20 per cent of the heat produced.

∴ Work done = $16,750 \times 0.2 = 3,350$ MJ per hour.

Problem - 8 : (i) One kg of steam at 700 kPa contains 2,760 kJ of heat. Change this total heat to equal amount of mechanical energy in newton-metres (N.m).

(i) Find the heat equivalent of work done in kJ, when a weight of 500 kg is raised through a height of 60 metres.

(i) Now, 1 kJ = 1kN.m

∴ 2,760 kJ = 2,760 kN.m = $2,760 \times 1,000 = 27,60,000$ N.m

(ii) Work done = force \times distance through which it acts

= mass \times gravitational acceleration \times distance through which it acts

= $(500 \times 9.81) \times 60 = 2,94,300$ N.m, or 2,94,300 J, or 294.3 kJ.

Problem - 9 : Find the mechanical energy in N.m given out when one kilowatt is maintained for one hour. Find the heat equivalent of this energy in kJ.

One kW = 1,000 N.m per second

One kW-hour = $1,000 \times 3,600 = 36,00,000$ N.m-hr.

or = 36,00,000 J per hour or 3,600 kJ per hour.

1.9 Specific Heat

The specific heat of a substance may be defined as the amount of heat that must be supplied to the substance to raise the temperature of unit mass of the substance through one degree.

In differential terms, specific heat k of a substance is defined as

$$k = \frac{dq}{dT} \quad \dots(1.12)$$

where dq is heat supplied per unit mass and dT is change in its temperature.

When a body is heated, the heat energy is used to speed up the molecules and also to provide the work necessary to expand the body. In a solid or a liquid, the amount of expansion is very small and the work of expansion is similarly small. When heating a gas, however, the expansion may be considerable, and value of specific heat will depend on nature of heating process. Gas has two important values of specific heat, namely, *specific heat at constant volume* and *specific heat at constant pressure*.

Consider 1 kg of gas being heated in a closed vessel (fig. 1-5), so that no expansion of the gas is allowed. The number of heat units required to raise the temperature of 1 kg of gas through 1°C under these conditions is called the specific heat at constant volume (k_v). In differential form it is expressed as

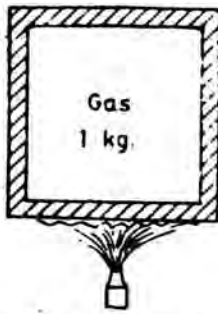


Fig 1 5 Heating at constant volume.

$$k_v = \left(\frac{\partial q}{\partial T} \right)_v \quad \dots(1.13)$$

In this case there is no work of expansion, because the gas cannot move and all the heat supplied is used to increase the internal energy, i.e., kinetic energy and potential energy of molecules. The value of k_v for air is 0.7165 kJ/kg K.

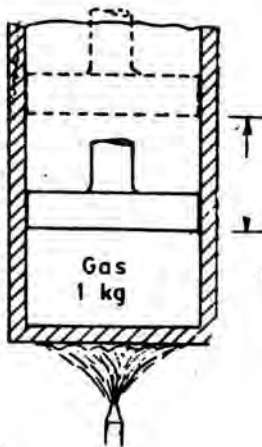


Fig. 1-6. Heating at constant pressure.

Consider now 1 kg of gas being heated in a cylinder (fig.1-6) fitted with a movable piston which exerts a constant pressure on the gas. When the gas is heated it will expand and move the piston through some distance h . In this case, in addition to the heat required to increase the kinetic energy of the molecules, further heat must be added to perform the work of moving the piston through the distance h .

The number of heat units required to raise the temperature of 1 kg of gas through 1°C under these conditions, is called the *specific heat at constant pressure* (k_p). In differential form it is expressed as

$$k_p = \left(\frac{\partial q}{\partial T} \right)_p \quad \dots(1.14)$$

The value of the specific heat of gas at constant pressure will always be greater than that at constant volume by the amount of expansive work done. The value of k_p for air is 1.0035 kJ/kg K.

The *ratio of two specific heats*, k_p and k_v of any given gas is assumed to be constant. This is expressed by the symbol γ (gamma). Thus,

$$\gamma = \frac{k_p}{k_v} \quad \dots(1.15)$$

For atmospheric air the value of k_p and k_v are 1.0035 kJ/kg K and 0.7165 kJ/kg K respectively.

Then, for air

$$\gamma = \frac{k_p}{k_v} = \frac{1.0035}{0.7165} = 1.4$$

It should be noted that no such term like γ is in use for vapours since there is no definite value for the specific heat of vapour.

Values of k_p and k_v at temperatures between 15°C and 30°C for some common gases are given in table 1-1.

Table 1 - 1 Values of specific heats for gasses

| Gas | Chemical formula | k_p kJ/kg K | k_v kJ/kg K | $\frac{k_p}{k_v}$ | $R = k_p - k_v$ kJ/kg K |
|-------------------|--------------------------------|------------------|------------------|-------------------|----------------------------|
| Air | — | 1.0035 | 0.7165 | 1.40 | 0.2870 |
| Carbon dioxide | CO ₂ | 0.8419 | 0.653 | 1.289 | 0.1889 |
| Oxygen | O ₂ | 0.9216 | 0.6618 | 1.393 | 0.2598 |
| Nitrogen | N ₂ | 1.0416 | 0.7448 | 1.40 | 0.2968 |
| Ammonia | NH ₃ | 2.177 | 1.69 | 1.288 | 0.4870 |
| Carbon monoxide | CO | 1.0413 | 0.7445 | 1.40 | 0.2968 |
| Hydrogen | H ₂ | 14.209 | 10.085 | 1.409 | 4.1240 |
| Steam | H ₂ O | 1.8723 | 1.4108 | 1.33 | 0.4615 |
| Argon | Ar | 0.52 | 0.312 | 1.667 | 0.2080 |
| Gasoline (Octane) | C ₈ H ₁₈ | 1.711 | 1.6385 | 1.044 | 0.0725 |
| Helium | He | 5.1926 | 3.1156 | 1.667 | 2.0770 |
| Methane | CH ₄ | 2.2537 | 1.7354 | 1.299 | 0.5183 |

Problem - 10 : A copper vessel weighs 2.5 kg. Calculate the quantity of heat required to raise its temperature from 20°C to 70°C. Take specific heat of copper as 0.377 kJ/kg K.

Quantity of heat required,

$$Q = \text{mass of copper, } m \times \text{specific heat of copper, } k \times \text{rise in temperature, } (t_2 - t_1) \\ = 2.5 \times 0.377 \times 50 = 47.125 \text{ kJ}$$

Problem - 11 : The specific heat of a gas at constant pressure (k_p) is 0.984 kJ/kg K and the value of γ for the gas is 1.351. If 0.5 kg of this gas is heated at constant volume from 25°C to 375°C, how many kJ need be supplied.

$$\gamma = \frac{k_p}{k_v}, k_v = \frac{k_p}{\gamma} = \frac{0.984}{1.351} = 0.728 \text{ kJ/kg K}$$

$$\text{Heat supplied} = m \times k_v \times (t_2 - t_1) = 0.5 \times 0.728 \times (375 - 25) = 127.4 \text{ kJ}$$

1.10 Perfect Gas Laws

There are three primary phases of a substance, namely, solid, liquid and gas.

Perfect gas (or ideal gas) is a gas which remains in gaseous phase at all pressures and temperatures. There are no perfect gases in nature, but from thermodynamic point of view, to simplify the formulae and calculations, some substances like oxygen, hydrogen, nitrogen, air, and carbon dioxide in gaseous phase are regarded as perfect gases.

A gas is a phase of a substance whose evaporation from its liquid phase is complete.

The behaviour of a perfect gas, undergoing changes of temperature and pressure is governed by certain laws. There are four such fundamental laws governing the behaviour of gases under the specific conditions, and these laws have been established from experimental results. These are not applicable to vapours for the reason stated above. Usual practice is to represent initial state of gas by the suffix 1 and final state by suffix 2.

A vapour is a secondary phase between liquid and gas. Thus, vapour is a phase of a substance whose evaporation from its liquid phase is partial. A vapour, therefore,

contains particles of the liquid in suspension. Steam, carbon dioxide, sulphur dioxide and ammonia are some vapours used in engineering practice. Since a vapour is liable to further evaporation or condensation on changes of either its temperature or pressure, the laws of gases do not apply to vapours. A vapour becomes dry when it is completely evaporated. Any further heating of a dry vapour is termed superheating and such a state of the vapour is termed superheated state. The behaviour of a superheated vapour approaches that of a perfect gas.

1.10.1 Boyle's Law : Boyle experimentally established that *when a perfect gas is heated at constant temperature, the volume of a given mass of gas is inversely proportional to the absolute pressure.* Hence, volume increases as the absolute pressure decreases and vice versa.

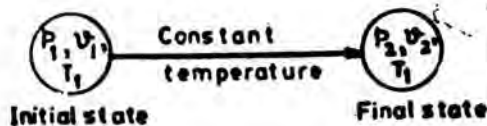


Fig. 17

$$\text{Thus, } v \propto \frac{1}{p} \quad \therefore v = \frac{C}{p}$$

i.e. $pv = C$, where $C = \text{a constant}$

$$\text{Applying the above law for initial and final states,} \\ p_1v_1 = p_2v_2 = pv = \text{a constant} \quad \dots(1.16)$$

where p and v are the corresponding pressure and volume for any instantaneous condition of a process in which temperature is constant. In other words, when we have constant temperature (*isothermal*) process, the product of pressure and volume at any state of the process is always equal to the same number as at any other state of the same process.

The expansion of a given mass of gas under the condition $pv = c$ is termed as *hyperbolic expansion*.

Problem - 12 : 4 m^3 of air is compressed isothermally to a final volume of 0.6 m^3 . If the initial pressure is 5 MPa , what will be the final pressure of the air ?

Given, $p_1 = 5\text{ MPa} = 5,000\text{ kPa}$, $v_1 = 4\text{ m}^3$ and $v_2 = 0.6\text{ m}^3$.

Since for isothermal process, $p_1v_1 = p_2v_2$ i.e. $5,000 \times 4 = p_2 \times 0.6$

\therefore Final pressure, $p_2 = 33,333\text{ kPa}$ or $p_2 = 33.333\text{ MPa}$.

1.10.2 Charles's Law : It states that, *if a perfect gas is heated at constant pressure, its volume varies directly with the absolute temperature.* In other words, the Charles's law states that coefficient of expansion is constant at constant pressure, i.e. its change of volume per degree of temperature change is constant. This change in volume, he found to be same for all perfect gases. For each degree centigrade change in temperature, the change in volume he found was $1/273$ th of the initial volume of gas at 0°C when pressure is constant. If for example, the temperature of gas is changed from 0°C to 10°C , its volume will increase by $10/273$ th of the original volume no matter what the pressure is, so long the pressure is held constant.

Thus, when the pressure is constant, the volume varies directly as the absolute temperature, i.e. $v \propto T$ $\therefore \frac{v}{T} = \text{a constant}$

Applying the above law for initial and final states,

$$\frac{v_1}{T_1} = \frac{v_2}{T_2} \quad \text{or} \quad \frac{v_1}{v_2} = \frac{T_1}{T_2} \quad \dots(1.17)$$

1.10.3 Gay-Lussac Law : This law expresses relationship between temperature and pressure of a perfect gas when the volume is kept constant. It is stated as

With volume remaining constant, the absolute pressure varies directly as the absolute temperature,

i.e. when v is constant,

$$p \propto T \therefore \frac{p}{T} = \text{a constant}$$

Applying the above law for initial and final states,

$$\frac{p_1}{T_1} = \frac{p_2}{T_2} \text{ or } \frac{p_1}{p_2} = \frac{T_1}{T_2} \quad \dots(1.18)$$

Problem - 13 : A quantity of gas at 0°C occupies 0.6 m^3 . What would be its volume at 400°C if the pressure is same at both temperatures ?

Given, $v_1 = 0.6 \text{ m}^3$, $t_1 = 0^\circ\text{C}$ and $t_2 = 400^\circ\text{C}$.

$$\text{Increase in volume} = \frac{1}{273} \times 0.6 \text{ m}^3 \text{ per degree centigrade rise}$$

$$\therefore \text{Total increase in volume} = \frac{1}{273} \times 0.6 \times 400 = 0.88 \text{ m}^3$$

$$\therefore \text{Final volume, } v_2 = 0.6 + 0.88 = 1.48 \text{ m}^3$$

Alternatively, using eqn. (1.17), $\frac{v_1}{v_2} = \frac{T_1}{T_2}$,

$$\text{i.e. } v_2 = v_1 \times \frac{T_2}{T_1} = 0.6 \times \frac{(400 + 273)}{(0 + 273)} = 1.48 \text{ m}^3 \text{ (same as before)}$$

1.11 Characteristic Equation for a Perfect Gas

An ideal or perfect gas can change its thermodynamic state without one of its characteristics p , v and T remaining constant. In other words, during the change of state, the pressure, volume and temperature may all be varied. This necessitates the derivation of another equation that will apply to such changes.

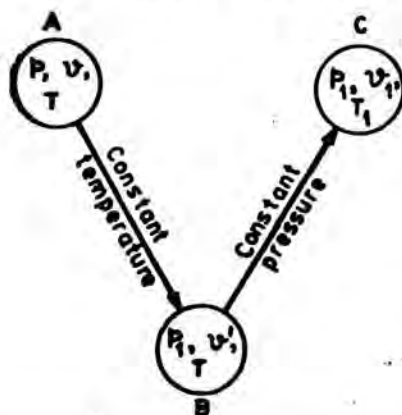


Fig. 1-8

This equation is known as the *characteristic gas equation* or *equation of state for a perfect gas*. It is derived by combining laws of Boyle and Charles.

Let a kilogram of gas be initially at pressure p , volume v and absolute temperature T at state represented by A (fig. 1-8). This gas is to be ultimately in the state represented by C where its characteristics have all changed becoming p_1, v_1 and T_1 . Let us assume that it does not change directly from A to C , but passes through intermediate state B . From A to B the temperature is to remain constant so that the temperature at B is T . The pressure at B will be taken as p_1 , the final pressure. Hence, the volume to permit this change is v' . The gas changes from state B to state C with its pressure held constant, so that the pressure at C is p_1 . The volume and temperature will change to their final values v_1 and T_1 .

Considering the change of state from A to B at constant temperature which follows the Boyle's law and using eqn. (1.16), $p v = p_1 v'$

$$\therefore v' = \frac{p v}{p_1} \quad \dots (i)$$

The change from B to C being at constant pressure, then according to Charle's law and using eqn. (1.17),

$$\frac{v'}{v_1} = \frac{T}{T_1} \quad \text{i.e. } v' = \frac{T v_1}{T_1} \quad \dots(ii)$$

Comparing the values of v' from eqn. (i) and eqn. (ii),

$$\frac{p v}{p_1} = \frac{T v_1}{T_1} \quad \text{or} \quad \frac{p v}{T} = \frac{p_1 v_1}{T_1}$$

Thus, if mass remains unchanged, $\frac{p v}{T} = \text{constant}$.

This constant is designated by R and is called the 'Characteristics Gas Constant, and its value is different for different gases.

$$\text{Then, } p v = R T \quad \dots(1.19)$$

The above equation is called the Characteristic Gas Law or Equation of state of a perfect gas.

For any mass m kg of gas, v denotes valume of m kg of gas instead of specific volume and R is replaced by mR . Hence, the most general equation for all masses, volumes, pressures and temperatures of a perfect gas is

$$p v = m R T \quad \dots(1.20)$$

It can be shown that the value of R represents work to be supplied when one kg of gas is raised in temperature by one degree centigrade at constant pressure. Thus, unit of R is N.m or joules per kg per degree centigrade temperature.

The value of R for air is 287 J/kg K or 0.287 kJ/kg K.

Problem - 14 : *The pressure of a gas supplied to an engine is measured as 100 mm of water gauge when barometer reads 756 mm of mercury. Determine the volume of 1.5 kg of this gas if its temperature is 85°C. The gas constant of the gas is 0.686 kJ/kg K.*

$$\text{Pressure of gas, } p = 756 + (100/13.6) = 763.36 \text{ mm of Hg ab.}$$

$$\text{or } = 763.36 \times 0.1333 = 101.756 \text{ kPa}$$

Applying characteristic gas eqn. (1.20), $p v = m R T$

$$\text{Volume of gas, } v = \frac{m R T}{p} = \frac{1.5 \times 0.686 \times (85 + 273)}{101.756} = 3.62 \text{ m}^3.$$

It should be noted that if the pressure is expressed in kPa or kN/m², the unit of R would be kJ/kg K.

Problem - 15 : *A gas at a temperature of 20°C and pressure of 150 kPa occupies a volume of 0.105 m³. If the gas is compressed to a pressure of 750 kPa and volume of 0.04 m³, what would be the final temperature of gas ?*

$$\text{Given, } p_1 = 150 \text{ kPa, } v_1 = 0.105 \text{ m}^3, \quad t_1 = 20^\circ\text{C, } p_2 = 750 \text{ kPa and } v_2 = 0.04 \text{ m}^3.$$

Applying characteristic gas eqn. (1.20) for initial and final states,

$$p_1 v_1 = mRT_1 \text{ and } p_2 v_2 = mRT_2$$

Dividing one by the other and re-arranging, $\frac{p_1 v_1}{T_1} = \frac{p_2 v_2}{T_2}$

$$\text{i.e. } \frac{150 \times 0.105}{(20 + 273)} = \frac{750 \times 0.04}{T_2}$$

For which, $T_2 = 558 \text{ K}$ \therefore Final temperature, $t_2 = 558 - 273 = 285^\circ\text{C}$.

1.12 Avogadro's Law

A mol of gas has a mass numerically equal to the molecular weight of the gas. If M represents the molecular weight, $1 \text{ kg-mol} = M \text{ kg}$.

Since, the molecular weight of Hydrogen is 2, one kg-mol of Hydrogen is equal to 2 kilograms. The molecular weight of Nitrogen (N_2) is 28, therefore, one kg-mol of Nitrogen is equal to 28 kg. It will be shown a little later that the volume of one kilogram-mole or kg-mol of any gas at N.T.P. (0°C and 760 mm of Hg) is 22.4 cubic metres.

Avogadro's law states that *equal volumes of all gases at the same temperature and pressure contain the same number of molecules*. Hence, under identical conditions of the temperature and pressure, one cubic metre of oxygen (O_2) contains the same number of molecules as one cubic metre of hydrogen (H_2). Hydrogen has a molecular weight of 2, while the molecular weight of oxygen is 32. Therefore, molecules of O_2 has a weight which is $32/2 = 16$ times the weight of the molecules of H_2 . Since, one cubic metre of these gases contain the same number of molecules and a molecule of O_2 weighs 16 times as much as a molecule of H_2 , it is evident that the density of O_2 is 16 times the density of hydrogen. So this law indicates that *the specific weight or density of any of the two gases are directly proportional to their molecular weights if the gases are at the same temperature and pressure*.

The density of O_2 is 1.429 kg/m^3 at N.T.P. (0°C and 101.325 kPa). Since, the specific volume is reciprocal of the density, the specific volume of O_2 at N.T.P. = $\frac{1}{1.429} \text{ m}^3/\text{kg}$.

If one kilogram of O_2 has volume of $\frac{1}{1.429} \text{ m}^3$, 32 kg or 1 kg-mol will have a volume of $\frac{1}{1.429} \times 32 \text{ m}^3$, which is equal to 22.4 m^3 at N.T.P. (0°C and 101.325 kPa),

i.e. at N.T.P. the *volume of one kg-mol is 22.4 m^3* .

Similarly, it can be proved that at N.T.P., volume of one kg-mol of any gas is 22.4 m^3 .

One g-mol (gram-mol) of all gases occupies a volume of 22.4 litres at N.T.P.

Avogadro's law may also be expressed as :

"The volume of one kg-mol (molar volume) is the same for all gases provided that temperature and pressure are equal".

Density of a gas (kg/m^3) at 0°C and 760 mm of Hg

$$= \frac{\text{Molecular weight of gas in kg}}{22.4} \quad \dots(1.21)$$

Equation (1.21), will enable us to determine the density of gases at N.T.P. (at 0°C and 760 mm of Hg).

1.12.1 Universal Gas Constant : In the equation $pv = mRT$, let $p = 760$ mm of Hg or 101.325 kPa, $T = 273$ K and $m = M$, the number of kilograms in one kg-mol. Then, v in equation $pv = mRT$ becomes the volume of one kg-mol which under the N.T.P. conditions equals 22.4 m^3 . Substituting these values in the equation $pv = mRT$, we get

$$101.325 \times 22.4 = MR \times 273$$

$$\therefore MR = 8.314 \text{ kJ/kg-mol K or } = 8,314 \text{ J/kg-mol K} \quad \dots(1.22)$$

Equation (1.22) states that the product of molecular weight, M and the gas constant, R of any gas is equal to $8.314 \text{ kJ/kg-mol K}$. This constant MR is known as *Universal Gas Constant* and its value is constant for all perfect gases. It is usually denoted by the letter G .

$$\therefore G = MR \quad \therefore R = \frac{G}{M} = \frac{8.314}{M} \text{ or } M = \frac{G}{R} = \frac{8.314}{R} \quad \dots(1.23)$$

where R is gas constant in kJ/kg K, and
 G is in kJ/kg-mol K.

Since, the molecular weights of all gases are available, the gas constant R can be calculated from the eqn. (1.23).

The values of molecular weight of some common gases are listed in Table 7-1.

If we use the symbol \bar{v} as molar volume ($\text{m}^3/\text{kg-mol}$), then the characteristic gas equation can be written as

$$p\bar{v} = GT \quad \dots(1.24)$$

Problem - 16 : 0.16 kg of gas at a pressure of 100 kPa and a temperature of 300 K occupies a volume of 0.14 m^3 . Calculate the value of the gas constant and the molecular weight of the gas.

As $pv = mRT$,

(where p is absolute pressure of gas in kPa, v is volume of gas in m^3 , T is temperature of gas in K, R is characteristic gas constant in kJ/kg K, and $m =$ mass of gas in kg)

$$\text{Gas constant, } R = \frac{pv}{mT} = \frac{100 \times 0.14}{0.16 \times 300} = 0.2917 \text{ kJ/kg K}$$

$$\text{Using eqn. (1.23), Molecular weight of the gas, } M = \frac{G}{R} = \frac{8.314}{0.2917} = 28.5$$

1.13 Regnault's Law and Joule's Law

Regnault's law hints that *the specific heat of a perfect gas at constant pressure is constant and its value at constant volume is also constant.*

This is assumed to hold good for many thermodynamic calculations. However, actually a variation in the values of specific heat at constant pressure and constant volume for any gas is found. The value of the specific heat may increase to a certain extent with the increase in temperature. However, the law is assumed to hold good within small range of variation of temperature from which it follows that the ratio of the two specific heats k_p and k_v of any given gas is a constant. Thus,

$$\gamma = \frac{k_p}{k_v} = \text{a constant} \quad \dots(1.25)$$

Joule's Law states that the *internal energy of a gas is a function of the temperature only and is independent of the pressure or volume of the gas*. Thus, internal energy of a gas is proportional to absolute temperature.

Joule's experiment was carried out with two insulated pressure vessels, connected by a pipe and a valve. One vessel was at a higher pressure than the other. The valve was opened and the gas was allowed to have free unresisted expansion.

Applying the law of conservation of energy,

$$Q = \Delta u + W$$

$Q = 0$ because no heat was supplied or rejected, and

$W = 0$ because no work was done.

$\therefore \Delta u = 0$ i.e. internal energy did not change.

After free expansion it was found that the temperature did not change and hence it was concluded that the internal energy of a given mass of gas depends upon its temperature only.

1.13.1 Change of Internal Energy of a gas : Any convenient process of thermodynamics change may be selected, but the change of internal energy evaluated between any two temperatures will be the same.

Consider that heat is added to a gas at constant volume. Since, the volume does not change in such a process, no external work is done, that is, $p \cdot dv = 0$. Hence, the energy equation for the process is,

Transferred heat, $Q = u_2 - u_1$ where $u_2 - u_1$ is change of internal energy.

Considering m kg of gas, the heat transferred in constant volume process,

$$Q = m \int_{T_1}^{T_2} k_v dT \quad \text{But, } Q = u_2 - u_1$$

$$\therefore u_2 - u_1 = m \int_{T_1}^{T_2} k_v dT$$

The equation for a constant value of k_v becomes

$$u_2 - u_1 = m k_v \int_{T_1}^{T_2} dT = m k_v (T_2 - T_1) \quad \dots(1.26)$$

This equation applies to all processes of a perfect gas between the temperature range from T_1 to T_2 . This also shows that the heat added during a constant volume process goes merely to increase the internal energy of the gas.

A perfect or ideal gas is one which obeys the laws, namely, Boyle's, Charles', Gay-Lussac's, Regnault's and Joule's. It is assumed that these laws are very closely obeyed by gases such as hydrogen, oxygen, nitrogen and air, but not by vapours. A perfect gas obeys characteristic gas equation $p v = RT$ and has constant specific heats k_p and k_v .

1.14 Relation between Gas Constant and Two Specific Heats of a Gas

Let one kilogram of gas at initial condition p_1 , v_1 and T_1 be heated at constant pressure. Let the final condition be p_1 , v_2 and T_2 .

The external work done in increasing the volume under constant pressure heating,

$$W = \int_1^2 p \, dv = p_1 (v_2 - v_1)$$

The heat transferred to the gas during this heating process,

$$Q = k_p (T_2 - T_1)$$

Applying the law of conservation of energy, $Q = \Delta u + W$

i.e. change in internal energy, $u = Q - W = k_p (T_2 - T_1) - p_1 (v_2 - v_1)$..(i)

Now, if the same one kilogram of the gas be heated at constant volume from temperature T_1 to T_2 , and as there is no change in volume, there is no external work done.

$$\therefore \Delta u = k_v (T_2 - T_1) \quad \dots(ii)$$

Since, the gas is heated through same range of temperature, the change in internal energy is the same in both cases. Hence, by equating eqns. (i) and (ii), we have

$$k_p (T_2 - T_1) - p_1 (v_2 - v_1) = k_v (T_2 - T_1)$$

$$\therefore p_1 (v_2 - v_1) = k_p (T_2 - T_1) - k_v (T_2 - T_1)$$

$$\text{Since } p_1 (v_2 - v_1) = R (T_2 - T_1) \quad (\because p_2 v_2 = RT_2 \text{ and } p_1 v_1 = RT_1)$$

$$R(T_2 - T_1) = k_p (T_2 - T_1) - k_v (T_2 - T_1)$$

Dividing both sides by $(T_2 - T_1)$, we have

$$R = k_p - k_v \quad \dots(1.27)$$

This proves that the numerical difference between values of specific heat at constant pressure and constant volume is equal to gas constant (R).

Problem - 17 : A gas of certain mass is expanded from an initial state of 400 kPa and 0.04 m^3 to another condition of 120 kPa and 0.1 m^3 . The temperature fall was observed to be 146°C . If the values of k_p and k_v are 1.0216 kJ/kg K and 0.7243 kJ/kg K respectively, calculate the change in the internal energy of the gas.

Here, $p_1 = 400 \text{ kPa}$, $v_1 = 0.04 \text{ m}^3$, $p_2 = 120 \text{ kPa}$, $v_2 = 0.1 \text{ m}^3$ and $T_1 - T_2 = 146$.

$$\text{From eqn. (1.27), } R = k_p - k_v = 1.0216 - 0.7243 = 0.2973 \text{ kJ/kg K}$$

Applying characteristic eqn. (1.20) for initial and final states to evaluate mass of the gas.

$$p_1 v_1 = mRT_1 \text{ and } p_2 v_2 = mRT_2$$

$$\text{i.e. } mRT_1 - mRT_2 = p_1 v_1 - p_2 v_2$$

$$\therefore m = \frac{p_1 v_1 - p_2 v_2}{R(T_1 - T_2)} = \frac{(400) 0.4 - (120) 0.1}{0.2973 \times 146} = 0.0915 \text{ kg}$$

Using eqn. (1.26), Change in internal energy, $u_2 - u_1 = m k_v (T_2 - T_1)$

$$= 0.0915 \times 0.7243 (-146) = -9.745 \text{ kJ(decrease).}$$

Tutorial-1

1. (a) Explain the term thermodynamic medium.
(b) Explain the terms "systems and surroundings."
(c) Classify systems.
2. (a) Explain isolated, closed, and open systems.
(b) Explain the following terms as related to thermodynamics : System, State, Property, Process and Cycle.
3. State and explain basic thermodynamic properties.
4. (a) What is the concept of temperature ? How is temperature measured ?
(b) Explain gauge pressure, vacuum and absolute pressure. State and explain devices used to measure pressure.
5. Write a brief note on 'energy' and its various forms.
6. (a) Differentiate between :
(i) stored energy and energy in transition, and
(ii) mechanical energy and internal energy.
(b) Explain the energy forms : Work and Heat.
(c) Explain the term 'enthalpy'.
7. (a) Explain thermal equilibrium and Zeroth law of thermodynamics.
(b) Write brief note on thermodynamic equilibrium.
8. (a) State the first law of thermodynamics and discuss its importance.
(b) Show that internal energy is the consequence of the first law of thermodynamics.
9. (a) Explain the second law of thermodynamics with reference to (i) Kelvin-Planck and (ii) Clausius statements.
(b) State some important statements of the second law of thermodynamics formulated by different thermodynamits.
10. (a) Explain reversible and irreversible processes.
(b) Explain the term 'entropy'.
11. (a) Define specific heat, and explain specific heat at constant volume and specific heat at constant pressure.
(b) Why specific heat of a gas at constant pressure is always greater than its specific heat at constant volume.
12. (a) Gas in a tank is at a pressure of 450 mm of Hg gauge. Barometer reads 750 mm of Hg. What is the absolute pressure of gas in the tank in kPa ?
(b) A vacuum gauge on a condenser reads 600 mm of mercury and at the same time barometer reads 740 mm of mercury. What is the absolute pressure in the condenser in kPa ?
[(a) 160 kPa, (b) 18.665 kPa]
13. The pressure of gas supplied to an engine is measured as 100 mm of water gauge. If the barometer reads 730 mm of mercury, what is the absolute pressure of gas in mm of mercury and in kPa ?
[737.353 mm of Hg, 98.304 kPa]
14. (a) Convert the following readings of pressure to kPa :
(a) 1 MPa, (b) 5 atm, (c) 1,50,000 N/m^2 , (d) 10 bar, (e) 100 kN/m^2 , (f) 1,200 mm of Hg, (g) 1,500 mm H_2O , and (h) 0.01 N/mm^2 .
(b) Convert the following readings of pressure to bar :
(i) 800 kPa, (ii) 10 atm, (iii) 2 MPa, (iv) 1,12,000 N/m^2 , (v) 200 kN/m^2 , (vi) 1,520 mm of Hg, and (vii) 1,520 mm of H_2O .
(c) A pressure gauge reads 1.6 MPa and the barometer reads 95 kPa. Calculate the absolute pressure.
[(a) 1,000, (b) 506.625, (c) 150, (d) 1,000, (e) 100, (f) 160, (g) 14.706, (h) 10];
[(b) (i) 8, (ii) 10.1325 (iii) 20, (iv) 1.12, (v) 2, (vi) 2.0265 (vii) 0.149];
[(c) 1.695 MPa]
15. (a) 5 kg of gas occupy 4 m^3 . What is the specific volume and density of the gas ?
(b) Find work done in kJ when a weight of 2 tons ascends through a height of 100 metres.
[(a) 0.8 m^3/kg ; 1.25 kg/m^3 , (b) 962 kJ]
16. (a) Find the energy given out when one kW power is maintained for 30 minutes.
(b) One kg of steam at 8 bar (0.8 MPa) contains 2,700 kJ of heat. Express this heat in newton-metres (N.m)
[(a) 1,800 kJ; (b) 27,00,000 N.m]

17. When a body was heated, 5.0 kJ were used in doing external work, 6.7 kJ were used in increasing the internal potential energy and 14.7 kJ were used in increasing the internal kinetic energy of the body. Determine : (a) the increase in internal energy and (b) the heat added to the body.
 [(a) 21.4 kJ; (b) 26.4 kJ]
18. (a) Under certain conditions, 142.77 kJ are required to raise 2 kg of hydrogen from a temperature of 10 °C to a temperature of 15°C. Find the mean specific heat of hydrogen under these conditions.
 (b) Mass of a copper vessel is 0.5 kg. Calculate the quantity of heat required to raise its temperature from 20°C to 810°C. Take specific heat of copper as 0.377 kJ/kg K.
 [(a) 14.277 kJ/kg K; (b) 7.54 kJ]
19. (a) The value of γ for a certain gas is 1.381 and its specific heat at constant pressure is 1.05 kJ/kg K. Find the heat given out when 0.3 kg of this gas is cooled at constant volume from 180 °C to 10 °C.
 (b) The values of specific heat at constant pressure and constant volume for a gas are 0.984 kJ/kg K and 0.729 kJ/kg K respectively. Find the value of γ for the gas.
 If two kg mass of this gas is heated from 30 °C to 180 °C, find the heat absorbed if the heating takes place at constant volume and at constant pressure.
 [(a) 38.775 kJ; (b) $\gamma = 1.35$, 218.7 kJ, 295.2 kJ]
20. Define perfect gas and state and explain the following laws :
 (i) Boyle's law, (ii) Charles' law, and (iii) Gay-Lussac's law.
21. Using Boyle's and Charles' laws, derive the characteristic equation for a perfect gas. What is its utility in thermodynamics ? What is a gas constant ?
22. (a) What is kg-mol ?
 (b) State and explain Avogadro's law.
 (c) What is universal gas constant ? What is the relationship between universal gas constant and gas constant ?
 (d) Write characteristic equation for a perfect gas using universal gas constant.
23. (a) State and explain Regnault's law and Joule's law.
 (b) How is change in internal energy of a gas determined ?
24. Establish the relation between gas constant R and two specific heats, k_p and k_v of a gas.
-