

# **THERMAL PHYSICS**

**(16sccPH3)**

(Brief notes for reference)

**BY**

Dr. V. S. Kumar

Assistant Professor

Department of Physics

Swami Dayananda College of Arts and Science

Manjakkudi

Note: This material is helpful for the students those who are in exam point of view only and creates the idea(especially for the students 2016-2021). For more materials students are advised to refer the prescribed text and other references. This material is not enough. Students are instructed to refer book for study and reference respectively for further elaborate points as prescribed by the University.

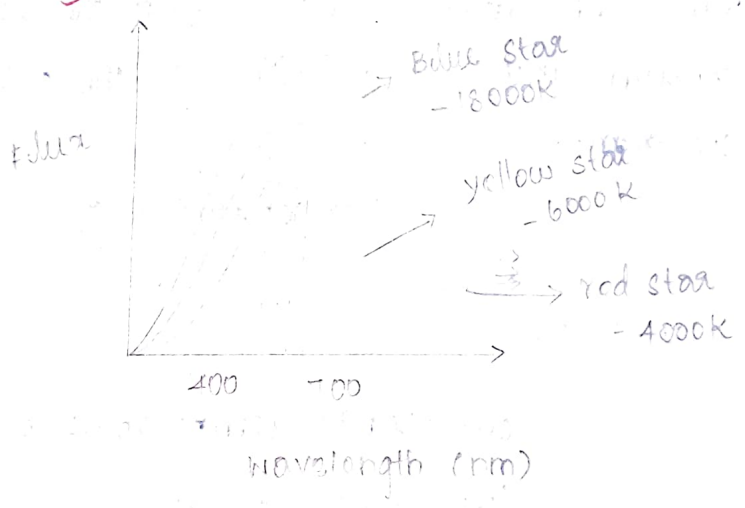
1. Planck's law: 310

In physics, planck's law describes the spectral density of electromagnetic radiation emitted by a blackbody in thermal equilibrium at a given temperature  $T$ , when there is no net flow of matter or energy between the body and its environment.

$$B_{\lambda}(T) = \frac{2hc^2}{\lambda^5} \frac{1}{e^{\frac{hc}{\lambda kT}} - 1}$$

2. Black body radiation: 301

Black - body radiation is the thermal electromagnetic radiation within or surroundings a body in thermodynamic equilibrium with its environment, emitted by a black body.



3. Wien's displacement law: 308

\* From thermodynamic considerations, Wien has shown that the product of the wavelength corresponding to maximum energy  $\lambda_m$  and the absolute temperature  $T$  is constant.

$\lambda_m T = \text{constant}$

\* This constant is called Wien's displacement constant and has a value  $0.2892 \text{ cm} \cdot \text{K}$ . In laboratory, it is evident that when a blackened platinum wire is electrically heated, it becomes dull red at about  $500^\circ\text{C}$ , cherry red at about  $900^\circ\text{C}$ , orange red  $1100^\circ\text{C}$ , yellow at  $1250^\circ\text{C}$  and finally becomes white at  $1600^\circ\text{C}$ . This shows that as the temperature rises, the radiation emitted contains more and more of shorter wavelengths. In other words, as the temperature is raised, the maximum intensity of emission is displaced towards the shorter wavelength side.

\* This is therefore, known as Wien's displacement law.

#### 4. Solar constant :

The solar constant is a flux density measuring mean solar electromagnetic radiation per unit area. It is measured on a surface perpendicular to the rays, one astronomical unit from the sun. The solar constant includes radiation over the entire electromagnetic spectrum.

$$\text{solar constant} = \frac{W}{\text{m}^2}$$

#### 5. Surface temperature of the sun :

Our sun's temperature is about  $6000 \text{ K}$ .

Accurately  $5,778 \text{ K}$

It's Fahrenheit  $9,941^\circ\text{F}$

#### 6. Radiation :

\* Radiation is defined as an energy that travels in the form of waves electromagnetic radiations or high speed particles.



\* Particulate radiation happens when an unstable (radioactive) atom disintegrates.

\* Electromagnetic radiations, on the other hand, has no mass and travels in waves.

\* And has wave like properties

\* Radiation also call electromagnetic waves.

## 7. Principle of Refrigeration:

The refrigeration cycle is also known as Vapour Compression cycle. The cycle operates at two pressures high and low, to produce a continuous cooling effect.

Ex: If you dip your finger in a volatile liquid like gasoline or alcohol and then allowed the liquid to evaporate, you can feel a cooling effect. The same thing will happen with water but will not be as noticeable, as the evaporation process is slower.

## 8. Specific heat capacity:

The amount of heat required to raise the temperature of a substance by one unit

$$C = \frac{Q}{m\Delta T}$$

$Q$  = Heat energy

$m$  = mass

$c$  = specific heat capacity

$\Delta T$  = change in temperature.

## 9. Dulong and Petit's law: 543

Dulong and Petit's in 1819, studied the specific heat of various elements in a solid state and enunciated a

law, called duLong and Petit's law.

## 10. Applications of low temperature:

- \* Low temperature is known as cryogenic from the Greek and meaning "producing cold".
- \* It is achieved by removing the energy from a substance.
- \* It is used to the simplest way to cool a substance is to bring it into contact with another substance.
- \* Ordinary ice, dry ice and liquid air may be used successively to cool a substance down to about  $80^{\circ}\text{K}$ .
- \* Various liquefied gases can be used in this manner to cool a substance to as low as  $4.2^{\circ}\text{K}$ .

## 11. Special cases for the porous plug experiment:

- \* There are three possible cases.
  - i) Below the Boyle temperature,  $P_1 V_1 < P_2 V_2$ .
  - ii) At the Boyle temperature if  $P_1$  is not very high  $P_1 V_1 = P_2 V_2$  and  $P_2 V_2 - P_1 V_1 = 0$ .
  - iii) Above the Boyle temperature  $P_1 V_1 > P_2 V_2$  and  $P_2 V_2 - P_1 V_1$  is -ve.

## 12. Limitations of Einstein's Theory:

- \* Although the values of atomic heats agree well at very high and very low temperature with the experimental curves, but the variation in between them does not exactly follow some elements like Cu, Al, Fe etc.
- \* In Einstein theory, frequency  $\nu$  and  $h\nu/kT$  have been obtained empirically and cannot be verified from any other independent physical data.

Part - A

1. Zeroth law of thermodynamics:

The zeroth law of thermodynamics states that if two systems, A and B are in thermal Equilibrium with a third system C, then A and B are in thermal Equilibrium with each other.

2. Irreversible process:

It is a process that is irreversible. Irreversible process cannot be plotted in a  $p-v$  diagram, because these process cannot have unique values of pressure, temperature at every stage of the process.

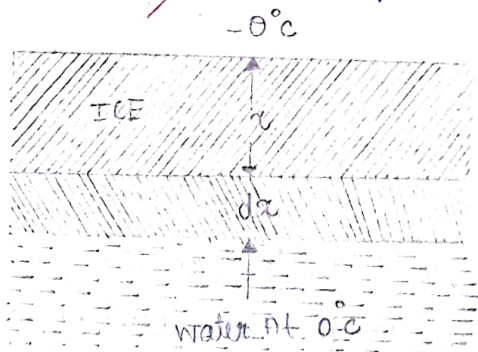
3. Isothermal process:

It is a process in which the temperature remains constant but the pressure and volume of a thermodynamic system will change. The ideal gas Equation is

$$PV = nRT$$

4. Accretion of ice on ponds:

consider a layer of ice  $x$  cm thick on the surface of a pond. Let the temperature of air over the surface of ice be  $- \theta^{\circ}\text{C}$  and that of water below ice  $0^{\circ}\text{C}$ . Suppose a thickness  $dx$  of ice is formed in time  $dt$ .





Mass of ice formed

$$= A \cdot dx \cdot \rho$$

Here  $A$  is the area of the pond,  $\rho$  the density of ice and  $L$  the latent heat of fusion of ice.

Heat lost by water

$$= A \cdot dx \cdot \rho \cdot L \text{ calories} \rightarrow \text{(i)}$$

The heat is conducted across a layer of ice of thickness  $x$  upwards.

$$\text{Heat conducted} = KA \cdot \frac{\theta}{x} dt \text{ calories.}$$

Equating (i) and (ii)

$$KA \frac{\theta}{x} dt = A dx \cdot \rho \cdot L$$

$$\frac{dx}{dt} = \frac{K\theta}{\rho L x}$$

$\frac{dx}{dt}$  represents the rate of growth of the thickness of ice,

$$dt = \left( \frac{\rho \cdot L}{K \cdot \theta} \right) x dx$$

Total time taken by the layer of ice to increase in thickness by  $x$ .

$$\int dt = \frac{\rho L}{K \theta} \int x \cdot dx$$

$$t = \frac{\rho L}{K \theta} \frac{x^2}{2} + \text{constant}$$

When

$$t = 0, x = 0$$

Hence the constant is zero,

$$\therefore t = \frac{\rho L}{2 K \theta} x^2.$$

## 5. Green house effect :

\* The greenhouse effect is a natural process that warms the Earth's surface.

\* When the sun's energy reaches the Earth's

atmosphere, some of it is reflected back to space and some is absorbed and re-radiated by greenhouse gases.

\* The absorbed energy warms the atmosphere and the surface of the earth.

\* The main greenhouse gases:

i) Methane

ii) Chlorofluorocarbon

iii) Carbon oxide

6. Photovoltaic cells:

A solar cell or photovoltaic cell is a solid state electrical device that converts the energy of light directly into electricity by the photovoltaic effect.

Principle: photoelectric effect.

They produce D-c electricity.

7. Dry ice:

Dry ice is the solid form of carbon dioxide ( $\text{CO}_2$ ), a molecule consisting of a single carbon atom bonded to two oxygen atoms. Dry ice is colorless, odorless, and non-flammable, and can lower the pH of a solution when dissolved in water, forming carbonic acid ( $\text{H}_2\text{CO}_3$ ).

8. Second law of thermodynamics:

Clausius statement:

It is impossible to design a device which works on a cycle and produces no other effect other than Heat Transfer from a cold body to hot body.

Kelvin statement:

It is impossible for any system to operate in a thermodynamic cycle and deliver a net amount of energy by work to its surroundings while receiving energy by heat transfer from a single thermal reservoir.

9. Wiedemann - Franz law :

The ratio of the thermal conductivity of the material and the electrical conductivity of the material is directly relative to the temperature.

$$\frac{k}{\sigma} = LT$$

$k$  = Materials conductivity

$\sigma$  = electrical conductivity

$L$  = Lorenz number [ $2.44 \times 10^{-8}$ ]

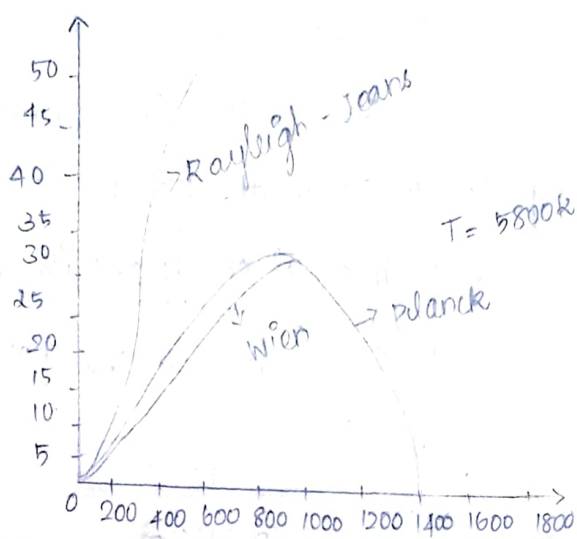
10. Rayleigh - Jean's law :

\* In physics, the Rayleigh - Jeans law is an approximation to the spectral radiance of electromagnetic radiation as a function of wavelength from a blackbody at a given temperature through classical argument.

\* The Rayleigh - Jeans law agrees with experimental results at large wavelengths but strongly disagrees at short wavelengths.

\* The inconsistency between observation and the predictions of classical physics is commonly known as the ultraviolet catastrophe its resolution in 1900 with the derivation by Max Planck of Planck's law, which gives the correct radiation at all frequencies, was a foundational aspect of the development of Quantum Mechanics in the early 20<sup>th</sup> century.





## 11. Joule - Thomson effect :

\* If a gas initially at a constant high pressure is allowed to suffer throttle expansion through the porous plug of silk wool or cotton wool having a number of the fine pores, to a region of constant lower pressure adiabatically, a change of temperature of the gas is observed. This effect is called Joule - Thomson or Joule - Kelvin.

\* Joule in collaboration with William Thomson devised a very sensitive technique known as porous plug experiment and performed number of experiments from 1852 to and established beyond doubt the existence of intermolecular attraction. In this effect, the total heat function.

$$H = U + PV \text{ remains constant.}$$

\* At ordinary temperatures, all gases except hydrogen show cooling effect on passing through the porous plug, but hydrogen shows a heating effect. At sufficiently low temperatures all gases show a cooling effect.

## 12. Entropy :

The expression  $\int_A^B \frac{dq}{T} = \int_{S_A}^{S_B} ds$  is a function of the thermodynamic coordinates of a system. This function is

represented by symbol  $s$  and is called entropy. Hence "entropy of a system is a function of the thermodynamical coordinates defining the state of the system viz., the pressure, volume, temperature or internal energy and its change between two state of equal to  $\int \frac{dq}{T}$  between the states along any reversible path joining them".

### Part - B

#### 1. Mayer's relation:

\* consider  $n$  mole of an ideal gas in a container with volume  $V$ , pressure  $p$  and temperature  $T$ .

\* when the gas is heated at constant volume the temperature increases by  $dT$ .

\* As no work is done by the gas, the heat that flows into the system will increase only the internal energy.

\* Let the change in internal energy be  $du$ .

\* If  $C_V$  is the molar specific heat capacity at constant volume.

$$du = n C_V dT \rightarrow \textcircled{1}$$

\* suppose the gas is heated at constant pressure so that the temperature increases by  $dT$ .

\* If ' $Q$ ' is the heat supplied in this process and ' $dV$ ' the change in volume of the gas.

$$Q = n C_P dT \rightarrow \textcircled{2}$$

\* If  $w$  is the work done by the gas in this process

$$W = PdV \rightarrow \textcircled{3}$$

\* But from the first law of thermodynamics

$$Q = du + W \rightarrow \textcircled{4}$$

From ①, ②, ③, ④ we get

$$\mu C_p dT = \mu C_v dT + PdV \rightarrow \textcircled{5}$$

For mole of ideal gas

$$PV = \mu RT \Rightarrow PdV + RdP = \mu R dT$$

\* Since, the pressure is constant,  $dP = 0$

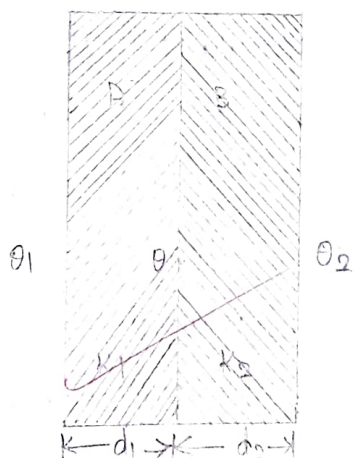
$$\therefore C_p dT = C_v dT + R dT$$

$$\therefore C_p = C_v + R$$

\* This relation is called Meyer's relation.

2. Heat flow through a compound wall :

Consider a compound wall (or a slab) made of two materials A and B of thickness  $d_1$  and  $d_2$ . Let  $k_1$  and  $k_2$  be the coefficients of thermal conductivity of the two materials.  $\theta_1$  and  $\theta_2$  are the temperatures of the end faces ( $\theta_1 > \theta_2$ ) and  $\theta$  is the temperature of the surface in contact. After the steady state is reached, the heat flowing per second ( $Q$ ) across any cross section is the same.



For the material A,

$$Q = \frac{k_1 A (\theta_1 - \theta)}{d_1} \rightarrow \textcircled{1}$$

For the material B,

$$Q = \frac{k_2 A (\theta - \theta_2)}{d_2} \rightarrow \textcircled{2}$$



From eqn ① and ②

$$\frac{K_1 A (\theta_1 - \theta)}{d_1} = \frac{K_2 A (\theta - \theta_2)}{d_2}$$

$$\theta = \frac{\frac{K_1 \theta_1}{d_1} + \frac{K_2 \theta_2}{d_2}}{\frac{K_1}{d_1} + \frac{K_2}{d_2}}$$

Substituting the value of  $\theta$  in equation (i)

$$Q = \frac{A (\theta_1 - \theta_2)}{\frac{d_1}{K_1} + \frac{d_2}{K_2}} \rightarrow \textcircled{3}$$

In general, for any number of walls or slabs,

$$Q = \frac{A (\theta_1 - \theta_2)}{\sum \left( \frac{d}{K} \right)} \rightarrow \textcircled{4}$$

2. Practical Applications of conduction of heat:

\* Metals are good conductors of heat and wood, felt, brick, glass, granite, cotton, wool, cork, ebonite, rubber are bad conductors of heat.

\* Sauce pans, hot water buckets, kettles and other utensils are made of metal. They are provided with wooden or ebonite handles so that heat from the utensil is not conducted to the hand.

\* Ice box has a double wall made of tin or iron. The space between the walls is filled with cork or felt. This is done because cork and felt are poor conductors of heat and prevent the flow of the outside heat into the box.

\* Thick brick walls are used in the construction of a cold storage. Brick is a bad conductor of heat and does not allow outside heat to flow inside the cold storage.

\* Woollen clothes have fine pores filled with air. Air and wool are bad conductors of heat. Heat from the body does not flow outside to the atmosphere. Therefore, woollen clothes keep the body warm in winter.

\* Two shirts keep the body warmer than a single shirt of the same material and double the thickness. Between the two shirts a fine layer of air acts as a bad conductor and does not allow the heat from the body to flow out to the surroundings.

\* quilts and bed coverings filled with cotton are used in winter. The air layers in the pores of the cotton are bad conductors of heat. Therefore, the flow of heat to outside is prevented.

\* A steel blade appears colder than a wooden handle in winter. Steel is a good conductor of heat. As soon as a person touches the blade, heat flows from the hand to the blade. Therefore, it appears colder. Since wood is a bad conductor of heat, heat does not flow from the hand to the handle.

\* In cold countries, the windows are provided with double doors. Air in between the two doors forms a non-conducting layer and does not allow heat to flow from inside to outside. In hot countries also, double door windows are used. Heat does not flow from outside to inside because air forms a non-conducting layer in between the two doors.

\* When a stopper fitted tightly to the bottle is to be removed the neck is gently heated. Glass is a poor conductor of heat. Neck expands but heat is not conducted to the stopper. The stopper can be removed easily.



#### 4\* Einstein's theory of specific heat:

Dulong and Petit's law has been explained by Einstein in 1907 for the first time on the basis of quantum theory of heat radiation. According to quantum theory, heat is radiated in the form of discrete particles called photons. Each particle has an energy equal to  $h\nu$  where  $h$  is Planck's constant and  $\nu$  is the frequency of heat radiation. Einstein proposed his theory under the following assumption.

#### Assumption:

\* A solid is constituted of atoms. At absolute zero of temperature, these atoms are absolute zero under the action of mutual attractions and separation. The energy of the solids in this state is zero. When the temperature is raised.

\* Each atom of solid has 3 degrees of freedom like a monoatomic gas molecule. The mean energy per degree of freedom is not  $KT$ , as given by equipartition law but  $\frac{h\nu}{e^{h\nu/KT} - 1}$  calculated by Planck by using quantum theory. Every atom has 3 degrees of freedom like a monoatomic gas molecule.

\* The mean energy per degree of freedom is not  $KT$ , as given by equipartition but  $\frac{3h\nu}{e^{h\nu/KT} - 1}$ .

\* This energy content of one gram of solid consisting of  $N$  atoms is given by

$$E = \frac{3Nh\nu}{e^{h\nu/KT} - 1}$$

\* Therefore, the atomic heat at constant



volume will be

$$C_v = \frac{dE}{dT} = 3Nh\nu \left[ \frac{-1}{(e^{h\nu/KT} - 1)^2} \right] e^{h\nu/KT} \left( \frac{-h\nu}{KT^2} \right)$$

$$= \frac{3Nh^2\nu^2}{KT^2} \frac{e^{h\nu/KT}}{(e^{h\nu/KT} - 1)^2}$$

$$= 3Nk \frac{e^{h\nu/KT}}{(e^{h\nu/KT} - 1)^2} \left( \frac{h\nu}{KT} \right)^2 \rightarrow \textcircled{1}$$

\* This equation can be conveniently written as

$$C_v = 3R \left[ \frac{e^{\theta/T}}{(e^{\theta/T} - 1)^2} \left( \frac{\theta}{T} \right)^2 \right] \rightarrow \textcircled{2}$$

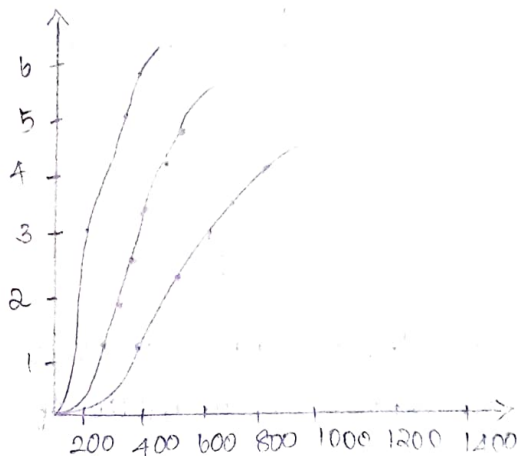
\* Where  $Nk = R$ , gas constant for a gram atom and

$$\theta = \frac{h\nu}{k}$$

\* At high temperatures, the atomic heat approaches the constant value  $3R$ , as given by Dulong and Petit's law.

\* The atomic heat decreases with decreases of temperature and tends to zero at absolute zero of temperature.

\* The experimental curves drawn for atomic heat against temperature show that the curves have the same form of all substance.



## 5. Newton's law from stefan's law :

\* stefan's law is applicable for all temperature of a hot body. But Newton's law is applicable when the difference of temperature between the hot body and the surrounding is small.

\* Consider a hot body at temperature  $T_1$  placed in a uniform temperature enclosure at  $T_2$ .

\* According to stefan's law.

$$R = e\sigma(T_1^4 - T_2^4)$$

\* Here  $e$  is the emissivity of the surface of the hot body.

$$R = e\sigma(T_1 - T_2)(T_1^3 + T_1^2T_2 + T_1T_2^2 + T_2^3)$$

\* As  $(T_1 - T_2)$  is small,  $T_1$  can be taken approximately equal to  $T_2$ .

Then,

$$R = e\sigma(T_1 - T_2)(T_2^3 + T_2^3 + T_2^3 + T_2^3)$$

$$R = 4e\sigma T_2^3 (T_1 - T_2)$$

$$4e\sigma T_2^3 = k$$

$$R = k(T_1 - T_2)$$

$$R \propto (T_1 - T_2)$$

\* This equation represents Newton's law of cooling and is true when the difference of temperature is small.

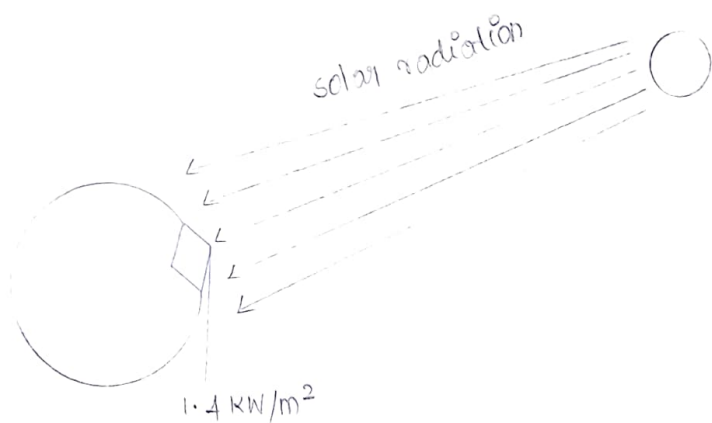
## 6. Sources of solar energy :

\* Solar energy reaches the earth at the rate of about  $1.4 \text{ kW}$  per square metre of surface  $\perp$  to the direction of the sun.

\* By how much does the mass of the sun decrease per second owing to this energy loss? The mean radius of the earth's orbit is  $1.5 \times 10^8 \text{ m}$ .

\* The solar energy reaching the Earth's surface is estimated as ~~under~~ the surface area of a sphere of radius  $r$  is  $A = 4\pi r^2$ .

$$P = \frac{P}{A} A = \frac{P}{A} (4\pi r^2) = (1.4 \times 10^3 \text{ W/m}^2) (4\pi) (1.5 \times 10^8 \text{ m})^2$$



\* Thus, the sun loses  $E_0 = 4.0 \times 10^{26} \text{ J}$  of rest energy per second, which means that the sun's rest mass decreases by

$$m = \frac{E_0}{c^2} = \frac{4.0 \times 10^{26} \text{ J}}{(3.0 \times 10^8 \text{ m/s})^2} = 4.4 \times 10^9 \text{ kg}$$

\* The sun's mass is  $2.0 \times 10^{30} \text{ kg}$ , of each helium nucleus is accompanied by the release of  $4.0 \times 10^7 \text{ J}$  of energy, so  $10^{37}$  helium nuclei are produced in the sun per second.

\* According to solar energy utility system are broadly divided into two categories.

i) Active system

ii) passive system.

\* Both passive and active solar systems can be installed very easily. Neither produces air pollution and both have a very low environment impact to achieve the goal.



1. Lee's disc method for bad conductors:

\* The apparatus consists of a cylindrical steam chamber A, the specimen disc D and brass or copper block C.

\* The whole apparatus is suspended from the stand T<sub>1</sub> and T<sub>2</sub> are the thermometer used to determine the temperature after the steady state is reached.

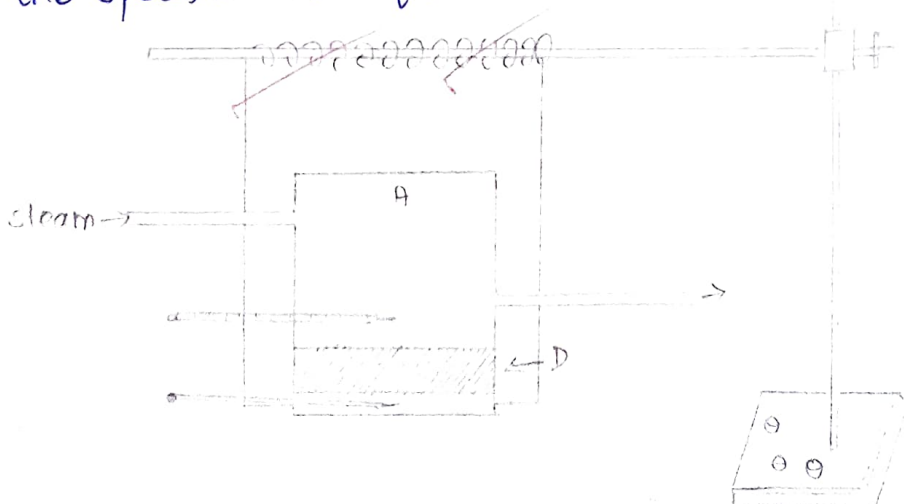
\* Steam is passed through the chamber and the readings of the thermometer T<sub>1</sub> and T<sub>2</sub> are noted.

\* The heat passing through D in one second is equal to the heat radiated by the exposed surface of C in one second.

$$\therefore \frac{KA(\theta_1 - \theta_2)}{d} = ms \frac{d\theta}{dt} \left[ \frac{A+s}{2A+s} \right] \rightarrow \text{①}$$

\* Here,  $\left[ \frac{A+s}{2A+s} \right]$  is the fraction of the total area exposed to the surroundings.

\* Here A is the area of cross-section D and C. S is the area of the curved surface of C,  $\frac{d\theta}{dt}$  is the rate of cooling at temperature  $\theta_2$ , m is the mass and s is the specific heat of C.



$\frac{d\theta}{dt}$ , the disc D is removed and C makes contact with the steam chamber. C is removed when its temperature is about  $10^\circ\text{C}$  higher than  $\theta_2$ .

\* It is placed over two knife edges and temperature is observed after equal intervals of time (say one minute). A graph is drawn between temperature and time. From the graph, the value of  $\frac{d\theta}{dt}$  at temperature  $\theta_2$  is found.

\* From equation (i),  $k$  can be calculated.

2. Forbes' method to find k:

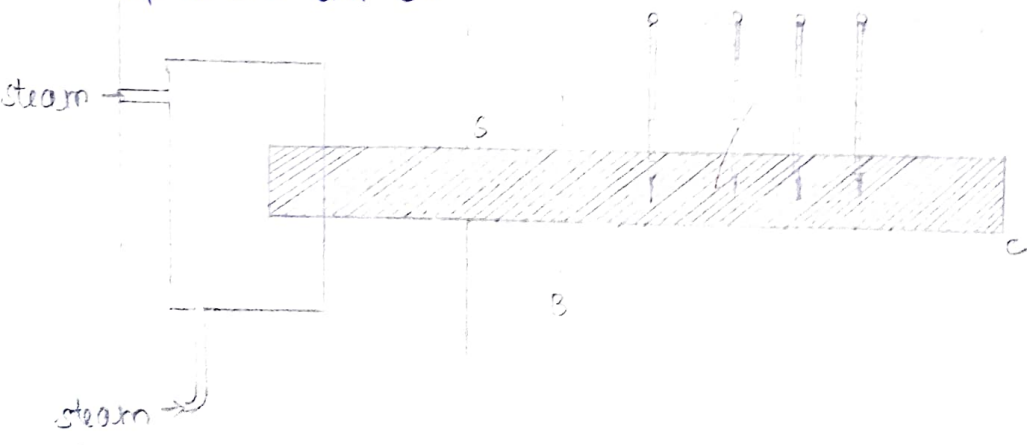
\* Forbes method is used to determine the absolute conductivity of different metals.

\* Consider a long rod of uniform area of cross-section heated at one end.

\* After the steady state is reached, the amount of heat passing per second across the cross-section at the point B =  $KA \left(\frac{d\theta}{dx}\right)_B$ .

\* Here  $\left[\frac{d\theta}{dx}\right]_B$  is the temperature gradient at B.

The amount of heat lost by radiation from the point B up to the end C.



$$= \int_B^C (PA dx) s \frac{d\theta}{dt}$$

$$\therefore KA \left[ \frac{d\theta}{dx} \right]_B = \int_B^C (PA dx) s \frac{d\theta}{dt}$$

$$K = \frac{Ps \int_B^C \frac{d\theta}{dt} dx}{\left[ \frac{d\theta}{dx} \right]_B} \rightarrow \textcircled{1}$$

\* To find  $\int_B^C \frac{d\theta}{dt} dx$  and  $\left[ \frac{d\theta}{dx} \right]_B$  the experiment is divided into two parts.

(i) static Experiment :

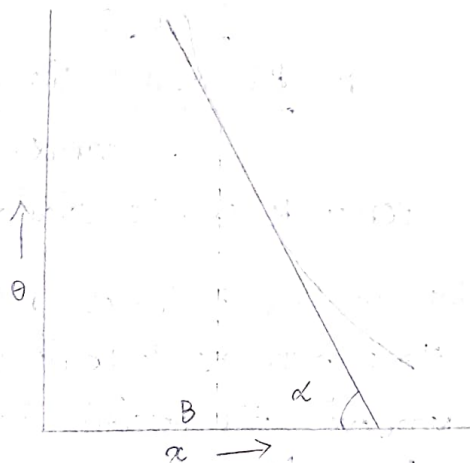
\* A long rod about 2 metres in length is taken and its one end is heated.

\* Forbes heated the rod for about six hours.

\* After the steady state is reached, the thermometers fixed in the rod at various positions are read.

\* A graph is plotted b/w the temperature and the distance ( $x$ ) from the hot end. The graph is an exponential curve. Take the point B and draw a tangent to the curve corresponding to the point B.

\* Here  $\left[ \frac{d\theta}{dx} \right]_B = \tan \alpha$ .

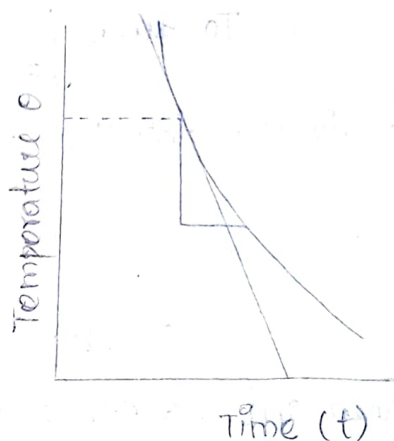
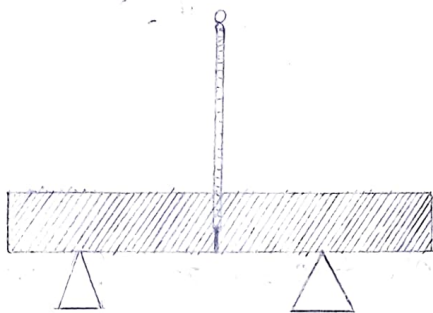




## ii) Dynamic Experiment :

\* The original bar or a small bar of the same material having the same material having the same area of cross-section is heated to the temperature of steam.

\* The bar is exposed to the atmosphere and a thermometer is fixed at its middle portion.



The various value of  $\theta \frac{d\theta}{dt}$  is determined. This is done by drawing tangents to the curve at various points on the curve.

\* The area of the shaded portion =  $\int_B^C \frac{d\theta}{dt} dx$ .

The area is measured with the help of the planimeter or from the graph directly.

$$K = \frac{\rho S \int_B^C \frac{d\theta}{dt} dx}{\left[ \frac{d\theta}{dx} \right]_B}$$

$$K = \frac{\rho S (\text{area of the shaded portion})}{\tan \alpha}$$

Hence  $K$  can be calculated.

\* This method is tedious because it takes a long time and three graph are to be drawn.

\* Moreover the specific heat  $S$  does not remain constant at all temperature.

\* Therefore this experiment is not accurate.

\* But the advantage of this experiment is that the absolute conductivity of the material of the rod can be determined.

### 3. Carnot's Theorem :

Statement :

From the second law of thermodynamics two important results are derived ; these conclusions are taken together to constitute Carnot's theorem which may be stated in the following forms.

Proof :

First Part :

\* To prove the first part of the theorem, we consider two engines R and I working between the temperatures  $T_1$  and  $T_2$  where  $T_1 > T_2$ . Of these two engines R is reversible and I is irreversible.

$$\frac{Q_1' - Q_2'}{Q_1'} > \frac{Q_1 - Q_2}{Q_1}$$

(or)

$$\frac{W}{Q_1'} > \frac{W}{Q_1}$$

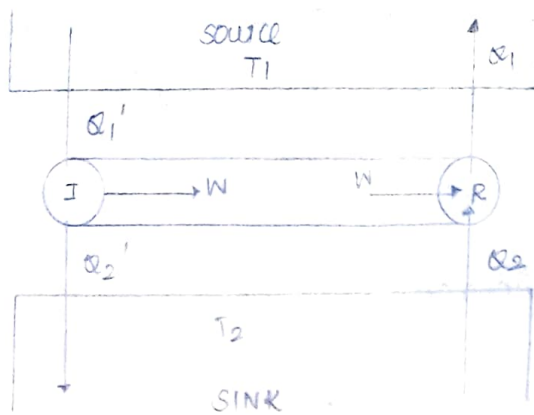
$$Q_1 > Q_1'$$

$$Q_1' - Q_2' = Q_1 - Q_2,$$

$$Q_2 - Q_2' = Q_1 - Q_1'$$

$$Q_1 > Q_1'$$

$$Q_2 > Q_2'$$



\* The net result of the complete cycle of the coupled engines is given by

\* Gain of heat by the source at  $T_1 = Q_1 - Q_1'$

\* Loss of heat by the sink at  $T_2 = Q_2 - Q_2'$

\* External work done on the system = 0.

\* Thus, the coupled engines forming a self-acting machine unaided by any external agency transfer heat continuously from a body at low temperature to a body at a higher temperature.

Second part:

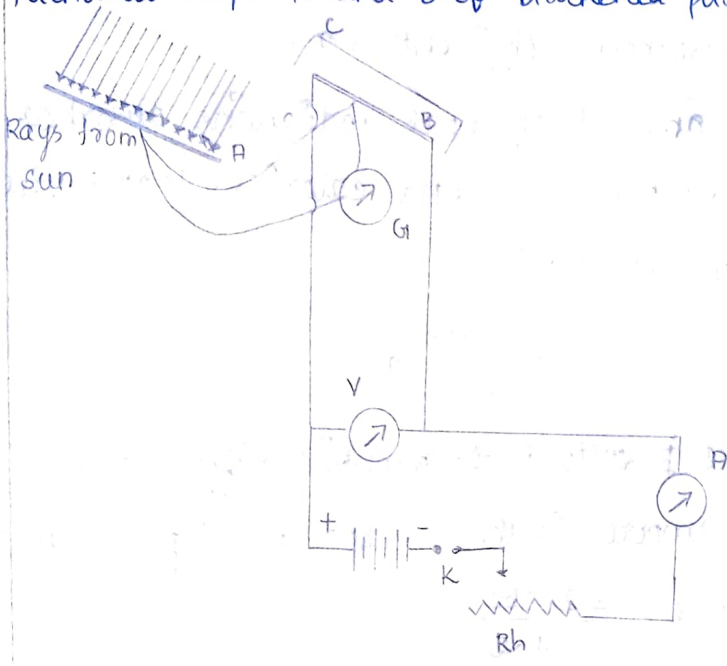
\* The second part of the theorem may be proved by the same arguments as before. Therefore, all reversible engines working between the same two temperatures have the same efficiency.

\* Thus, the efficiency of a perfectly reversible engine depends only on the temperatures between which the engine works, and is independent of the nature of the working substances.



#### 4. Angstrom's pyrheliometer:

\* Pyrheliometer is an instrument which is used to find the amount of incident heat radiations and the solar constant. Angstrom's pyrheliometer consists of two identical strips A and B of blackened platinum foil.



\* The strip A is exposed to the sun and B is shielded by a cover C. A thermocouple having a sensitive galvanometer with A as one junction and B as the other junction is used. The strip B can be heated by an electrical arrangement and suitable current passing through B can be adjusted with the help of a rheostat.

\* When both the strips A and B are shielded from the sun, their junctions are at the same temperature and the galvanometer shows no deflection. The strip A is exposed to the sun and B is kept shielded. The strip A receives heat radiations from the sun and its temperature rises and the galvanometer shows deflection. The strip B is gradually heated by passing current through it and the current is adjusted so that there is no deflection in the galvanometer.

\* It means the strip A and B are again at the same temperature and they are receiving heat energy at the same rate.

\* Let  $H$  calories of heat be incident on one sq cm surface of the strip in one minute. The area of the plate A =  $A$  sq cm and absorption coefficient =  $a$ .

\* The amount of heat radiations absorbed in one minute by the plate A =  $H A a$  calories. Heat produced in one minute in the strip B.

$$= \frac{E I \times 60}{4.2} \text{ cal.}$$

\* Here  $E$  volts is the potential difference across the strip B and  $I$  amperes is the current flowing through it.

$$H A a = \frac{E I \times 60}{4.2}$$

Hence  $H$  can be calculated.

## 5. Clausius - Clapeyron's Equation:

\* The equation  $\frac{dp}{dT} = \frac{L}{T(v_2 - v_1)}$  was first derived by Clapeyron using Carnot's reversible cycle. Therefore, it is sometimes called Clapeyron's equation.

\* Whenever there is a change of state, either from a solid state to liquid state or from liquid state to vapour state, the temperature remains constant; as far as the change takes place. This temperature depends upon the pressure and is a characteristic of each substance. The point vary with pressure and was derived by Clapeyron by applying the second law of thermodynamics.

Derivations :

\* From second thermodynamical relation

$$\left[ \frac{\partial S}{\partial V} \right]_T = \left[ \frac{\partial P}{\partial T} \right]_V$$

(x) both side by T, we have

$$T \left[ \frac{\partial S}{\partial V} \right]_T = T \left[ \frac{\partial P}{\partial T} \right]_V$$

But

$$T \delta S = \delta Q$$

$$\therefore \left[ \frac{\partial Q}{\partial V} \right]_T = T \left[ \frac{\partial P}{\partial T} \right]_V$$

\* The quantity  $\left[ \frac{\partial Q}{\partial V} \right]_T$  represent the quantity of heat absorbed or liberated per unit change in volume at constant temperature, the heat represents the latent heat used when a substance changes from solid to liquid or liquid to vapour state when the temperature remains constant, during the change of state.

\* If  $L$  is the quantity of heat, required to change the state of a unit mass of the substance,  $V_2$  and  $V_1$  the corresponding specific volumes then

$$\delta Q = L \text{ and } \delta V = V_2 - V_1$$

$$\text{Hence } \left[ \frac{\partial Q}{\partial V} \right]_T = \frac{L}{V_2 - V_1}$$

$$\therefore \frac{L}{V_2 - V_1} = T \left( \frac{\partial P}{\partial T} \right)_V$$

$$\textcircled{v} \quad \frac{dP}{dT} = \frac{L}{T(V_2 - V_1)} \quad \text{where } dT \text{ is the change in}$$

Melting point or boiling point due to a change in pressure  $dP$ .  
This is Clausius - Clapeyron latent heat Equation.



## b. Refrigerating Mechanism and AC Mechanism:

### Refrigerating Mechanism

A refrigerator does not cool items by lowering their original temperature. Instead, an evaporating gas called a refrigerant draws heat energy, leaving the surrounding area much colder. Refrigerators and air conditioners both work on the principle of cooling through evaporation.

A refrigerator is basically a heat engine in which work is done on a refrigerant substance so it could collect energy from a cold region; deliver it in a higher temperature region with that cooling the cold region even more. From evaporator coils refrigerant gas goes into compressor and cycle repeats. In the refrigeration cycle, there are five basic components; fluid refrigerant; a compressor, which controls the flow of refrigerant; the condenser coils [on the outside of the fridge] the something called an expansion device the purpose of refrigeration.

### AC Mechanism

The fanance draws air through an evaporator coil, which cools the air. As the refrigerant passes across the coil, the air passes heat from the refrigerant which cause the refrigerant to condense from a gas to a liquid state.

A central air conditioner cool with an outdoor compressor and condenser coil connected to an indoor fanance fitted with an evaporator coil. The refrigerant then passes through an expansion device that converts it to a low-pressure, low-temperature liquid, which return to the indoor coil. And so the cycle goes. AC is the process of removing that heat and moisture from the interior of an occupied space to improve the comfort of occupants. AC can be used in both domestic and commercial environments. Freon gas; we use air conditioning to improve thermal comfort and indoor air quality.

The fundamental reason for having a refrigerator is to keep food cold temperatures help food stay fresh longer. The basic idea behind refrigeration is to slow down the activity of bacteria.

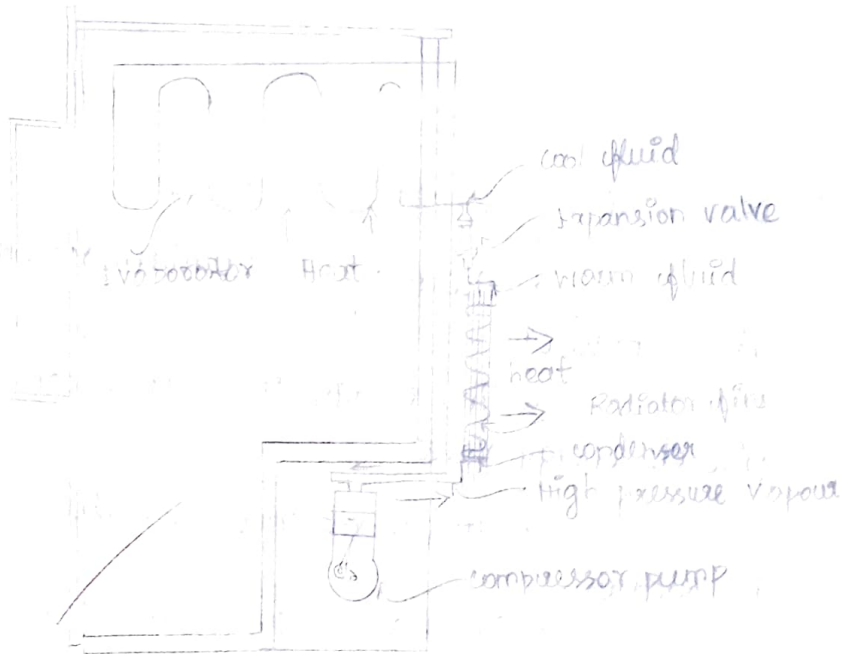
The unit draws in the cold liquid refrigerant, pressurized and condenses it and raises the temperature, turning it into a gas.

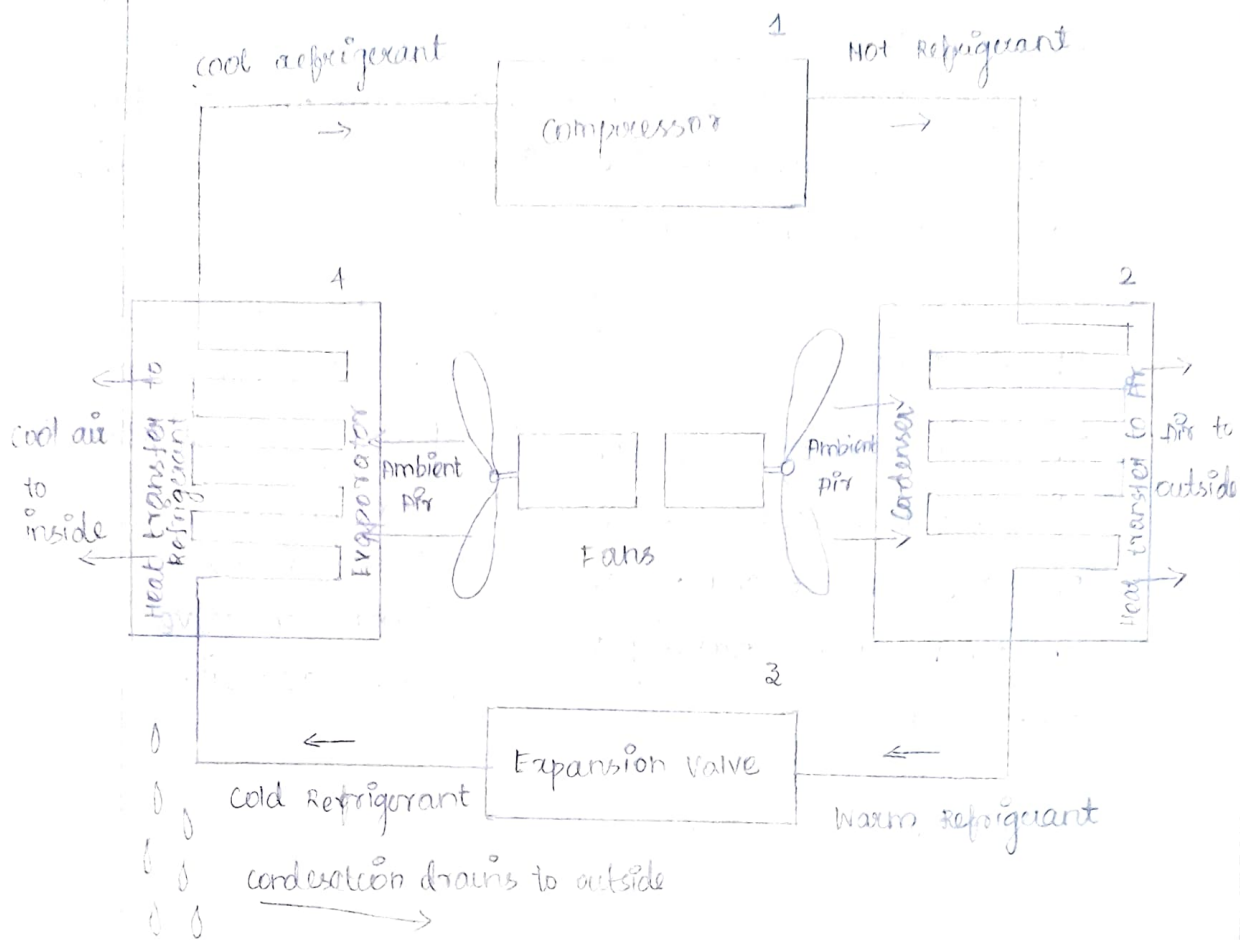
An air conditioner has 5 main parts: The outside unit, called the AC contains a compressor, cooling fins and tubes and a fan.

Refrigerant is a special fluid that is vital to cooling and freezing technology.

- Compressor
- Condenser coil
- Expansion valve
- Evaporator coil.

### Refrigerating Mechanism :





WORKING OF AIR-CONDITIONER

### 7. Debye's theory of specific heat :

- \* According to quantum mechanics if a particle is constrained.
- \* The energy of particle can only have special discrete energy value.
- \* It cannot increase infinitely from one value to another.
- \* It has to go up in steps.
- \* These steps can be so small depending on the system that the energy can be considered as continuous.
- \* This is the case of classical mechanics.
- \* But on atomic scale the energy can only jump by a discrete amount from one value to the another.
- \* In some cases, each particular energy level can be associated with more than one different state.



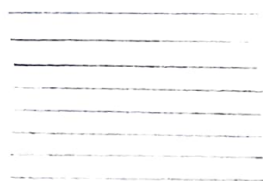
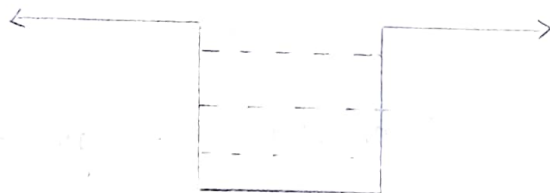
\* This energy level is said to be degenerate.

\* The density of states  $P(E)$  is the no. of discrete states per unit energy interval, and so that the no. of state between  $E$  and  $E+dE$  will be  $P(E)dE$ .

\* There are two sets of waves for solution.

i) Running waves

ii) Standing waves



Definite energy levels



steps get small



energy is continuous



\* These steps can be so small depending on the system that the energy can be considered as continuous.

\* This is the case of classical mechanics.

\* But on atomic scale the energy can only jump by an discrete amount from one value to another.

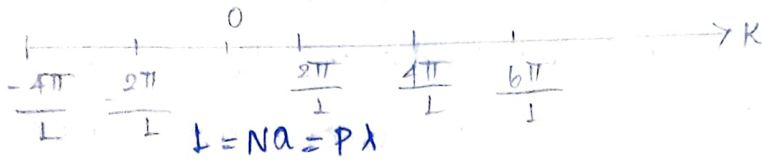
\* In some case, each particular energy level can be associated with more than one different state.

\* This energy level is said to be degenerate

\* The density of states  $P(E)$  is the no. of discrete states per unit energy interval, and so that the no. of state bet.

$$P_R(k) dk = \frac{L}{2\pi} dk.$$

Running waves :



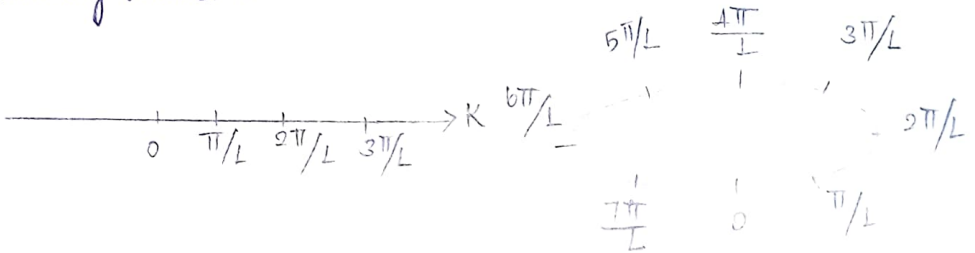
$$\lambda = \frac{Na}{p} = \frac{2\pi}{k}$$

$$k = \frac{2\pi}{Na} p$$

$$k = \frac{2\pi}{L} p$$

$p =$  an integer ;  $L =$  length of the 1D chain

standing waves :



\* In some cases it is more suitable to use standing waves, i.e. chain with fixed ends. Therefore we will have an integral no. of Half wavelength in the chain.

$$k = \frac{2\pi}{L} p \rightarrow \text{for running waves.} \quad k = \frac{\pi}{L} p \rightarrow \text{for standing waves}$$

\* These allowed  $k$ 's are uniformly distributed between  $k$  and  $k+dk$  at the density of  $P_S(k)$ .

$$P_S(k) dk = L/\pi dk \Rightarrow \text{DOS of standing waves.}$$

$$P_R(k) dk = L/2\pi dk \Rightarrow \text{DOS of running waves.}$$

$$dn = P_R(k) dk = g(\omega) d\omega'$$

$$dn = P_S(k) dk = g(\omega) d\omega.$$

\* Choose standing wave to obtain  $g(\omega)$

$$g(\omega) = P_S(k) \frac{dk}{d\omega}$$

$$\omega^2 = \frac{4k}{m} \sin^2 \frac{ka}{2} \Rightarrow \omega = 2\sqrt{\frac{k}{m}} \sin \frac{ka}{2}$$

$$\frac{d\omega}{dk} = \frac{2a}{2} \sqrt{\frac{k}{m}} \cos \frac{ka}{2} \Rightarrow g(\omega) = P_3(k) \frac{1}{a\sqrt{\frac{k}{m}} \cos \frac{ka}{2}}$$

$$g(\omega) = P_3(k) \frac{1}{a} \sqrt{\frac{m}{k}} \frac{1}{\cos(ka/2)}$$

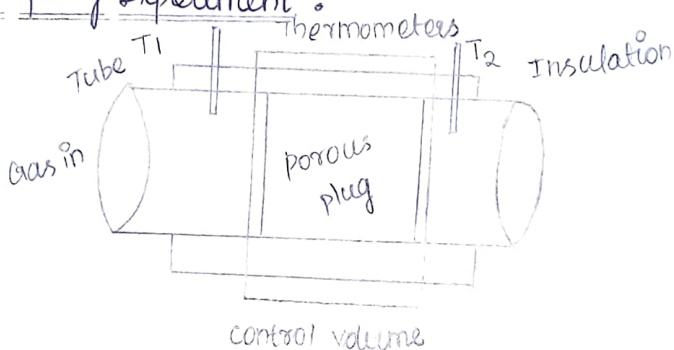
$$\sin^2 \alpha + \cos^2 \alpha = 1 \Rightarrow \cos \alpha = \sqrt{1 - \sin^2 \alpha}$$

$$\cos\left(\frac{ka}{2}\right) = \sqrt{1 - \sin^2\left(\frac{ka}{2}\right)}$$

$$g(\omega) = P_3(k) \frac{1}{a} \frac{2}{\sqrt{4k/m - \frac{4k}{m} \sin^2\left(\frac{ka}{2}\right)}}$$

$$g(\omega) = \frac{4}{\pi} \frac{2}{a} \frac{1}{\sqrt{\omega^2 - \omega^2_{\text{max}}}}$$

### 8. Porous plug Experiment :



\* In this experiment gas is forced through a porous plug and is called a throttling process.

\* In a actual experiment, there are no pistons and there is a continuous flow of gas.

\* A pump is used to maintain the pressure difference between the two sides of the porous plug.

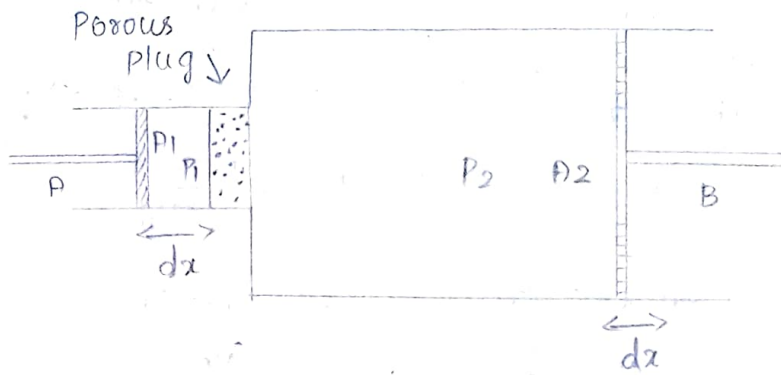
\* In this experiment, as pressures are kept constant work is done.

### Porous plug Experiment :

\* Lord Kelvin along with Joule devised a modified Joule experiment to test Joules law.

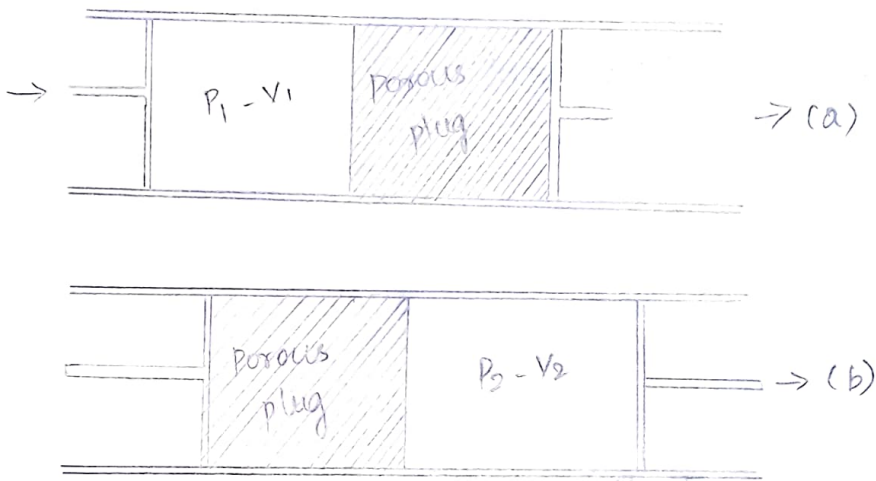
\* This is called porous plug experiment.





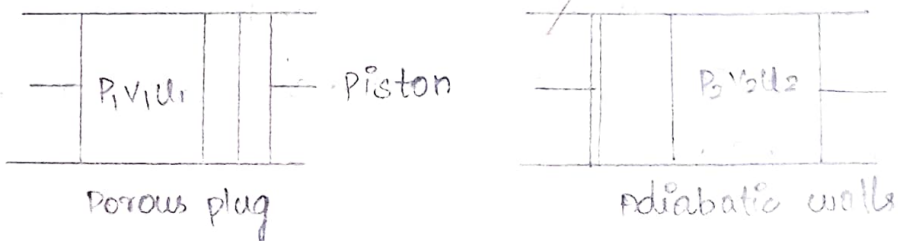
\* Highly compressed gas is being continuously forced at constant pressure through a narrow nozzle or porous plug.

\* The porous plug is cotton or wool etc, having number of fine holes.



Throttling process:

\* A porous plug divides an adiabatic cylinder into two parts and both the parts have adiabatic piston piston up from two ends.



\* In this experiment work is obviously done, the pressure are kept constant

$$W = \int_{V_1}^{V_2} P_1 dV + \int_0^{P_2} P_2 dV = P_2 V_2 - P_1 V_1$$

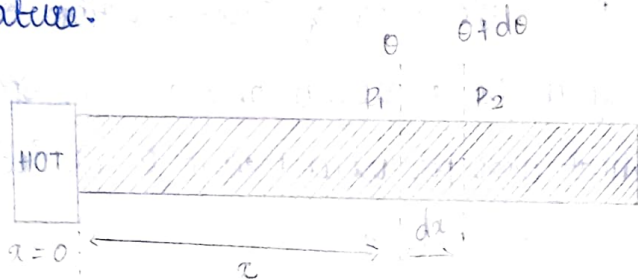
$$dQ = dU + dW \quad 0 = (U_2 - U_1) + (P_2 V_2 - P_1 V_1) \quad \text{or} \quad U_2 + P_2 V_2 = U_1 + P_1 V_1$$

## 9. Rectilinear flow of heat along a bar :

Fourier equation of heat flow :

\* consider a uniform flow area of cross-section which is heated one end. Heat is flowing along the length of the bar. Consider two planes  $P_1 + P_2$  perpendicular to the length of the bar at distances.

\*  $x$  and  $x + \delta x$  from the hot end. The temperature gradient at the plane  $P_1 = \frac{d\theta}{dx}$ . Here  $\theta$  is the excess of temperature of the bar at  $P_1$ . The excess of temperature.



$$\text{at } P_2 = \theta + \frac{d\theta}{dx} \delta x$$

The temperature gradient at  $P_2 = \frac{d}{dx} \left( \theta + \frac{d\theta}{dx} \delta x \right)$

\* Heat flowing through  $P_1$  in one second

$$Q_1 = -KA \frac{d\theta}{dx}$$

\* Heat flowing through  $P_2$  in one second

$$Q_2 = -KA \frac{d}{dx} \left( \theta + \frac{d\theta}{dx} \delta x \right)$$

\* Heat gained per second by the rod between the planes  $P_1 + P_2$ .

$$\begin{aligned} Q &= Q_1 - Q_2 \\ &= KA \frac{d\theta}{dx} + KA \frac{d}{dx} \left( \theta + \frac{d\theta}{dx} \delta x \right) \end{aligned}$$

$$Q = KA \frac{d^2\theta}{dx^2} \delta x.$$

Before the steady state is reached :

\* The quantity of heat  $Q$  is used in two ways before the steady state is reached. partly the heat is used to raise the temperature of the rod and the rest is lost due to radiation. Let the rate of rise of temperature of the bar be  $\frac{d\theta}{dt}$ . The heat used per second to raise the temperature of the rod.

$$= \text{mass} \times \text{specific heat} \times \frac{d\theta}{dt}$$

$$= (A \times \delta x) \rho \times s \frac{d\theta}{dt}$$

\* Where  $A$  is the area of cross-section of the rod,  $\rho$  is the density of the material and  $s$  is the specific heat.

\* The heat lost per second due to radiation

$$= EP \delta x \theta$$

\* Where  $E$  is the emissive power of the surface,  $P$  is the perimeter and  $\theta$  is the average excess of temperature of the bar between the planes  $P_1$  and  $P_2$ .

$$Q = A \delta x \rho \times s \frac{d\theta}{dt} + EP \cdot \delta x \cdot \theta$$

$$KA \frac{d^2\theta}{dx^2} \delta x = A \delta x \rho s \frac{d\theta}{dt} + EP \delta x \theta$$

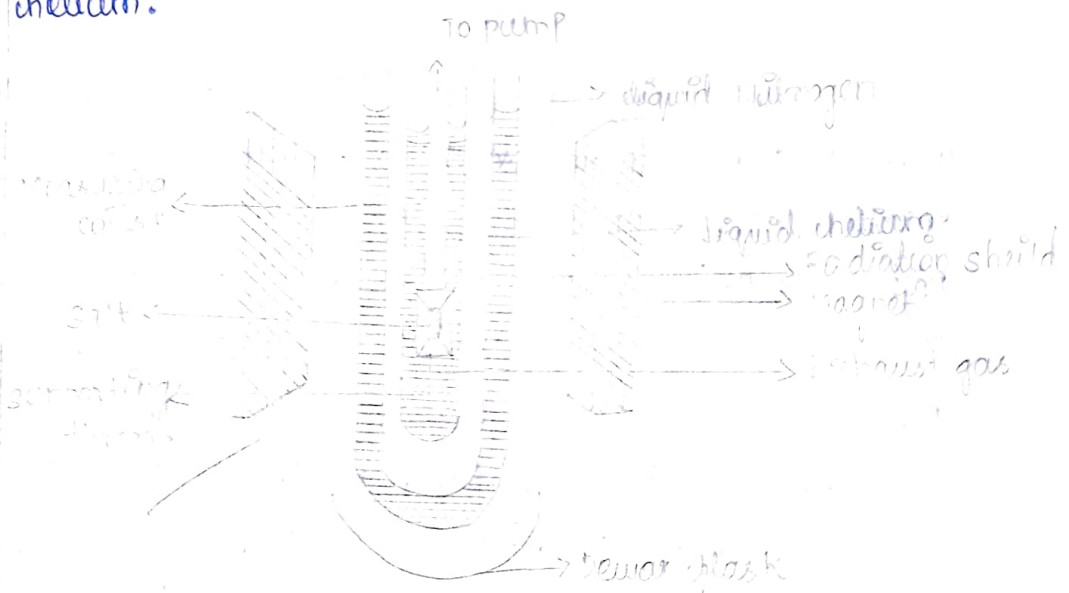
$$\frac{d^2\theta}{dx^2} = \frac{\rho s}{K} \cdot \frac{d\theta}{dt} + \frac{EP}{KA} \theta$$

\* This is the general equation that represent the rectilinear flow of heat along a bar of uniform area of cross-section and is known as Fourier's differential Equations.



## 10. Adiabatic Demagnetisation:

- \* Debye, CIAUQUE, MacDougall.
- \* Below 1K with help of gadolinium sulphate - low temperature was produced.
- \* <sup>Haas and</sup> Kramer - magnetic balance with paramagnetic substance found that - 1K and co gives low temperature pressure.
- \* Next the salt is exposed to a strong magnetic field of about approx - 25000 gauss - Heat produced due to magnetization of the salt is transferred to the liquid helium without causing an increase in rate temperature.
- \* with the magnetic field still present, the inner chamber containing the salt is evacuated of gaseous helium.



\* Finally the magnetic field is removed. The molecules misalign themselves, which requires energy.

\* This energy is obtained by the salt getting cooler in the process.

\* Repetition of the process lowers down the temperature of the salt. Temperature as low as 0.0001K have been achieved so far.

\* Salt is hung dry on fine nylon thread inside the salt tube such that it does not touch the sides.

\* In the neighborhood of absolute zero, all ordinary methods of temperature measure fail.

\* Curie's law gives the most convenient method for measurement of at low temperature.

$y = c/T$   
\* Where  $y$  is the magnetic susceptibility of the salt.  
 $T$  is the absolute temperature.  
 $c$  is the Curie's constant.

\* The fundamental features of all cooling process are that the lower the temperatures achieved, the harder it is to go still lower.

## 11. Maxwell's Thermodynamical relations:

\* From the first & second law of thermodynamics, Maxwell was able to derive six fundamental thermodynamical relations. The state of a system can be specified by any pair of quantities viz. pressure ( $P$ ), volume ( $V$ ), temperature ( $T$ ) and entropy ( $S$ ). In solving any thermodynamical problem, the most suitable pair is chosen and the quantities constituting the pair are taken as independent variables.

\* From the first law of thermodynamics,

$$\delta Q = du + \delta W$$

$$\delta Q = du + p dv$$

$$dv = \delta Q - p dv$$

(or)

For the second law of thermodynamics,

$$ds = \frac{\delta Q}{T}$$

$$\delta Q = T ds \rightarrow \text{①}$$

(or)

sub this value of  $\delta Q$ , we get

$$du = Tds - pdv$$

considering  $u, s$  and  $v$  to be function of two independent variables  $x$  and  $y$

$$du = \left[ \frac{\partial u}{\partial x} \right]_y dx + \left[ \frac{\partial u}{\partial y} \right]_x dy$$

$$ds = \left[ \frac{\partial s}{\partial x} \right]_y dx + \left[ \frac{\partial s}{\partial y} \right]_x dy$$

$$dv = \left[ \frac{\partial v}{\partial x} \right]_y dx + \left[ \frac{\partial v}{\partial y} \right]_x dy$$

$$\begin{aligned} \left[ \frac{\partial u}{\partial x} \right]_y dx + \left[ \frac{\partial u}{\partial y} \right]_x dy &= T \left[ \left( \frac{\partial s}{\partial x} \right)_y dx + \left( \frac{\partial s}{\partial y} \right)_x dy \right] - \\ &\quad P \left[ \left( \frac{\partial v}{\partial x} \right)_y dx + \left( \frac{\partial v}{\partial y} \right)_x dy \right] \\ &= \left[ T \left( \frac{\partial s}{\partial x} \right)_y - P \left( \frac{\partial v}{\partial x} \right)_y \right] dx + \left[ T \left( \frac{\partial s}{\partial y} \right)_x - P \left( \frac{\partial v}{\partial y} \right)_x \right] dy \end{aligned}$$

comparing the co-efficient of  $dx$  and  $dy$ , we get.

$$\left( \frac{\partial u}{\partial x} \right)_y = T \left( \frac{\partial s}{\partial x} \right)_y - P \left( \frac{\partial v}{\partial x} \right)_y \rightarrow \textcircled{2}$$

$$\left( \frac{\partial u}{\partial y} \right)_x = T \left( \frac{\partial s}{\partial y} \right)_x - P \left( \frac{\partial v}{\partial y} \right)_x \rightarrow \textcircled{3}$$

Diff equation  $\textcircled{2}$  with respect to  $y$  and equation  $\textcircled{3}$  with respect to  $x$ ,

$$\frac{\partial^2 u}{\partial y \partial x} = \left( \frac{\partial T}{\partial y} \right)_x \left( \frac{\partial s}{\partial x} \right)_y + \frac{T \partial^2 s}{\partial y \partial x} - \left( \frac{\partial P}{\partial y} \right)_x \left( \frac{\partial v}{\partial x} \right)_y - P \frac{\partial^2 v}{\partial x \partial y}$$

and

$$\frac{\partial^2 u}{\partial x \partial y} = \left( \frac{\partial T}{\partial x} \right)_y \left( \frac{\partial s}{\partial y} \right)_x + \frac{T \partial^2 s}{\partial x \partial y} - \left( \frac{\partial P}{\partial x} \right)_y \left( \frac{\partial v}{\partial y} \right)_x - P \frac{\partial^2 v}{\partial x \partial y}$$

The change in internal energy brought about by changing  $v$  and  $T$ , whether  $v$  is changed by  $dv$  first and  $T$  by  $dT$  later or vice versa is the same.



It means  $du$  is a perfect differential

$$\therefore \frac{\delta^2 u}{\delta y \delta x} = \frac{\delta^2 u}{\delta x \delta y} \text{ and}$$

$$\begin{aligned} & \left(\frac{\delta T}{\delta y}\right)_x \left(\frac{\delta s}{\delta x}\right)_y + T \frac{\delta^2 x}{\delta y \delta x} - \left(\frac{\delta P}{\delta y}\right)_x \left(\frac{\delta v}{\delta x}\right)_y - P \left(\frac{\delta^2 v}{\delta y \delta x}\right) \\ &= \left(\frac{\delta T}{\delta x}\right)_y \left(\frac{\delta s}{\delta y}\right)_x + T \frac{\delta^2 s}{\delta x \delta y} - \left(\frac{\delta P}{\delta x}\right)_y \left(\frac{\delta v}{\delta y}\right)_x - P \frac{\delta^2 v}{\delta y \delta x} \end{aligned}$$

since  $ds$  and  $dv$  are also perfect diff, we have

$$\frac{\delta^2 s}{\delta x \delta y} = \frac{\delta^2 s}{\delta y \delta x} \text{ and } \frac{\delta v}{\delta x \delta y} = \frac{\delta v}{\delta y \delta x}$$

$$\begin{aligned} \left(\frac{\delta T}{\delta y}\right)_x \left(\frac{\delta s}{\delta x}\right)_y - \left(\frac{\delta P}{\delta y}\right)_x \left(\frac{\delta v}{\delta x}\right)_y &= \left(\frac{\delta T}{\delta x}\right)_y \left(\frac{\delta s}{\delta y}\right)_x - \\ &\left(\frac{\delta v}{\delta y}\right)_x \rightarrow \textcircled{5} \end{aligned}$$

This is the general expression for Maxwell's thermodynamical relations. In place of the independent variables  $x$  and  $y$ , any two of the four variables  $s, T, P$  and  $v$  can be substituted so that there may be one mechanical variable ( $P$  or  $v$ ) and one thermal variable ( $s$  or  $T$ ). Thus, there may be four sets of possible sub ( $s, v$ ) ( $T, v$ ) ( $s, P$ ) and ( $T, P$ ) providing the four Maxwell's thermodynamical relations.

First relation:

Put  $x = s$  and  $y = v$  in eqn  $\textcircled{5}$

$$\frac{\delta s}{\delta x} = 1, \frac{\delta v}{\delta y} = 1$$

and

$$\frac{\delta s}{\delta y} = 0, \frac{\delta v}{\delta x} = 0$$

sub in eqn  $\textcircled{5}$ , we get

$$\left(\frac{\delta T}{\delta y}\right)_x = - \left(\frac{\delta P}{\delta x}\right)_y$$

But  $\delta y = \delta v$  (as  $y = v$ ) and  $\delta s = \delta s$  (as  $x = s$ ). Hence

$$\left(\frac{\delta T}{\delta V}\right)_S = -\left(\frac{\delta P}{\delta S}\right)_V$$

This is Maxwell's first thermodynamical relations.

Second Relation:

Put  $x = T$  and  $y = V$  in eqn ⑤

$$\text{Then, } \frac{\delta T}{\delta x} = 1, \frac{\delta V}{\delta y} = 1$$

$$\text{and } \frac{\delta T}{\delta y} = 0, \frac{\delta V}{\delta x} = 0$$

$$\text{sub ⑤ we get } \left(\frac{\delta S}{\delta V}\right)_T = \left(\frac{\delta P}{\delta T}\right)_V$$

This is the Maxwell's second thermodynamical relations.

Third relation:

Put  $x = S$  and  $y = P$ , in eqn ⑤ then

$$\frac{\delta S}{\delta x} = 1, \frac{\delta P}{\delta y} = 1, \frac{\delta S}{\delta y} = 0, \frac{\delta P}{\delta x} = 0$$

sub these in eqn ⑤, we get

$$\left(\frac{\delta T}{\delta P}\right)_S = \left(\frac{\delta V}{\delta S}\right)_P$$

This is the Maxwell's third thermodynamical relations.

Fourth relation:

Put  $x = T$  and  $y = P$ , then eqn ⑤ gives

$$\frac{\delta T}{\delta x} = 1, \frac{\delta P}{\delta y} = 1, \frac{\delta T}{\delta y} = 0 \text{ and } \frac{\delta P}{\delta x} = 0$$

sub these values the eqn ⑤, we get

$$\left(\frac{\delta S}{\delta P}\right)_T = -\left(\frac{\delta V}{\delta T}\right)_P$$

This is Maxwell's fourth thermodynamical relation.

Fifth relation:

put  $x = P$  and  $y = V$

$$\frac{\delta P}{\delta x} = 1, \frac{\delta V}{\delta y} = 1, \frac{\delta P}{\delta y} = 0 \text{ and } \frac{\delta V}{\delta x} = 0$$

sub these values in eqn ⑤, we get

$$\left(\frac{\delta T}{\delta P}\right)_V \left(\frac{\delta S}{\delta V}\right)_P - \left(\frac{\delta T}{\delta V}\right)_P \left(\frac{\delta S}{\delta P}\right)_V = 1$$

sixth relation:

put  $x = T$  and  $y = S$

$$\frac{\delta T}{\delta x} = 1, \frac{\delta S}{\delta y} = 1, \frac{\delta T}{\delta y} = 0 \text{ and } \frac{\delta S}{\delta x} = 0$$

sub in eqn ⑤ we get

$$\left(\frac{\delta P}{\delta T}\right)_S \left(\frac{\delta V}{\delta S}\right)_P - \left(\frac{\delta P}{\delta S}\right)_T \left(\frac{\delta V}{\delta T}\right)_S = 1$$

out of these six thermodynamics relations, the one suited for a particular problem is used and the problem is solved.