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Thermodynamics

Mechanical Engineering

Comprehensive Theory *with* Solved Examples

Civil Services Examination

Thermodynamics

Contents
Thermodynamics

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Basic Concepts & Zeroth Law of Thermodynamics

1.1 Introduction

Thermodynamics is the branch of science which deals with the energy and energy interactions. More specifically it deals with energy conversions, energy exchange and the direction of exchange.

1.1.1 Macroscopic and Microscopic Approach

There are two points of view from which the behaviour of matter can be studied: the macroscopic and the microscopic. In the macroscopic approach, a certain quantity of matter is considered, without the events occuring at the molecular level being taken into account. From the microscopic point of view, matter is composed of myriads of molecules. If it is a gas, each molecule at a given instant has a certain position, velocity, and energy, and for each molecule these change very frequently as a result of collisions. The behaviour of the gas is described by summing up the behaviour of each molecule. Such a study is made in microscopic or statistical thermodynamics.

Macroscopic thermodynamics is only concerned with the effects of the action of many molecules, and these effects can be perceived by human senses. For example, the macroscopic quantity, pressure, is the average rate of change of momentum due to all the molecular collisions made on a unit area. The effects of pressure can be felt. The macroscopic point of view is not concerned with the action of individual molecules, and the force on a given unit area can be measured by using, e.g., a pressure gauge. These macroscopic observations are completely independent of the assumptions regarding the nature of matter. All the results of classical or macroscopic thermodynamics can, however, be derived from the microscopic and statistical study of matter.

1.2 Thermodynamic System, Surroundings and Properties

1.2.1 System, Surroundings and Properties

- **System:** A thermodynamics system is defined as the fixed mass or fixed region in space (also called control volume) upon which our study is focused.

- **Surroundings:** Everything external to the system is called surroundings.

- **Boundary:** It is a real or imaginary surface which separates system from the surroundings. A boundary can be fixed or movable. A boundary has zero thickness, no mass and no volume.

A thermodynamic system   **A closed system**   **An open system**

An isolated system   **Fixed Region in space Control volume**
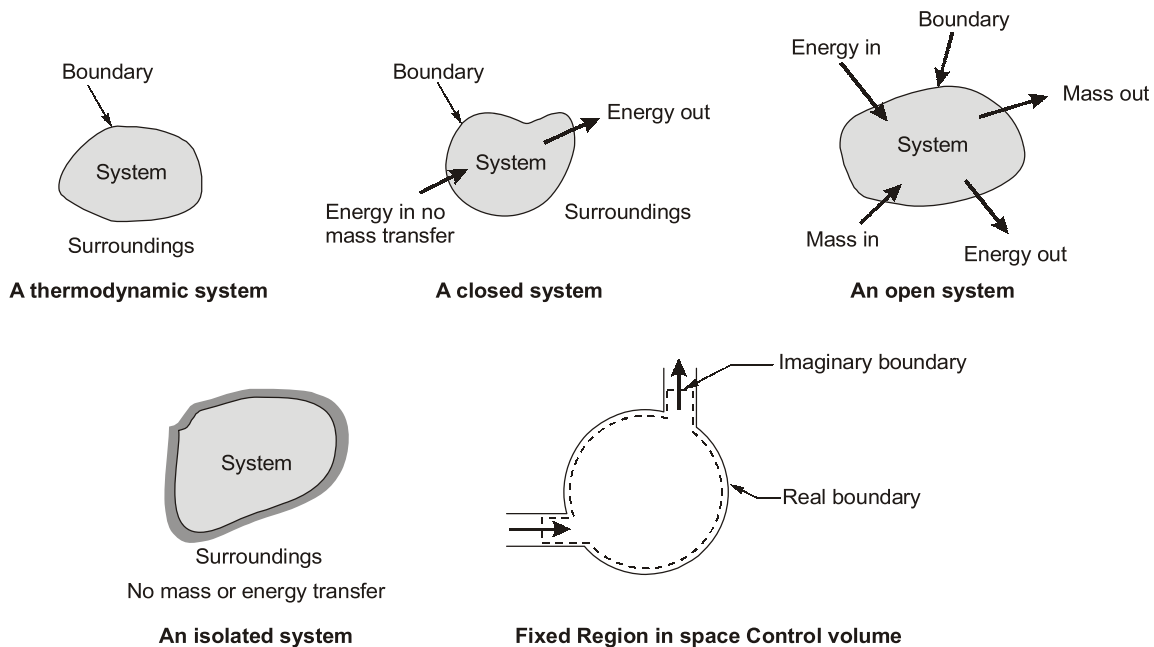
1.2.2 Types of System

Based on energy-mass interaction with the surroundings, the system has been categorized as given below.

Table: Types of Systems and Conditions

Type of system	Energy transfer	Mass transfer	Example
Open	Yes	Yes	Piston cylinder arrangement with valves
Closed	Yes	No	Piston cylinder arrangement without valves
Isolated	No	No	Universe

1.2.3 Properties of a System

- Properties are macroscopic characteristics of a system such as mass, volume, energy, pressure and temperature to which numerical values can be assigned at a given time without knowledge of the past history of the system. They have been classified as follows:

  1. **Intensive (Intrinsic) Properties:** The properties which are independent of the mass of system under consideration.
     For examples: Pressure, temperature, density, viscosity etc. Specific extensive properties, i.e., extensive properties per unit mass, are called intensive properties, e.g., specific volume, specific heat, specific internal energy etc.

  2. **Extensive (Extrinsic) Properties:** The properties which are dependent on the mass of system under consideration. For examples: Mass, energy, volume etc. While deciding the type of property we should not change the system under consideration.

- An easy way to determine whether a property is intensive or extensive is to divide the system into two equal parts with an imaginary partition as shown in figure. Each part will have same value of the property in case it is intensive but half the value in case it is extensive.
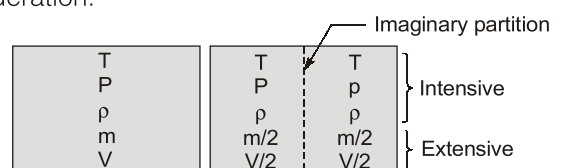

Fig.

- Important points with respect to properties:
  1. They are point or state functions.
  2. They are independent of past history.
  3. They are exact differentials.

1.2.4 Homogeneous and Heterogeneous Systems

A quantity of matter homogeneous throughout in chemical composition and physical structure is called a phase. Every substance can exist in any one of the three phases, viz. solid, liquid and gas. A system consisting of a single phase is called a homogeneous system, while a system consisting of more than one phase is known as a heterogeneous system.

1.3 State of the System & Process

- Any equilibrium condition of the system is called state of the system. At a given state all the properties of a system has fixed values throughout the entire system (may/may not be uniform).
- A change in state is called a process.
- The infinite number of states through which the system passes while going from an initial to a final state is called the path of the process. A process can be classified as:
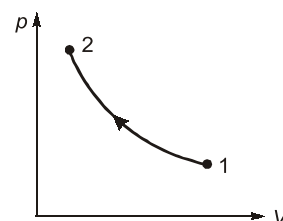
Fig. (a) Quasistatic Process

1. **Quasistatic and Non-Quasistatic Process:** If a process takes place infinitely slowly it is called a quasistatic process, otherwise a non-quasistatic process. A quasistatic process is generally represented by a joined line [Fig. (a)] on property diagrams. Whereas a non-quasistatic process is represented by dotted lines. [Fig. (b)] [i.e. every point on the path represents an equilibrium state and hence can be represented on the curve.]
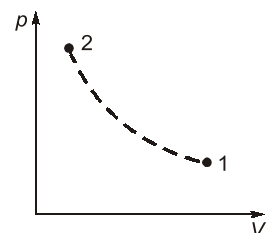
Fig. (b) Non-Quasistatic Process

2. **Reversible and Irreversible Process:** A process is said to be reversible if it can be reversed in direction following the same path as that of the forward process without leaving any change in the system as well as the surroundings. The process is said to be reversible otherwise irreversible.

   Quasistatic and reversible processes are not always same but for our study we take them as same. All reversible processes are quasistatic but all quasistatic processes may not be reversible. Frictionless quasistatic process is reversible.

1.3.1 Thermodynamic Equilibrium

A system is said to exist in a state of thermodynamic equilibrium when no change in any macroscopic property is registered. If the system is isolated, it always reaches in course of time a state of thermodynamic equilibrium and can never depart from it spontaneously.

Therefore, there can be no spontaneous change in any macroscopic property if the system exists in an equilibrium state. Thermodynamics studies mainly the properties of physical systems that are found in equilibrium states. A system will be in a state of thermodynamic equilibrium, if the conditions for the following three types of equilibrium are satisfied:

1. Mechanical equilibrium
2. Chemical equilibrium
3. Thermal equilibrium

In case the absence of any unbalanced force within the system itself and also between the system and the surroundings, the system is said to be in a state of mechanical equilibrium. If an unbalanced force exists, either the system alone or both the system and the surroundings will undergo a change of state till mechanical equilibrium is attained.

If there is no chemical reaction or transfer of matter from one part of the system to another, such as diffusion or solution, the system is said to exist in a state of chemical equilibrium.

When a system existing in mechanical and chemical equilibrium is separated from its surrounding by a diathermic wall (diathermic means 'which allows heat to flow') and if there is no spontaneous change in any property of the system, the system is said to exist in a state of thermal equilibrium. When this is not satisfied, the system will undergo a change of state till thermal equilibrium is restored.

1.4   Concept of Continuum

From the macroscopic viewpoint, we are always concerned with volumes which are very large compared to molecular dimensions. Even a very small volume of a system is assumed to contain large number to molecules so that statistical averaging is meaningful and a property value can be assigned to it. Disregarding the behaviour of individual molecules, matter is here treated as continuous. Let us consider the mass δm in a volume δV surrounding the point p. The ratio $\delta m/\delta V$ is the average mass density of the system within the volume δV. We suppose that at first δV is rather large, and is subsequently shrunk about the point P. If we plot $\delta m/\delta V$ against δV, the average density tends to approach an asymptote as δV increases. However, when δV becomes so small as to contain relatively few molecules, the average density fluctuates substantially with time as molecules pass into and out of the volume in random motion, and so it is impossible to speak of a definite value of $\delta m/\delta V$. The smallest volume which may be regarded as continuous is $\delta V'$. The density ρ of the system at a point is thus defined as:

$$\rho = \lim_{\delta V \to \delta V'} \frac{\delta m}{\delta V}$$
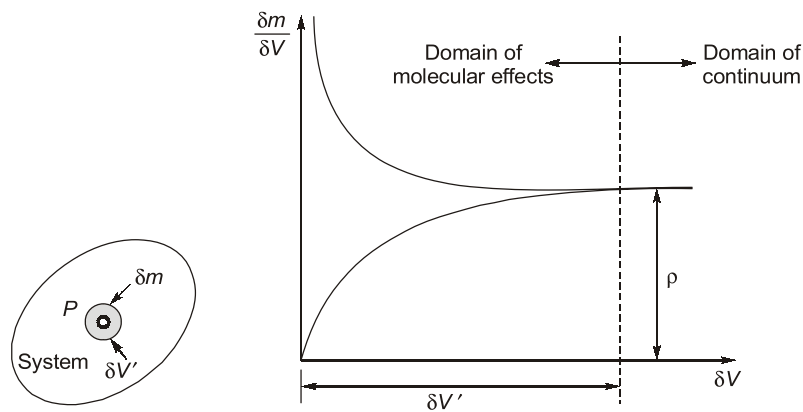
Fig. (a)   Fig. (b) Definition of the macroscopic property, density

Similarly, the fluid velocity at a point P is defined as the instantaneous velocity of the centre of gravity of the smallest continuous volume $\delta V'$.

The concept of continuum loses validity when the mean free path of the molecules approaches the order of magnitude of the dimension of the vessel, as, for instance, in highly rarefied gases encountered in high vacuum technology, in rocket flights at high altitudes and in electron tubes. In most engineering applications, however, the assumption of a continuum is valid and convenient, and goes hand in hand with the macroscopic point of view.

1.5 Pure Substances

- A substance is said to be a pure substance if it is of homogeneous and invariable chemical composition throughout.
- It does not have to be a single chemical element or compound. A mixture of various chemical elements or compounds also qualifies as a pure substance as long as the mixture is homogeneous. For example, air.
- Some more examples are shown in figure.
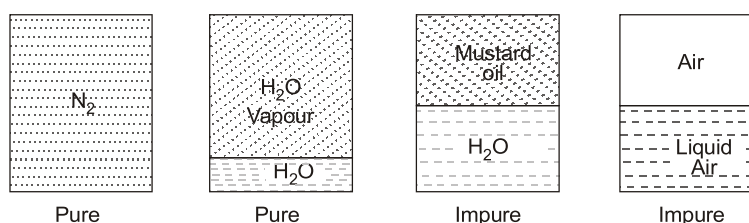
Fig.

- The mixture of refrigerants which behaves as a pure substance is called Azeotrope.
- Mixture of ethyl alcohol and water is also a pure substance due to molecular level hydroxyl bond formation.

1.5.1 Gibbs Phase Rule

- Phase is defined as a quantity of mass that is homogeneous throughout in chemical composition and physical structure. For example, solid, liquid, vapour, gas.
- In general the minimum number of independent intensive variables required to fix the state of the system for multiphase, multi-component system is given by the Gibbs phase rule, expressed as:

$$F = C - P + 2$$

where, F = Degree of freedom or minimum number of independent intensive variables required

C = Number of chemical components

P = Number of phases present in equilibrium

Example 1.1   Determine the degree of freedom of the following systems and comment on the result:

(i) Water and water vapour system

(ii) A mixture of oxygen and nitrogen gas as system

(iii) Water at its triple point

Solution :

(i)

In the given system it can be asserted that:

Number of phases, P = 2   (liquid + vapour)

Number of components, C = 1   (only water)

∴   From Gibbs phase rule, we know $F = C - P + 2$

Substituting the values in above equation

$$F = 1 - 2 + 2 = 1$$

Comment : Only one variable is enough to fix the state of the system e.g., two phase systems in evaporators of a RAC system.

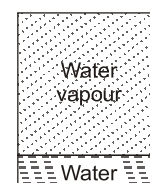**(ii)** It can be asserted that in the given system

$$P = 1 \quad \text{(only gas)}$$
$$C = 2 \quad (O_2 + N_2)$$

From the Gibbs phase rule, we know $\quad F = C - P + 2$

Substituting the values in above equation

$$F = 2 - 1 + 2 = \mathbf{3}$$

Comment : We will require three independent intensive variables to fix the state of the system. Even though air is mixture of several gases but it is considered as one component (in gaseous phase).

(iii) Triple point of any substance is a state at which it can exist in equilibrium in solid, liquid and gaseous phase i.e. all 3 phases can co-exist.

∴ It can be asserted from above definition that at triple point of water
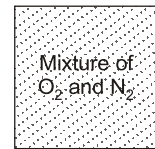
$$P = 3 \quad \text{(solid, liquid and gas)}$$
$$C = 1 \quad \text{(only water)}$$

From the Gibbs phase rule, we know $\quad F = C - P + 2$

Substituting the values in above equation

$$F = 1 - 3 + 2 = 0$$

Comment : The degree of freedom comes out to be zero which suggests that the triple point of water is a very specific condition and occurs at a particular value of temperature and pressure.

1.5.2   State Postulate

The state of a pure substance of given mass can be fixed by specifying two independent intensive properties, provided the system is in equilibrium. This is known as the 'two-property rule'. The state can thus be represented as a point on thermodynamic property diagrams. Once any two property of a pure substance are known, other properties can be determined from the available thermodynamic relations.

Temperature and specific volume, for example, are always independent properties, and together they can fix the state of a simple compressible system. Temperature and pressure, however, are independent for single-phase systems, but are dependent for two-phase systems.

1.6   Zeroth Law of Thermodynamics

- When a body A is in thermal equilibrium with body B, and also separately with a body C, then B and C will be in thermal equilibrium with each other.

Explanation :

Let us say T_A, T_B and T_C are the temperatures of 3 bodies A, B, and C respectively.

Fig.

Given: A and C are in thermal equilibrium $i.e.$, $T_A = T_C$ and B and C are in thermal equilibrium $i.e.$, $T_B = T_C$ then as a consequence of zeroth law: A and B will also be in thermal equilibrium $i.e.$, $T_A = T_B$

- Zeroth law was first formulated by R. H. Fowler in 1931.

- It's fundamental value was recognized more than half a century after the formulation of the first and second laws and hence it was named zeroth law as it should have preceded the first and second laws.
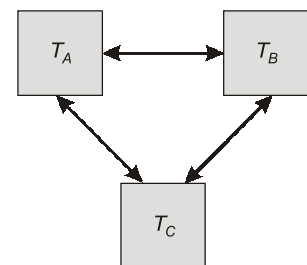
1.6.1   Thermometry

It is the science which is based on finding the thermometric property. The temperature cannot be quantified on the basis of feeling and hence we need a property which is easily measurable and then that property is used to find the temperature of the body.

Since 1954 only one fixed point has been in use, viz, the triple point of water, the state at which ice, liquid water vapour co-exist in equilibrium. The temperature at which this state exists is arbitrarily assigned the value of 273.16 kelvin, or 273.16 K (the reason for using Kelvin's name will be explained later). Designating the triple point of water by θ_t, and with X_t being the value of the thermometric property when the body, whose temperature θ is to be measured, is placed in contact with water at its triple point, it follows that

$$\theta_t = aX_t$$

$$\therefore \qquad a = \frac{\theta_t}{X_t} = \frac{273.16}{X_t}$$

Therefore, $\qquad \theta = aX = \frac{273.16}{X_t} \times X$

or, $\qquad \theta = 273.16\frac{X}{X_t}$

The temperature of the triple point of water, which is an easily reproducible state, is now the standard fixed point of thermometry.

1.6.2   Different Types of Thermometers

1.   Thermistor or Resistance Thermometer

- It is based on working of a balanced Wheatstone bridge circuit.

  Here, P and Q = Resistance with fixed known values

  $\qquad\qquad G$ = Galvanometer

  $\qquad\qquad R$ = Variable resistance (helps in balancing of Wheatstone bridge)

  $\qquad\qquad S$ = Resistance very sensitive to temperature change

Fig.

- Initially let us assume that the circuit is balanced, hence there will be no deflection in the Galvanometer, G.

- By balanced Wheatstone bridge equation, we can write

$$\frac{P}{Q} = \frac{R}{S} \qquad\qquad\qquad ...(i)$$

- Now if we change the temperature of S, its resistance will change to S' (unknown value) and the bridge will become unbalanced.

- Thus we will change value of R (variable resistance) to R', to again balance the bridge.

  Now $\qquad\qquad \frac{P}{Q} = \frac{R'}{S'} \qquad\qquad\qquad ...(ii)$

- From equation (ii) we get the value of unknown S' at the new temperature.

- The resistance as a function of temperature for resistor S will be known to us and from that we can calculate the temperature.

- In thermistor, resistance is the thermometric property used to calculate temperature.
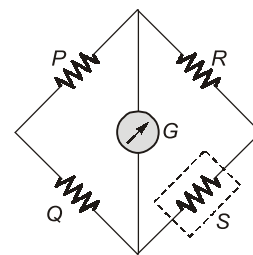
2.   Thermocouple

*   It's working is based on principle of Seebeck effect.
*   Seebeck effect: If two different metals are joined at two different junctions which are kept at different temperatures then an EMF is generated between the two junctions which is directly proportional to the temperature difference between them

    According to seebeck effect

$$\text{EMF} \propto T_2 - T_1$$

Fig.

*   Hence if one of the temperatures is known, the other can be found easily using the above relation.
*   In thermocouple, EMF is the thermometric property.
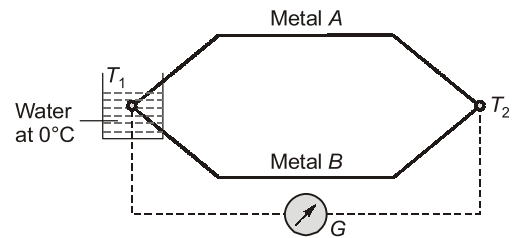*   The opposite of Seebeck effect is called Peltier effect and it is used in thermoelectric refrigeration.

3.   Constant Volume Gas Thermometer

*   It is based on Gay-Lussac's law which states that, for a given mass and constant volume of an ideal gas, the pressure is directly proportional to the absolute temperature, assuming closed system.

$$p \propto T$$

or

$$\frac{p_1}{T_1} = \frac{p_2}{T_2}$$

Fig.

*   Hence here temperature is measured by pressure change.
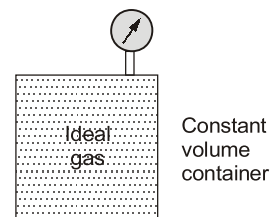*   Pressure is the thermometric property in this case.

4.   Constant Pressure Gas Thermometer

*   It is based on Charle's law which states that, for a given mass of an ideal gas at constant pressure, the volume is directly proportional to the absolute temperature, assuming closed system.

$$V \propto T$$

or

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

Fig. *Piston Cylinder Arrangement*

*   Here temperature is measured by volume change.
*   Volume is the thermometric property in this case.
*   Both constant volume and constant pressure gas thermometers are independent of the material of construction (which is ideal gas) i.e. any type of ideal gas can be used whether it is oxygen, nitrogen, air etc.
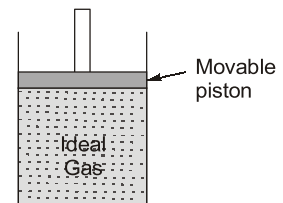
1.6.3   Temperature Scales

*   Temperature is the measure of random energy of molecules.
    Temperature scales enable us to use a common basis for temperature measurements and several have been used till date.
*   All scales are based on some easily reproducible states such as the freezing and boiling points of water also called ice point and steam point respectively.
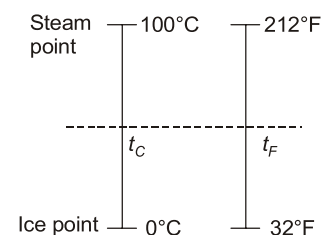

Fig.

- The Celsius scale and Fahrenheit scale are two most widely used scales.

  Let t_c be a temperature on Celsius scale and t_F, the corresponding value on Fahrenheit scale. We assume that the scale are linear

  $\therefore$ $\qquad \qquad \dfrac{t - t_i}{t_s - t_i} = \text{constant} \qquad$ {for any scale} $\qquad \qquad$ ...(i)

  t_i = temperature at ice point

  t_s = temperature at steam point

  t = temperature to be found

  Applying equation (i) to Celsius and Fahrenheit scale

  $$\dfrac{t_C - 0}{100 - 0} = \dfrac{t_F - 32}{212 - 32} \qquad \qquad \text{...(ii)}$$

  Solving equation (ii), we get

  $$t_F = \dfrac{9}{5} t_C + 32$$

  or $\qquad \qquad \qquad \qquad t_C = \dfrac{5}{9}(t_F - 32)$

- The above scales of °C and °F are called relative temperature scales.
- Later the second law of thermodynamics will help us to define an absolute temperature scale. Kelvin, which is the absolute temperature scale defined on Celsius scale.

  $$T_K = t_c + 273.15$$

- Kelvin is also called the thermodynamic temperature scale.
- Before 1954, temperature measurement was based on two reference points, namely ice point and steam point. After 1954, the temperature measurement has been based upon single reference point i.e. triple point of water.
- According to internationally accepted convention

  $$1K = \left(\dfrac{1}{273.16}\right)^{th} \text{of triple point of water}$$

1.6.4 Calibration of Thermometers

- If two different thermometers using alcohol and mercury respectively, are calibrated at ice point and steam point and the distance between ice point and steam point is divided into 100 equal parts then they are not guaranteed to give the same reading anywhere between the calibration points, but they will always give the same readings at the calibration points itself.
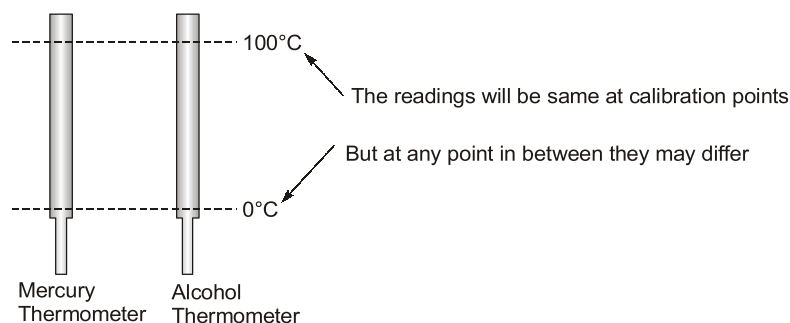

Fig. *Calibration of Thermometers*

Example 1.2 What does a temperature difference of 10 on °C scale correspond to on a Fahrenheit scale?

Solution :

Given:
$$\Delta t_c = 10$$

We know
$$t_F = \frac{9}{5}t_c + 32 \qquad \qquad ...(i)$$

Applying Δ on both sides of equation (i), we get

$$\Delta t_F = \frac{9}{5}\Delta t_c$$

Putting the value of Δt_c, we get $\quad \Delta t_F = \frac{9}{5} \times 10 = 18$

Example 1.3 Two mercury-in-glass thermometers are made of identical materials and are accurately calibrated at 0°C and 100 °C. One has a tube of constant diameter, while the other has a tube of conical bore, 10 percent greater in diameter at 100°C than at 0°C. Both thermometers have the length between 0 and 100 subdivided uniformly. What will be the straight bore thermometer read in a place where the conical bore thermometer reads 50°C?

Solution :

The volume of mercury in the tube at t°C, V_t, is given by
$$V_t = V_0\,[1 + \beta(t - t_0)]$$

where V_0 is the volume at 0°C, β is the coefficient of volume expansion of mercury, and t_0 is the ice point temperature which is 0°C. The volume change of glass is neglected.

Therefore,
$$V_t - V_0 = \beta\, V_0\, t$$

The temperature t is thus a linear function of volume change of mercury ($V_t - V_0$). Therefore,

$$\Delta V_{0-100} = \beta V_0 \times 100$$
$$\Delta V_{0-50} = \beta V_0 \times 50$$

$\therefore \qquad \qquad \dfrac{\Delta V_{0-50}}{\Delta V_{0-100}} = \dfrac{1}{2}$

That is, at 50°C, the volume of mercury will be half of that at 100°C, for the straight bore thermometer. But if the bore is conical, mercury will fill up the volume $ACDB$, which is less than half of the mercury volume at 100°C, i.e. volume $AEFB$. Let t be the true temperature when mercury rises half the length of the conical tube (the apparent temperature being 50°C). Let EA and FB be extended to meet at G. Let l represent the length of the thermometers and l' the vertical height of the cone ABG, as shown in the figure. Now,

$$\frac{l'}{l + l'} = \frac{d}{1.1d} = \frac{1}{1.1}$$
$$l' = 10$$

and
$$\frac{l'}{l' + l\,/\,2} = \frac{d}{CD}$$
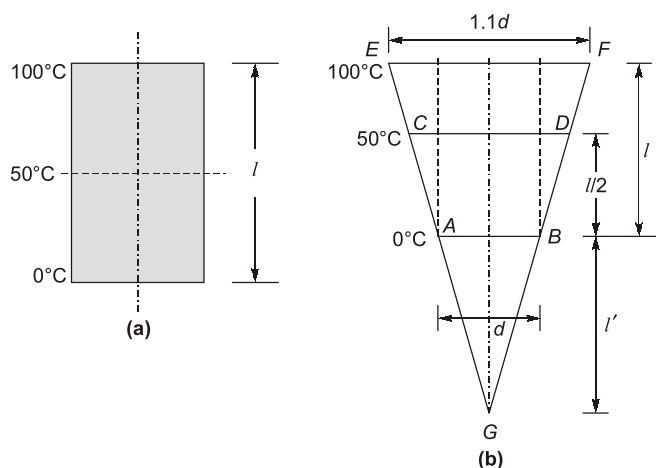
$$\therefore \qquad CD = \frac{10.5}{10}d = 1.05d$$

Again

$$\Delta V_{0-100} = V_0 \times \beta \times 100$$
$$\Delta V_{0-t} = V_0\beta t$$

$$\frac{\Delta V_{0-t}}{\Delta V_{0-100}} = \frac{t}{100}$$

or, $\qquad \dfrac{\text{Volume } ACDB}{\text{Volume } AEFB} = \dfrac{t}{100} \quad$ or, $\quad \dfrac{\frac{1}{3}\frac{\pi}{4}(1.05d)^2 \times 10.5l - \frac{1}{3}\frac{\pi}{4}d^2 \times 10l}{\frac{1}{3}\frac{\pi}{4}(1.1d)^2 \times 11l - \frac{1}{3}\frac{\pi}{4}d^2 \times 10l} = \dfrac{t}{100}$

or, $\qquad \dfrac{1.05 \times 1.05 \times 10.5 - 10}{1.1 \times 1.1 \times 11 - 10} = \dfrac{t}{100}$

$$\therefore \qquad t = \frac{1.58}{3.31} \times 100 = 47.73°\text{C}$$

1.7 Units and Dimensions

In the present text, the SI (System International) system of units has been used. The basic units in this system are given in below table:

Table: Basic units

Quantity	Unit	Symbol
Length (L)	Metre	m
Mass (M)	Kilogram	kg
Time (t)	Second	s
Amount of substance (H)	Mole	mol
Temperature (T)	Kelvin	K
Electric current (I)	Ampere	A
Luminous intensity (I_v)	Candela	cd
Plane angle (Q)	Radian	rad
Solid angle (Ω)	Steradian	sr

The dimensions of all other quantities are derived from these basic units which are given in below table:

Table : In system: Derived units

Quantity	Unit	Symbol	Alternative unit	In basic units
Force (F)	Newton	N		kgm/s^2
Energy (E)	Joule	J	Nm	kgm^2/s^2
Power	Watt	W	J/s	kgm^2/s^3
Pressure	Pascal	Pa	N/m^2	$kg/(ms^2)$
Frequency	Hertz	Hz		s^{-1}
Electric charge	Coulomb	C		As
Electric potential	Volt	V	W/A = J/C	$kgm^2/(s^3 A)$
Capacitance	Farad	F	C/V	$s^4 A^2/(kg\,m^2)$
Electrical resistance	Ohm	Ω	V/A	$kgm^2/(s^3 A^2)$
Magnetic flux	Weber	Wb	Vs	$kgm^2/(s^2 A)$
Magnetic flux density	Tesla	T	Wb/m^2	$kg/(s^2 A)$
Inductance	Henry	H	Wb/A	$kgm^2/s(s^2 A^2)$

1.7.1 Force

The force acting on body is defined by Newton's second law of motion. The unit of force is the newton (N). A force of one newton produces an acceleration of 1 ms^{-2} when applied to a mass of 1 kg.

$$1\ N = 1\ kg\ m/s^2$$

The weight of a body (W) is the force with which the body is attracted to the centre of the earth. It is the product of its mass (m) and the local gravitational acceleration (g), i.e.,

$$W = mg$$

The value of *g* at sea level is 9.80665 m/s^2. The mass of substance remains constant with elevation, but its weight varies with elevation.

1.7.2 Pressure

The $p = \lim_{A \to A'} \left(\dfrac{F_{normal}}{A} \right)$ where A' is the area at the 'point' in the same limiting sense as used in the definition of density.

If the area A was given new orientations by rotating it around the given point, and the pressure determined for each new orientation, it would be found that the pressure at the point is the same in all directions as long as the fluid is at rest. this is a consequence of the equilibrium of forces acting on an element of volume surrounding the point. However, the pressure can vary from point to point within a fluid at rest; examples are the variation of atmospheric pressure with elevation and the pressure variation with depth in oceans, lake, and other bodies of water.