HEAT AND THERMODYNAMICS

Thermometry : Measurement of temperature is called thermometry. Temperature may be defined as follows :

(i) The degree of hotness or coldness is known as temperature.

(ii) Temperature is the thermal condition of the body which determines the direction of flow of heat.

(iii) Temperature is the measure of average kinetic energy of the gas molecules, and heat is the measure of kinetic energy of all the gas molecules at constant volume.

Thermometer : A thermometer is an instrument used to measure the temperature.

Temperature Scales : To measure temperature two fixed points are taken on each thermometer. One of the fixed points is the freezing point of water, it is known as ice point of lower fixed point. The other fixed point is boiling point of water, it is known as steam point or upper fixed point. The difference in upper fixed point and lower fixed point is known as fundamental interval. A thermometer may be graduated in following scales :

(i) Centigrade scale (°C) or Celsius scale.
(ii) Fahrenheit scale (°F)
(iii) Reumur scale (°R)
(iv) Kelvin scale (K or °A)
(v) Rankine Scale (Ra)

- The upper and lower fixed points of centigrade scale are 100°C and 0°C and the fundamental interval is 100.
- The upper and lower fixed points of Fahrenheit scale are 212°F and 32°F and fundamental interval is 180.
- The upper and lower fixed points of Reaumur scale are 80°R and 0°R and the fundamental interval is 80.
- The upper and lower fixed points of Kelvin scale are 373 K and 273 K and the fundamental interval is 100.
- The upper and lower fixed points of Rankine scale are 672° Ra and 460° Ra and the fundamental interval is 212.

fundamental interval is 212.

So, following relation exists between different temperature scales.

$$\frac{C}{100} = \frac{F-32}{180} = \frac{R}{80} = \frac{K-273}{100} = \frac{Ra-460}{212}$$

If should be noted that, for simplicity absolute zero is taken at –273°C but its exact value is –273.16°C. Moreover $\Delta C = \Delta K$.

Difference between heat and temperature

Heat	Temperature
1. It is a form of energy.	1. It is thermal condition of a body.
2. It is total amount of internal energy.	2. It is proportional to average kinetic energy of the molecules of the body.
3. As a result of heat exchange between two bodies, total amount of heat of two bodies remains unchanged.	3. As a result of heat exchange between two bodies, sum of their temperatures before and after exchange is not same.
4. It is the cause.	4. It is the effect.
5. Its SI unit is joule (J).	5. Its SI unit is Kelvin (K).

Thermal Equilibrium : When two bodies at different temperatures are kept in contact with each other, heat energy flows from a body at higher temperature to that at lower temperature, till temperatures of the two become equal. At this stage, the two bodies are said to be in thermal equilibrium and the resulting temperature is said to be equilibrium temperature.

Advantage of mercury as thermometric substance :

(i) It is an opaque and shining liquid and hence can be easily seen through the glass of the thermometric tube.

(ii) It does not stick to glass.

(iii) It does not vaporise at moderate temperatures.

(iv) It has a fairly large expansion for all small change in temperature.

(v) Its expansion is fairly constant at different temperatures.

(vi) It is a good conductor of heat and hence quickly attains the temperature to be measured.

(vii) It has low freezing point of –39°C and higher boiling point of 357°C. Hence, it can be used over a fairly wide range of temperature.

(viii) It has low specific heat. Hence it does not takes much heat from the body whose temperature is to be measured.

(ix) It can be easily obtained in pure state.

Expressions for temperatures determined by various thermometers :

Value of unknown temperature determined by

- Jolly's constant volume thermometer

$$t = \frac{h_t - h_0}{h_{100} - h_0} \times 100$$

when h_0, h_{100} *and* h_t are mercury level differences at 0°C, 100°C and t°C.

- Standard constant volume hydrogen thermometer

$$t = \frac{P_t - P_0}{P_{100} - P_0} \times 100$$

where P_0, P_{100} and P_t are the pressures of the gas at 0°C, 100°C and t°C.

- Platinum resistance thermometer

$$t = \frac{R_t - R_0}{R_{100} - R_0} \times 100$$

Where R_0, R_{100} and R_t are the resistances of platinum wire at 0°C, 100°C and t°C.

Drawback of a gas thermometer

(i) As the size of the gas thermometer is large, it is quite difficult and inconvenient to take it from one place to another.

(ii) For taking measurements by this thermometer, the quantity of the substance whose temperature is to be measured, should be more enough.

(iii) It can find the temperature only after measuring the pressures at different temperatures and after making some calculations. Hence, it is quite likely that the chances of error are much in the measured value of temperature.

(iv) To complete all these things, i.e., observations of pressure, calculations etc. takes a lot of time.

(v) As no practical gas obeys the ideal gas equation over all range of temperature and pressure, there is a limitation for these type of thermometers, i.e., they can measure only those temperature ranges in which the gas behaves more or less like an ideal gas.

(vi) Correction factor has to be taken into account against the increase in volume of the glass bulb and also of connecting glass tubes while heating the bulb.

Coefficient of linear expansion (α) : It is defined as the increase in length per unit length per unit degree rise in temperature of the solid.

Mathematically,

$$\alpha = \frac{\Delta l}{l.\Delta T}$$

Where Δl = change of length

l = original length

ΔT = rise in temperature

Its unit is $^0C^{-1}$ or K^{-1}.

Coefficient of Superficial expansion (β) : It is defined as the increase in surface area per unit area per unit degree rise in temperature of the solid.

Mathematically,

$$\beta = \frac{\Delta S}{S.\Delta T}$$

Where ΔS = change in surface area

S = original surface area

ΔT = rise in temperature.

Its unit is $^0C^{-1}$ or K^{-1}.

Coefficient of volume expansion (γ) : It is defined as the increase in volume per unit volume per unit degree rise in temperature of the solid.

Mathematically,

$$\gamma = \frac{\Delta V}{V.\Delta T}$$

Where ΔV = change in volume
V = original volume
ΔT = rise in temperature.

Its unit is ${}^0C^{-1}$ or K^{-1}.

Relation between α, β, and γ :

$$\beta = 2\alpha$$
$$\gamma = 3\alpha$$

Work and Heat : According to Joule, the ratio of work done and heat produced is always a constant, i.e.,

$$\frac{W}{H} = \text{constant} = J$$

Where J is called the mechanical equivalent of heat. It is defined as the amount of work done to produce a unit quantity (1 calorie) of heat. The value of J is 4.18 J cal^{-1} or 4.18×10^7 erg cal^{-1}.

Calculation of heat transferred :

Heat transferred = mass × specific heat × change in temp.

or $Q = m\,c\,\Delta T$.

Units of heat : The most commonly used unit of heat is 'calorie'. One calorie is the amount of heat required to rise the temperature of water through 1°C (from 14.5°C to 15.5°C). It is written as 'cal'.

A bigger unit of heat is called 'Kilo calorie'. One kilocalorie is the amount of heat required to rise the temperature of 1 kg of water through 1°C (from 14.5°C to 15.5°C). It is written as 'k cal'.

Also 1 kcal = 1000 cal.

Since heat is a form of energy, its S.I unit is joule (J), which is the same as for energy.

Also 1 cal = 4.18 J.

Specific heat : The quantity of heat gained or lost by a body depends upon

(*i*) mass of the body

(*ii*) nature of the material of the body, and

(*iii*) change in temperature of the body

Also, the quantity of heat Q required to raise the temperature of a body of mass m through ΔT is given by,

$$Q = m.c.\,\Delta T$$

$$\text{If } m = 1\text{g},\ \Delta T = 1°\text{C}$$

Then Q= C.

Hence, specific heat of a substance is defined as the amount of heat required to raise the temperature of 1g of the substance through 1°C.

Molar specific heat : It is defined as the quantity of heat required to raise the temperature of one kilo-mole of the substance through 1K, keeping its volume unchanged.

Dulong and Petit's law : According to this law, the average molar specific heat at constant volume for all the metals (except a few very lightest ones) is approximately the same and is equal to 3R (about 25 J $mole^{-1}\ {}^{0}C^{-1}$).

Specific heat of gases :

(*i*) ***Specific heat of a gas at constant volume*** **:** It is defined as the amount of heat required to raise the temperature of 1g of a gas through 1°C, when its volume is kept constant. It is represented by c_v.

If molecular weight of a gas under consideration is M, then,

$$C_v = Mc_v.$$

(If instead of 1g of gas, its 1 mole is heated through 1°C at constant volume, it is known as molar specific heat at constant volume and represented by C_v).

(*ii*) ***Specific heat of a gas at constant pressure*** **:** It is defined as the amount of heat required to raise the temperature of 1g of a gas through 1°C at constant pressure. It is represented by c .

If instead of 1g of a gas, its 1 mole is heated through 1°C, keeping its pressure constant, then it is called as molar specific heat of a gas at constant pressure. It is represented by C_p, therefore,

$$C_p = Mc_p$$

Specific heat at constant pressure is always greater than specific heat at constant volume. Also,

$$C_p - C_v = \frac{R}{J} \text{ (Mayer's relation)}$$

Principle of Calorimetry : According to this principle,

Heat lost by any body = Heat gained by another body

Thermal capacity or heat capacity : It is defined as the amount of heat required to raise the temperature of the body through one degree.

$$\text{Thermal capacity} = mC.$$

Its unit are cal $^0C^{-1}$ or JK^{-1}.

Water equivalent : Water equivalent of a body is equal to the mass of water that requires the same heat to raise its temperature by 1°C as is required by the body under study. It is equal to the product of the mass of the body and its specific heat. Also, equivalent and heat capacity of a body are numerically equal quantities.

It is generally represented by w. Its unit is kg. Hence,

$$w = mC.$$

Latent Heat : The quantity of heat which is supplied to a substance to bring about a change in its state without change in temperature, is called its latent heat.

(i) Latent heat of fusion (or melting) : The quantity of heat required to change 1 kg of solid to its liquid at its melting point, without any change in temperature. is called as the latent heat of fusion or melting of the substance. Its unit is cal g^{-1} or kcal kg^{-1} or J kg^{-1}.

(ii) Latent heat of fusion of ice : It is the quantity of heat required to change 1 kg of ice at 0°C completely to 1kg of water at the same temperature. Its value is 80 kcal kg^{-1} or 3.36×10^5 J kg^{-1}.

(iii) Latent heat of vaporisation (or boiling) : It is the quantity of heat required to completely convert 1kg of a liquid to its vapours at its boiling point without change in temp. Its unit is cal g^{-1} or kcal kg^{-1} or J kg^{-1}.

(*iv*) Latent heat of steam : The amount of heat required to completely convert 1kg of water at 100°C to steam at 100°C is called latent heat of steam. Its value is 540 kcal kg^{-1} or 2.27×10^6 J kg^{-1}.

Thermodynamics : Thermodynamics is that branch of physics in which we study the relation of heat energy with chemical energy, electrical energy, light energy etc.

Thermodynamical system : A thermodynamical system is that system, the state of which can be expressed by pressure, volume, temperature etc.

Work done by a Thermodynamical System : The small work done by a thermodynamical system is given by

$$dW = \text{Force} \times \text{displacement}$$

$$dW = F.dx = P.A\,dx = PdV.$$

Now there are two cases :

(*a*) If the pressure is constant, then the work done by the thermodynamical system is

$$W = P(V_2 - V_1)$$

(*b*) If the pressure and volume both are variable, then the work done

$$W = \int_{V_1}^{V_2} PdV = \text{Area between P} - \text{V curve}$$

and volume axis.

First Law of thermodynamics : It states that the amount of heat supplied to a system is equal to the sum of the increase in the initial energy of the system and the external work done, i.e.,

$$\delta Q = dV + \delta W$$

Here heat and work are path dependent functions and hence written as δQ and δW, whereas internal energy is path independent functions and hence written as dV. All these three quantities must be expressed in the same unit, i.e., either in the units of work or in the units of heat.

Isothermal process : A process in which the system is perfectly conducting to the surrounding and the temperature remains constant throughout the process, is called an isothermal process. The gas equation governing isothermal process is ,

$$PV = \text{constant}$$

The expression for the amount of work done during an isothermal expansion of a gas is given by,

$$W = 2.303\, nRT \log_{10}\left(\frac{V_2}{V_1}\right)$$

Adiabatic process : A process in which the working substance is perfectly insulated from the surrounding, i.e., there is no transfer of heat between the working substance and the surroundings, but there is a change in temperature. is called as adiabatic process. The gas equation governing adiabatic process is ,

$$PV^{\gamma} = \text{constant}$$

The expression for the amount of work done during an adiabatic expansion of a gas is given by

$$W = \frac{1}{1-\gamma}(P_2V_2 - P_1V_1) = \frac{R}{\gamma - 1}(T_1 - T_2).$$

Reversible and irreversible processes : A process which can be retraced in the opposite direction so that the system and the surroundings pass through exactly the same states at each stage in the opposite direction as in the direct process, is called as reversible process.

A process which can not be exactly retraced in the opposite direction, i.e., the system and the surroundings do not pass through the same intermediate states as in the direct process, is called as irreversible process.

Heat engine : A heat engine is a device which converts heat energy into mechanical work. Thermal efficiency of a heat engine is defined as the ratio of the net external work done by it during one cycle (i.e., output) to the heat absorbed by it from the source during that cycle (i.e., input). It is denoted by η. Hence,

$$\eta = \frac{\text{output}}{\text{input}}$$

Vander Waal's equation of state :

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

This equation is known as Vander Waal's equation of state, for a gas 'a' and 'b' are known as Vander Waal's constants.

Second law of thermodynamics :

(i) *Kelvin-planck's statement* : According to this statement, it is not possible to get a continuous supply of work by cooling a body to a temperature. lower than that of coldest of its surroundings.

(ii) *Clausius's statement* : According to this statement, it is impossible to make heat flow from a body at a lower temperature to a body at a higher temperature without doing external work on the working substance.

Carnot's reversible engine : Remember that Carnot's engine is an ideal engine and cannot be realised in actual practice. The efficiency of Carnot's engine is given by

$$\eta = \frac{W}{H_1} = 1 - \frac{H_2}{H_1} = 1 - \frac{T_2}{T_1}$$

Where

H_1 = Heat absorbed by the working substance from the source

H_2 = Heat rejected by the working substance to the sink

T_1 = Temperature of the source

T_2 = Temperature of the sink.

It shows that the efficiency of Carnot's reversible engine does not depend upon the nature of working substance but simply depends upon the temperature of the source and sink only.

Carnot's Theorem : According to this theorem, working between the same two temperatures, the efficiency of all reversible engines will be the same, and no engine can be more efficient than Carnot's reversible engine working between the same two temperatures.

Conduction : It is a process in which transfer of heat takes place from one point to another through a substance in the direction of fall of temperature without actual motion of the particles themselves.

The amount of heat flowing ΔQ between two faces in time Δt is given by

$$\Delta Q = KA \frac{\Delta T}{\Delta x} . \Delta t$$

Where A = area of each face

$\frac{\Delta T}{\Delta x}$ = temperature gradient between the two faces.

K = constant of proportionality, called as coefficient of thermal conductivity of the material.

Coefficient of thermal conductivity or simply thermal conductivity of a material is defined as the rate of flow of heat through its unit area per unit temperature gradient.

Its SI unit is $Js^{-1}\ m^{-1}\ K^{-1}$.

Convection : It is a process in which transfer of heat takes from one part of a fluid to another by movement of the fluid itself.

Radiation or Thermal radiation : In this process, transmission of heat occurs when heat energy travels directly from one place (hot) to another place (cold) without heating the intervening medium. Heat radiations are electromagnetic in nature and their speed is equal to the speed of light.

Properties of thermal radiations :

(i) Thermal radiations travel in straight lines.

(ii) It also obeys the law of reflections and refractions as established in case of light.

(iii) It also obeys the inverse square law, i.e., its intensity falls off with distance according to the inverse square law.

(iv) Thermal radiations can be polarised like light.

(v) Heat radiations travel with the velocity of light.

(vi) Heat radiations can travel through vacuum.

(vii) Heat radiation get diffused like light.

Perfectly black body : When a unit quantity of thermal radiations of wavelength λ fall on a body, then

(i) a fraction r_λ is reflected,

(ii) a fraction a_λ is absorbed, and

(iii) a fraction t_λ is transmitted.

Hence, $$r_\lambda + a_\lambda + t_\lambda = 1$$

Where r_λ is called as reflection coefficient, a_λ as absorption coefficient and t_λ as transmission coefficient.

If $r_\lambda = 0$ and $t_\lambda = 0$, then $a_\lambda = 1$ i.e., the body absorbs all the radiations falling on it. Such a body is called as perfectly black body and is an ideal case.

Emissive power of a substance : The emissive power (ℓ) of a surface is the ratio of the amount of heat energy (ℓ_s) radiated by it per unit area per unit time to the amount of heat energy (ℓ_p) radiated by a perfectly black body per unit area per unit time under exactly similar conditions. Hence

$$\ell = \frac{\ell_s}{\ell_b}$$

Absorptive power of a substance : Absorptive power (a) of a substance can be defined as the ratio of the amount of heat energy (a_s) absorbed by it per unit area per unit time to the amount of heat energy (a_b) absorbed by a perfectly black body per unit, area per unit time under exactly similar conditions. Hence,

$$a = \frac{a_s}{a_b}$$

Kirchhoff's law : This law states that the ratio of the emissive power to the absorptive power for the radiations of a particular wavelength and at a particular temperature is the same for all substances and is also equal to the emissive power of a perfectly black body. Hence,

$$\frac{\ell_\lambda}{a_\lambda} = \text{constant} = E_\lambda$$

where, ℓ_λ = emissive power of body

a_λ = absorptive power of the body

E_λ = emissive power of a perfectly black body.

Newton's law of cooling : According to Newton's law of cooling, the rate of loss of heat from a body is directly proportional to the difference of temperature of the body and its surroundings *i.e.*,

$$\frac{-dQ}{dt} \propto (Q - Q_0)$$

$$\text{or } \frac{-dQ}{dt} = K(Q - Q_0)$$

where Q is the temperature. of the body and Q_0 that of its surroundings. This law holds good only when $(Q - Q_0)$ is very small.

Wien's displacement law : According to this law, the product of the wavelength corresponding to which maximum energy is emitted and absolute temperature. of the black body is always constant. It can mathematically be expressed as,

$$\lambda_m T = \text{constant} = b$$

where *b* is known as the Wien's constant. In SI system its value is 2.898×10^{-3} mK.

Stefan's law or Stefan-Boltzmann law : This law can be stated as, the total amount of energy radiated per second per unit area of the surface of a perfectly black body is directly proportional to fourth power of the absolute temperature of the surface of the body. It can mathematically be expressed as,

$$E \propto T^4$$

$$\text{or} \quad E \propto \sigma T^4$$

When σ is known as Stefan's constant. In SI system its value is $5.67 \times 10^{-8}\ Wm^{-2}\ K^{-4}$.

When perfectly black body at temperature. T is placed in an enclosure at temperature. T_0, then heat energy radiated per second per unit area can be expressed as

$$E = \sigma (T^4 - T_0^{\ 4}).$$