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SCHOOL OF SCIENCE AND HUMANITIES

DEPARTMENT OF PHYSICS

Thermal Physics– SPH1211

I. Thermometry and Calorimetry

Thermometry

- The branch of physics dealing with the measurement of temperature.
- The Science of the construction and use of thermometers.

What is meant by temperature?

Temperature is a measure of hotness or coldness of a substance.

It is also defined as a measure of the amount of kinetic energy, possessed by the particles.

SI unit of temperature is the Kelvin (K)

What is the everyday practical scale of temperature?

The Celsius Scale

The difference between heat and temperature.

S. No	Heat	Temperature
1	Heat is a form of energy	Temperature is a thermal condition of a body
2	It flows from one body to other	It a quantity that indicates whether the body is hot or not and in which direction heat will flow
3	It is a total amount of internal energy of a body	It is proportional to average kinetic energy of the molecules of a body
4	In the transmission of heat total amount of heat remain unchanged	In the transmission of heat total amount of heat, temperature does not remain same
5	It is a cause	It is an effect
6	SI unit of heat is Joule(J)	SI unit of temperature is the Kelvin(K)

Internal Energy:

- In a solid, the molecules are bonded to each other and cannot move about freely.
- They can however vibrate. The higher the temperature the greater its vibration.
- The energy possessed by the body due to the random vibration of its molecule is called **Internal Energy**.

- The higher the temperature of the body the greater the vibration of its molecules is and hence greater its internal energy.

Principles of Thermometry

- The physical properties which are used to measure the temperature is known to be thermometric properties
- Any property of a material which changes with temperature can be used to indicate or measure temperature.

For example,

- Pressure (e.g. constant volume gas thermometer)
- Volume (e.g. constant pressure thermometer)
- Resistance (e.g. thermistor)
- Thermal expansion coefficient (e.g. bi-metallic strips)
- Coefficient of liquid expansion (e.g. Mercury based thermometer i.e., Clinical thermometer which is used by doctors.)

A pyrometer in which high temperatures are judged by comparing the colour of a hot object with a reference colour scale.

Selection of thermometer

- Does the thermometer work over the **range** of temperatures required?
- Is the thermometer **sensitive** enough (Can it detect small enough changes of temperature)
- How quickly does the thermometer **respond**?
- How small, portable and convenient is the thermometer?
- Can the thermometer give **continuous** reading and be connected to an electrically operated chart-recorder or warning device
- How **expensive** is it?

Upper & Lower Fixed Points

- Temperature at **melting point** and at the **boiling point** is called the lower and upper fixed point.
- On the Celsius scale the lower fixed point is the temperature of melting pure ice, also known as the **ice point.** The ice point is fixed at 0 ^{o}C.
- The upper fixed point is the temperature of the steam just above boiling water and is known as the **steam point.**

- The steam point is 100 ^{o}C. We can then divide the temperature range between the two fixed points into number of equal parts called degrees.

  Absolute zero is the lowest temperature possible, it is -273 ^{o}C or 0 K (kelvin).
- On the Kelvin scale or the absolute scale, one division is called the Kelvin and is exactly equal to one division or degree on the Celsius scale.
- To convert degree Celcius to Kelvin, use the following equation

Kelvin = degree Celcius + 273

Sensitivity of Thermometers

A thermometer is sensitive if it can detect **small changes** in temperature. **Wide range** of temperatures can be measured.

For Example:

A clinical thermometer has a range of 35^{o}C to 42^{o}C that is suitable for measuring human temperature. It's fine tube give 1/5 or 1/10 degree sensitivity, making it easy to detect small changes in temperature.

Types of thermometers

Common types of thermometers are

- Medical thermometers,
- Infrared thermometers,
- Mercury thermometers,
- Thermocouple thermometers,
- Laboratory thermometers, Bimetallic strip thermometers,
- Pyrometers, etc.

Types of Thermometers on the basis of Technology

Nowadays, there are many different types of thermometers, namely

- Mercury thermometers
- Alcohol in glass thermometers
- Constant pressure gas thermometers
- Constant volume thermometers
- Platinum Resistance Thermometer (PRT)
- Thermistor
- Thermocouple
- Radiation thermometer etc

Why mercury used in thermometers instead of water?

Mercury is used mostly in thermometers because of the following properties:

- It is visible.
- It has a low freezing point (-39 °C).
- It has a very high boiling point (357 °C).
- It expands linearly.
- It gives accurate measurements.
- It is a good conductor of heat.
- Fast response time.
- It has a wide range of temperatures.

Why water cannot be a thermometric liquid?

- Its thermal expansion is not very large compared to other liquids like mercury.
- Its thermal expansion is not as linear as other liquids available.
- Its range of temperatures where it is liquid is very small.
- When it freezes, it expands a lot, breaking the container it is confined in.

Thermistor

- A thermistor is a type of resistor used to measure temperature changes, relying on the change in its resistance with changing temperature. Thermistor is a combination of the words thermal and resistor.
- Coined from the words “THERmally controlled resISTOR”, thermistor is a temperature controlled resistor.
- It is made of metallic oxides, pressed into a bead, disk, or cylindrical shape and then encapsulated with an impermeable material such as epoxy or glass.

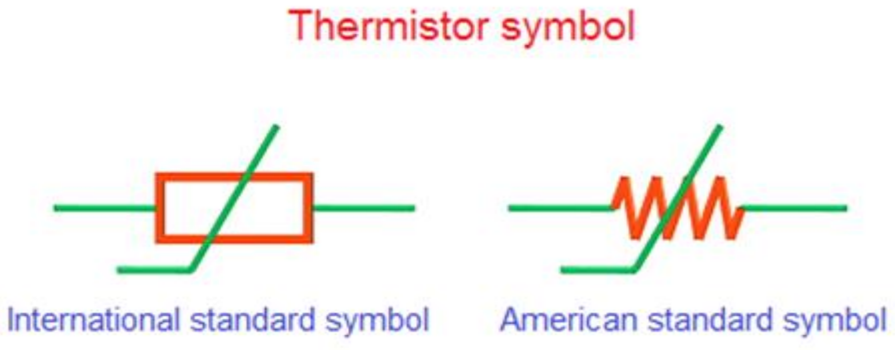


Fig. 1 Thermistor

Types of thermistors

Thermistors are classified into two types based on how they behave with the change in temperature:

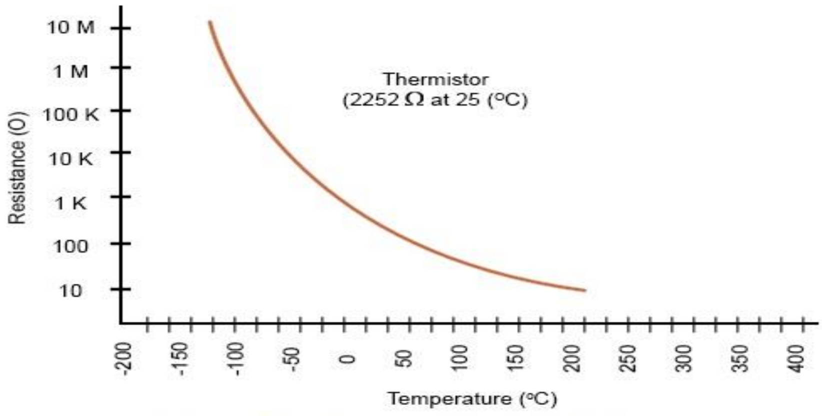
- Negative Temperature Co-efficient (NTC) thermistors
- Positive Temperature Co-efficient (PTC) thermistors

- Negative Temperature Co-efficient (NTC) thermistors

The resistance of the NTC (Negative Temperature Co-efficient) thermistors decreases with increasing temperature. In other words, the electric current flow through the NTC (Negative Temperature Co-efficient) thermistors increases with the increase in temperature.

Most of the NTC thermistors are made from a pressed disc, rod or cast chip of semiconductor material such as sintered metal oxides.

In NTC thermistors, charge carriers are generated by doping process. Because of this doping process, a large number of charge carriers are generated.



Thermistor Characteristic NTC Curve

www.CircuitsToday.com

Fig. 2. NTC Curve

If the temperature is slightly increased, a large number of charge carriers (free electrons) collides with the valence electrons of other atoms and provides them sufficient energy. The valence electrons which gains sufficient energy will breaks the bonding with the parent atom and moves freely from one place to another place. The electrons that move freely from one place to another place are called free electrons. These electrons carry the electric current while moving from one place to another place. The valence electron, which becomes a free electron will again collide with the other valence electrons and makes them free.

Likewise, a small increase in temperature produces millions of free electrons. More free electrons or charge carriers means more electric current. Thus, a small increase in temperature will rapidly decrease the resistance of NTC thermistor and allows a large amount of electric current.

- Positive Temperature Co-efficient (PTC) thermistors

The resistance of Positive Temperature Co-efficient (PTC) thermistors increases with increase in temperature. Most of the Positive Temperature Co-efficient (PTC) thermistors are made from doped polycrystalline ceramic. Thermistors with Positive Temperature Co-efficient (PTC) are also called posistors.

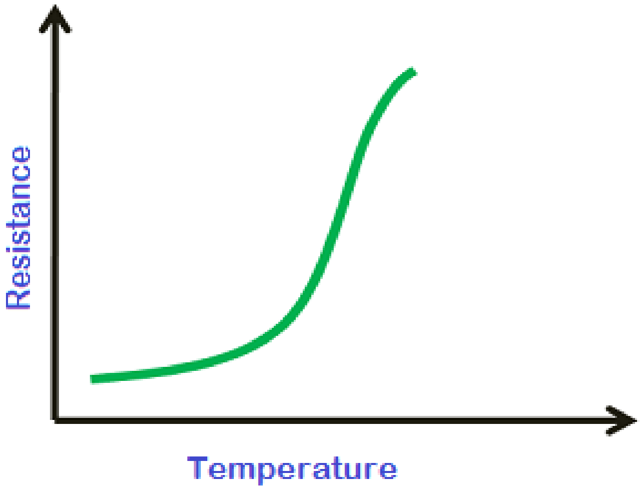


Fig. 3. PTC Curve

History of thermistors

The first NTC (Negative Temperature Co-efficient) thermistor was discovered by Michael Faraday in1833. Michael Faraday observed that the resistance of silver sulfide decreased rapidly when the temperature is increased.

Advantages and disadvantages of thermistors

Advantages of thermistors

- The resistance of thermistors changes rapidly with small change in temperature.
- Low cost
- Small size
- It is easy to carry thermistors from one place to another place.

Disadvantages of thermistors

- Thermistors are not suitable over a wide operating range
- The resistance versus temperature characteristics is non-linear.

Applications of thermistors

- Thermistors are used in medical equipments
- Thermistors are used in hot ends of 3d printers.
- Thermistors are used in home appliances such as ovens, hair dryers, toasters, refrigerators, etc.
- Modern coffee makers use thermistors to accurately measure and control water temperature.
- Thermistors are used in computers.
- Thermistors are used as temperature sensors.
- Thermistors are used as inrush current limiter.

Temperature coefficient of resistance

- Thermistor materials have a temperature coefficient of resistance (α) given by

$$\boldsymbol{\alpha = \Delta R / R_s (1/ \Delta T)}$$

where, Δ**R** is the change in resistance due to a temperature change ΔT

R_S *is* the material resistance at the reference temperature

Platinum Resistance Thermometer

Definition: The platinum thermal resistance (PTR) uses platinum for determining the temperature. It works on the principle that the resistance of platinum changes with the change of temperature. The thermometer measures the temperature over the range of 200°C to1200°C. The platinum is an unreactive metal and can easily be drawn into fine wires. Because of these properties of platinum, it is used as a sensing element in thermometer.

How Platinum Resistance Thermometer Works?

The resistance of platinum increases linearly with the temperature, and this property of the metal is used for measuring the temperature. The resistance of the platinum is measured by passing the alternating or direct current through it. Because of the current, the voltage induces across the metal which measures through the voltmeter. The reading of voltage is converted into the temperature with the help of the calibration equation.

Construction of Platinum Resistance Thermometer

The figure 4 below shows the platinum resistance thermometer. The platinum sensing coil is enclosed inside a bulb which is either made of glass or Pyrex. The insulator deposit on the surface of the glass tube is also used for sensing the temperature.

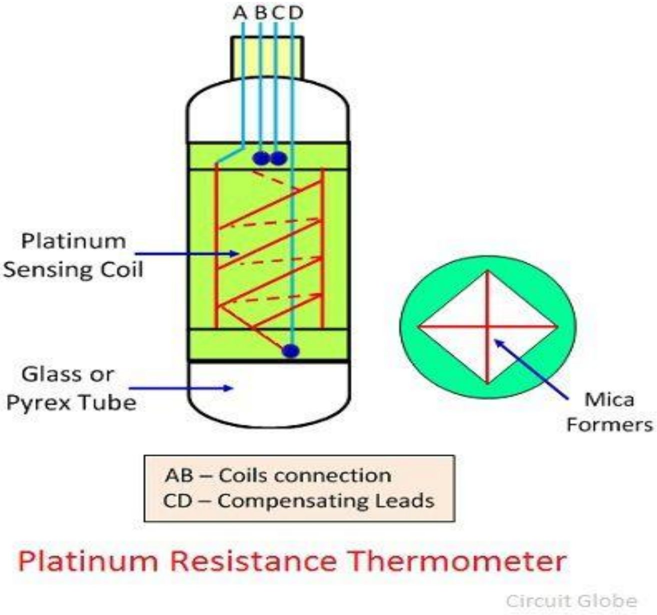


Fig. 4. Platinum resistance Thermometer

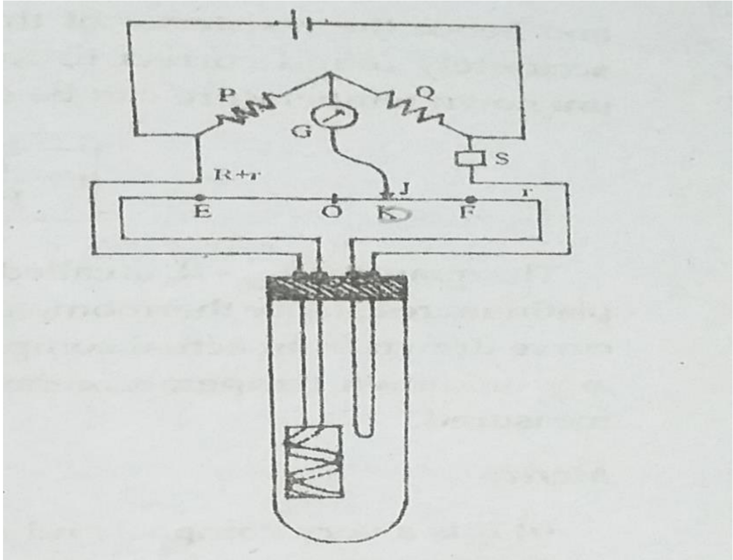


Fig. 5. Circuit diagram of PRT

In this PTR, the double wire of the platinum is wound on the strip of the mica. Here the double wires are used for reducing the inductive effect. The mica is used as an insulator, and it is placed at the ends of the tube.

The Ebonite cap is placed at the open end of the tube. The terminals of the copper wire are joined together with the help of the thick copper lead. The other ends of the copper leads are joined to the terminal AB fitted in the Ebonite cap. For reducing the effect of copper wire resistance on the thermometer, the two similar copper wires are connected to the upper-end terminals called CD. These wires are called the compensating lead.

The industrial type thermometer is shown in the figure 6 below. The platinum wire is protected by the stainless steel tube or by the glass coating. Glass or ceramic seal are the sensing elements. The sealing has two advantages. They provide the strength to the thermometer and protect the sensing element against the chemical reaction.

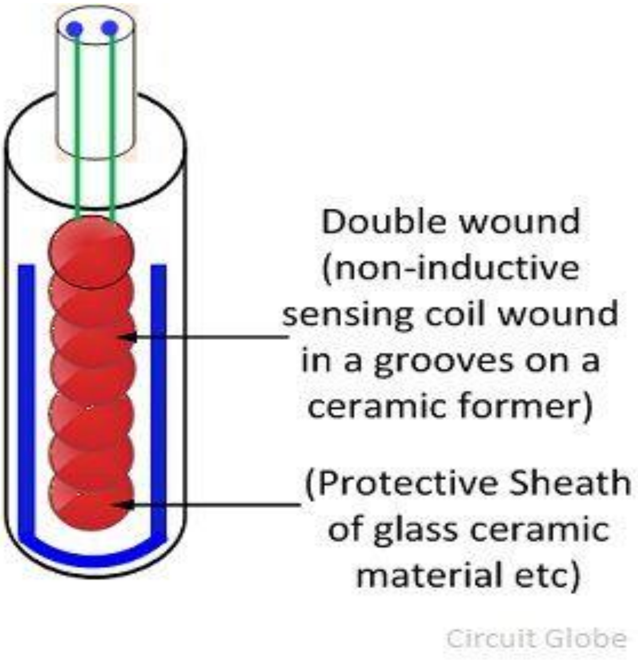


Fig. 6. Industrial type thermometer

Advantages of Platinum Resistance Thermometer

The temperature measurement through platinum resistance thermometer is easier as compared to the gas thermometer.

The meter gives the precise reading of temperature.

The thermometer has a wide range from 200 to 1200° Celsius.

The thermometer is quite sensitive.

The platinum has same resistance at the same temperature.

Disadvantages of Platinum Resistance Thermometer

The following are the disadvantages of platinum thermal resistance.

The thermometer gives the slow response. The melting point of the thermometer is 1800° Celcius. But when platinum measures the temperature higher than 1200°C they start evaporating. When the thermometer constructed carefully, it provides the excellent sensitivity and high range of measurement.

Expression for R_t

P=Q (P, Q -Equal resistance in the ratio arms)

Resistance of the arm AD = Resistance of the arm CD

Balancing point D is to the right of O

$R_t + r + (l+x)\,\rho = S + r + (l-x)\,\rho$

$R_t = S - 2x\rho$

R_t–resistance of the platinum wire

r – resistance of the compensating leads

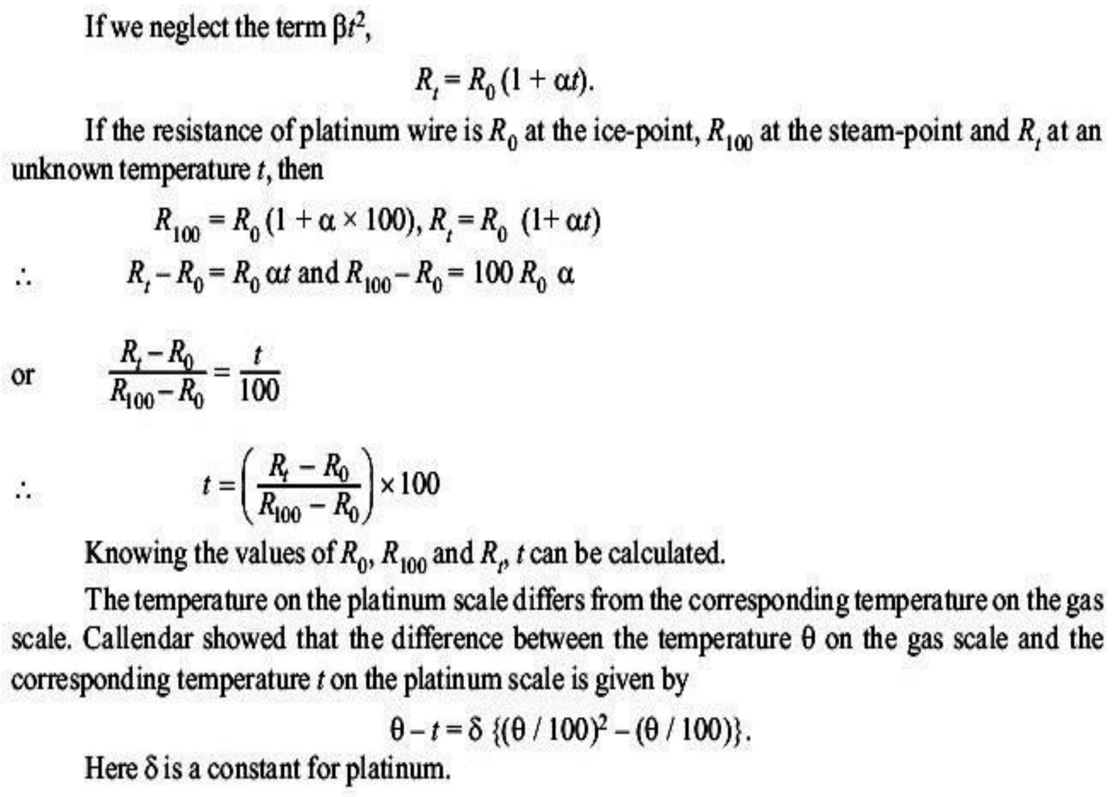
2I – length of the wire EF

ρ - resistivity of the compensating leads.

$$\boxed{R_t = S \pm 2x\rho}$$

Knowing **R_t**, the temperature can be determined.

Expression for temperature of PRT



If we neglect the term βt^2,

$$R_t = R_0\,(1 + \alpha t).$$

If the resistance of platinum wire is R_0 at the ice-point, R_{100} at the steam-point and R_t at an unknown temperature t, then

$$R_{100} = R_0\,(1 + \alpha \times 100),\ R_t = R_0\ (1 + \alpha t)$$

$$\therefore \qquad R_t - R_0 = R_0\,\alpha t \text{ and } R_{100} - R_0 = 100\,R_0\,\alpha$$

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

$$\therefore \qquad t = \left(\frac{R_t - R_0}{R_{100} - R_0}\right) \times 100$$

Knowing the values of R_0, R_{100} and R_t, t can be calculated.

The temperature on the platinum scale differs from the corresponding temperature on the gas scale. Callendar showed that the difference between the temperature θ on the gas scale and the corresponding temperature t on the platinum scale is given by

$$\theta - t = \delta\ \{(\theta / 100)^2 - (\theta / 100)\}.$$

Here δ is a constant for platinum.

CALORIMETRY

One technique we can use to measure the **amount of heat involved** in a chemical or physical process is known as **Calorimetry**.

Calorimetry is used to measure amounts of heat transferred to or from a substance. To do so, the heat is exchanged with a calibrated object (calorimeter).

The measurement of heat transfer using this approach requires the definition of

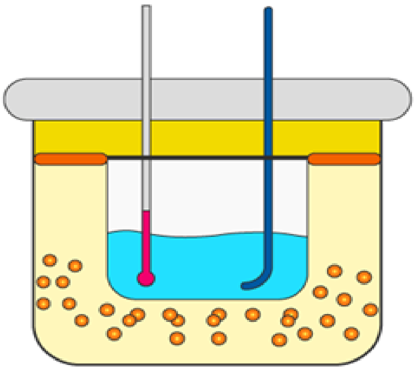
A **system** (the substance or substances undergoing the chemical or physical change)

Surroundings (the region or spaces that either provides heat to the system or absorb heat from the system).

Knowledge of the **heat capacity of the systems**, and careful measurements of the **masses** of the system and surroundings and their **temperatures** before and after the process allows one to calculate the heat transferred as described in this section.

Calorimeter

- A **calorimeter** is a device used to measure the amount of heat involved in a chemical or physical process.



Calorimeter

Fig. 7. Calorimeter

For example,

- When an **exothermic reaction** occurs in solution in a calorimeter, the heat produced by the reaction is absorbed by the solution, which increases its temperature.
- When an **endothermic reaction** occurs, the heat required is absorbed from the thermal energy of the solution, which decreases its temperature (Figure 1). The

temperature change, along with the specific heat and mass of the solution, can then be used to calculate the amount of heat involved in either case.

In a calorimetric determination, either

- (a) an **exothermic** process occurs and heat, *Q*, is **negative**, indicating that thermal energy is transferred from the system to its surroundings, or
- (b) an **endothermic** process occurs and heat, *Q*, is **positive**, indicating that thermal energy is transferred from the surroundings to the system.

Heat Capacity

- It is actually the heat needed for a substance’s temperature to change by one degree. This, therefore, shows that it is applicable to any type of matter. “Heat capacity” is the ratio of heat transfer “Q” to change in temperature “ΔT.”
- In formulaic expression, it is **$C = Q / \Delta T$.**
- In its SI unit notation, it uses units of energy / degree (energy per degree). C = **J / K.**

Specific Heat Capacity

- The specific heat is the amount of heat per unit mass required to raise the temperature by one degree Celsius.
- So, if the mass of the object whose specific heat capacity is calculated is m, the specific heat capacity is c, then the heat needed to raise the temperature of the system by θ is

$$\boxed{Q = mc\theta}$$

m = mass (kg)
c = specific heat capacity ($J\ kg^{-1}\ {}^{o}C^{-1}$)
θ = temperature change (°C)

Method of Mixtures (or) Law of Heat Exchange

- The Principle of Heat Exchange states that when two substances at different temperatures are mixed,
- The amount of heat lost by the HOT substance equals the amount of heat gained by the COOLER substance, assuming no heat is lost to the environment.

At equilibrium,

Heat lost Q is (m c θ) = Heat gained Q is (m c θ)

The specific heat of the substance is calculated with the help of the law of heat exchange.

Example

The heat loss from the 100g of 80°C water is gained by the 100g of 20°C water resulting in a final temperature of 50°C.

Experiment to find Specific heat capacity-Solid

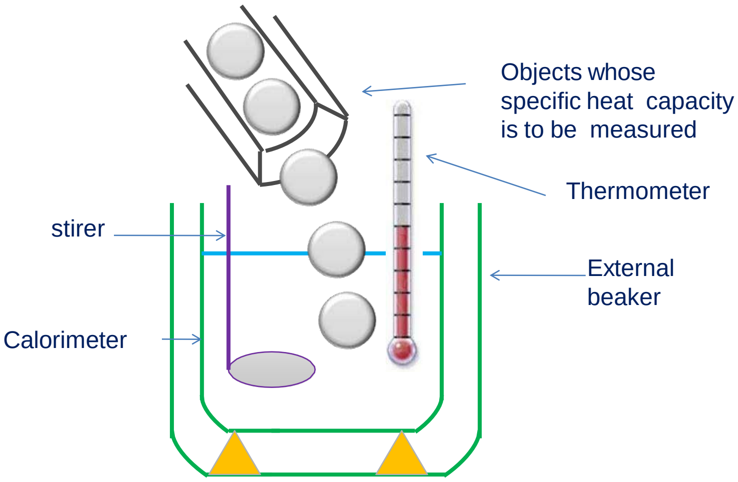


Fig. 8. Experimental setup

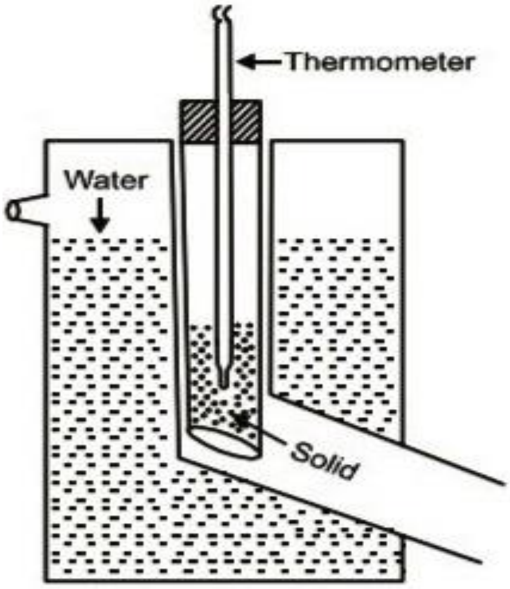


Fig. 9. Heating arrangement

Procedure

1. Measure the weight of the calorimeter and the stirrer (m_1).
2. Pour water to the calorimeter so that water fills about ⅓ of the calorimeter's volume.
3. Measure the weight of the calorimeter, the stirrer and water (m_2). So the weight of the water is (m_2-m_1).
4. Measure the initial temperature of calorimeter stirrer and water (**θ_1**)
5. Measure the total weight of the objects to be about thrice the weight of the total volume of water(m_3)
6. Heat the objects using a **Nicholson's heater** and record their initial temperature(**θ_2**).
7. Introduce the objects to the calorimeter + water system and stir the objects.
8. Record the final temperature of the system (**θ**)

Theory

Let the mass of calorimeter + stirrer = m_1,

Mass of calorimeter + stirrer + water = m_2

Total mass of the objects = m_3

Initial temperature of the calorimeter + stirrer +water = θ_1

Initial temperature of the objects = θ_2 and

Final temperature of the system = θ

The specific heat capacity of the calorimeter = C,

The specific heat capacity of the water = C_W

The specific heat capacity of the objects = C_s.

According to the Principle of method of Mixtures,

Heat gained (Q) = Heat lost (Q)

Heat gained by calorimeter& stirrer = $m_1 C (\theta - \theta_1)$

Heat gained by water = $(m_2 - m_1) C_w (\theta - \theta_1)$

Heat lost by the hot object = $m_3 C_s (\theta_2 - \theta)$

Assuming that the heat loss to the environment as negligible,

Heat emitted by the objects = Heat gained by (water + calorimeter)

Therefore,

$$m_3 C_s(\theta_2 - \theta) = \{ m_1 C (\theta - \theta_1) + (m_2 - m_1) C_W (\theta - \theta_1) \}$$

$$m_3 C_s(\theta_2 - \theta) = \{ m_1 C + (m_2 - m_1) C_W \} \{\theta - \theta_1\}$$

Thus,

$$\mathbf{C_s = [\{ m_1 C + (m_2 - m_1) C_W \} \{\theta - \theta_1\}] / [m_3 (\theta_2 - \theta)]}$$

By this relationship we can find the specific heat capacity of the hot objects.

Experiment to find Specific heat capacity-Liquid

- Measure the mass of the calorimeter &stirrer.
- Fill it with the given liquid whose specific heat capacity is to be determined. Follow the same procedure as solid.
- Specific heat capacity of the liquid can be calculated by using the formula

$$\mathbf{C_w = [\{ m_1 C (\theta - \theta_1) - m_3 C_s(\theta_2 - \theta) \} / \{ (m_2 - m_1) (\theta - \theta_1) \}]}$$

The two specific heat capacities of a gas

Gases can be expanded or compressed easily.

Hence in order to fix the value of the specific heat capacity of a gas, either the pressure or the volume should be kept constant. Hence, we have two specific heat capacities for a gas.

$$C_V = \left(\frac{\partial Q}{\partial T}\right)_v \text{ and } C_P = \left(\frac{\partial Q}{\partial T}\right)_P .$$

Subscripts *v* and *p* indicate the parameter kept constant during the process. C_v is known as the specific heat capacity at constant volume. C_p is the specific heat capacity at constant pressure.

Definitions

(*i*) *The specific heat capacity at constant volume* (C_v) *is defined as the amount of heat required to raise the temperature of 1 kg of the gas through 1 K when its volume is kept constant.*

(*ii*) *The specific heat capacity at constant pressure* (C_p) *is defined as the amount of heat required to raise the temperature of 1 kg of the gas through 1 K when its pressure is kept constant.*

Mayer's formula C_P-C_V= R

Difference between the two specific heat capacities

Consider one mole of a perfect gas kept in a non-conducting cylinder provided with a frictionless piston of area *A* [Fig.]. Let *T* be the temperature, *V* the volume and *P* the pressure of the gas. Let a certain amount of heat be given to the gas so that the temperature increases by *dT*. Assume that the piston is fixed so that the volume of the gas is constant.

Quantity of heat given to the gas = $1 \times C_v dT = C_v dT$

This quantity of heat is used in increasing the internal energy of the gas.

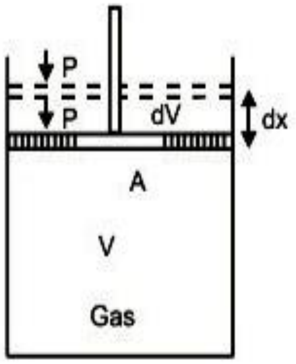


Fig.

Fig. 10. Cylinder with piston

Let us suppose that the same gas is now given a certain amount of heat at constant pressure P so that the temperature increases by dT. Since the gas is heated at constant pressure, the volume increases. The gas expands. Hence the piston moves up through a distance dx. Let dV be the increase in volume of the gas.

Quantity of heat supplied to the gas $= 1 \times C_p\,dT = C_p\,dT$.

This quantity of heat supplied to the gas at constant pressure is used in two ways.

(*i*) In raising the internal energy of the gas corresponding to a raise of temperature of dT. *i.e.*, by $C_v\,dT$.

(*ii*) In doing the work of expanding the gas against the external pressure.

External work done by the gas in expansion

$$= \text{Force} \times \text{distance}$$

$$= PA \times dx = P\,dV$$

Hence, $$C_p\,dT = C_v\,dT + P\,dV$$

For a perfect gas, $PV = RT$ or $P\,dV = R\,dT$

Hence $$C_p\,dT = C_v\,dT + R\,dT$$

$$\therefore \quad C_p - C_v = R$$

This formula is known as Mayer's formula.

$R = 8.31\ J\,mol^{-1}\,K^{-1}$. In SI units, $R = 8314\ J\,(kg\ mol)^{-1}K^{-1}$.

R is the universal gas constant.

Callender and Barnes' continuous flow method to determine C_p

The specific heat capacity of a gas at constant pressure can be determined by continuous flow method. The experimental arrangement is shown in Fig. 1.15. The gas is stored up in a large copper reservoir *R*. It is kept immersed in a constant temperature bath *W*. The pressure of the gas is read by the pressure gauge *G*. The regulating valve *V'* is used for allowing the gas to flow at a constant pressure through the calorimeter *D*. The manometer *E* measures the pressure of the gas flowing through *D*. A heating coil *C* is arranged axially inside the vessel *D*. The current passing through the coil *C* is measured by ammeter *A*. The P.D. across the coil is measured by the voltmeter *V*. The incoming gas is heated due to the heat generated in the coil *C*. The platinum resistance thermometers T_1 and T_2 measure the temperatures of the incoming and outgoing gas. The gas travels in the direction of the arrows through the zig-zag path and finally comes in contact with the heating coil *C*.

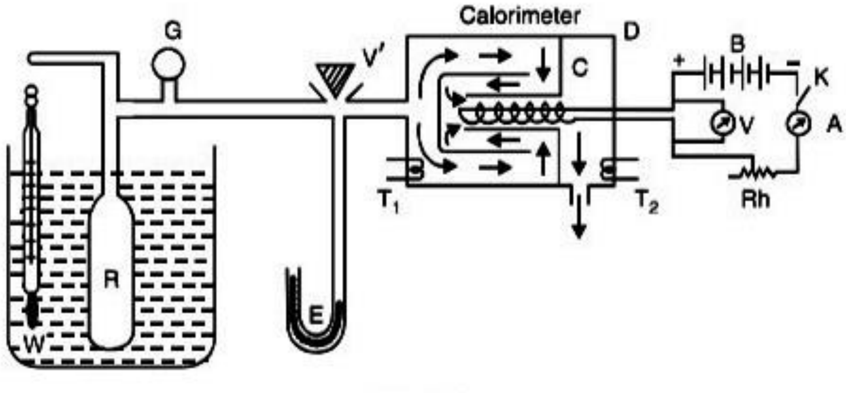


Fig. 1.15

Procedure :

The gas is allowed to flow through the apparatus for some time till the steady state is reached. When the steady state is reached, the thermometers T_1 and T_2 show constant readings. Let θ_1 and θ_2 be the temperatures of the incoming and outgoing gas, as shown by T_1 and T_2. The pressure (P_1) of the gas in the reservoir is noted by the pressure gauge *G*. The gas is allowed to flow through the vessel *D* for about 30 minutes. The final pressure (P_2) of the gas in the reservoir is noted.

Calculations :

The mass of the gas flowing out of the reservoir in *t* seconds is calculated from its initial and final pressures. Then,

heat gained by the gas $= mC_p(\theta_2 - \theta_1)$.

Let *E* and *I* be the voltmeter and ammeter readings. Then, heat produced in the heating coil in *t* seconds $= EIt$.

Hence, $$mC_p(\theta_2 - \theta_1) = EIt$$

$$\therefore \quad C_p = \frac{EIt}{m(\theta_2 - \theta_1)}$$

To find M. The gas in the reservoir is at constant temperature T. Suppose P_1 and P_2 are the initial and final pressures of the gas in the reservoir. Let V be the volume of the reservoir.

Mass of the gas escaped $= M = V\rho_1 - V\rho_2$

$$= V(\rho_1 - \rho_2) \quad \text{...(1)}$$

Here, ρ_1 and ρ_2 are the initial and final densities of the gas in the reservoir.

By the gas equation, $\frac{P_1}{\rho_1} = RT$ and $\frac{P_2}{\rho_2} = RT$

Hence, $\rho_1 = \frac{P_1}{RT}$ and $\rho_2 = \frac{P_2}{RT}$

$$\therefore \quad \rho_1 - \rho_2 = \frac{P_1 - P_2}{RT} \quad \text{...(2)}$$

Let ρ_o be the density of the gas at N.T.P. Then

$$0.76 \times \frac{1}{\rho_o} = R \times 273$$

or

$$R = \frac{0.76}{273\rho_o} \quad \text{...(3)}$$

Substituting for R in (2),

$$\rho_1 - \rho_2 = \frac{(P_1 - P_2)273\rho_o}{0.76\,T} \quad \text{...(4)}$$

Substituting for $\rho_1 - \rho_2$ in (1),

$$M = \frac{V(P_1 - P_2)273\,\rho_o}{0.76\,T}$$

Thus M is known. Hence C can be calculated.

Advantages :

1. The radiation loss is minimized by the zig-zag arrangement for the flow of gas.
2. The temperatures of the incoming and outgoing gas are measured accurately under steady state.
3. All electrical quantities can be measured with precision. Thus the results obtained are accurate.

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SCHOOL OF SCIENCE AND HUMANITIES

DEPARTMENT OF PHYSICS

Thermal Physics– SPH1211

II. Thermodynamics

Let us break the word **thermodynamics** into two words, **thermo** and **dynamics.** '**Thermo**' stands for heat while '**dynamics**' is used in connection with a mechanical motion which involves 'work'. Therefore, Thermodynamics is the branch of physics that deals with the relationship between heat and other forms of energy.

Now which quantities determine the state of the system?

They are pressure, volume, temperature, entropy, mass or composition, internal energy etc. These quantities are referred to as the state variables and State variables are measured only when the system is at equilibrium. The systems that we study in thermodynamics consist of very large numbers of atoms or molecules interacting in complicated ways. But, if these systems meet the right equilibrium, they can be described with a very small number of measurements.

Boundary & Surroundings

Boundary

- The system and surroundings are separated by a boundary. It may be fixed or movable or imaginary. It will not occupy any volume or mass in space.

Surroundings

- Anything outside the system which affects the behavior of the system is known as surroundings. (Fig. 2.1)

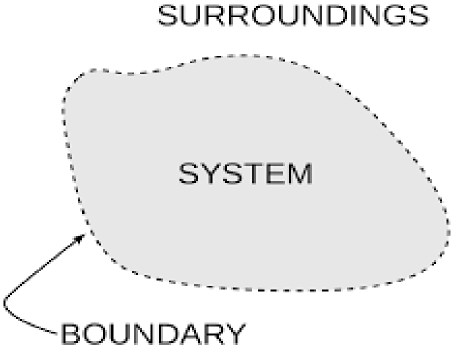

Fig. 2.1. System & surrounding

System

- In thermodynamics, the **system** is defined as a definite space or area on which the study of energy transfer and energy conversions is made.
- **Open system:** System in which both mass and energy cross the boundaries of the system.
- **Closed system:** System in which mass does not cross boundaries of the system, though energy may do so.
- **Isolated system:** System in which neither mass nor energy crosses the boundaries of the system.

Thermodynamic Processes

How does food stay cold and fresh in a refrigerator?
Alongside have you ever noticed even though the entire inner compartment of a refrigerator is cold, outside or the back of a refrigerator is warm?

- Here the refrigerator pulls heat from its inner compartment and transfers it to the region outside. This is why the back of a refrigerator is warm. '**Thermodynamic processes**' involve heat energy moving within a system or between systems. Let us study more about them.

Types of Thermodynamic Processes

- Isobaric process
- Isochoric process
- Isothermal process
- Adiabatic process
- Quasi-static process

Isobaric Process

- "Iso" means the same, and"baric" means pressure.
- The processes during which the **pressure of the system remains constant** are called **isobaric thermodynamic processes**. Suppose there is a fuel in piston and cylinder arrangement. When this fuel burns the pressure of the gases, generated inside

the engine. But if the gases are allowed to expand by allowing the piston to move outside, the pressure of the system can be constant.

PV Curve

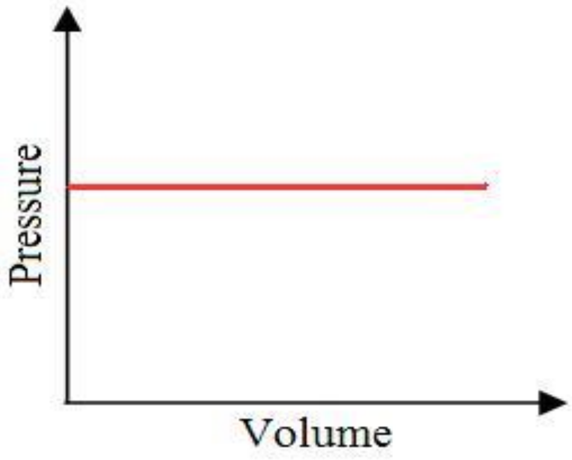

Fig. 2. 2. PV curve

Isochoric Process

- The process, during which the volume of the system remains constant, is an isochoric process.
- Heating of a gas in a closed cylinder is an example of the isochoric process.
- The change in temperature for a given amount of heat is determined by the specific heat of the gas at a constant volume.

Work done in an isochoric process = Force x displacement

$W = \int P\, dV$

Here, V = constant, dV = 0

Therefore, W = 0

Isothermal Process

In an isothermal process, there is no change in temperature that means the temperature remains constant.

Like when hot water is kept in a thermos flask, if we remove a certain quantity of water from the flask, but keep its temperature constant then the process is said to be an **isothermal process**.

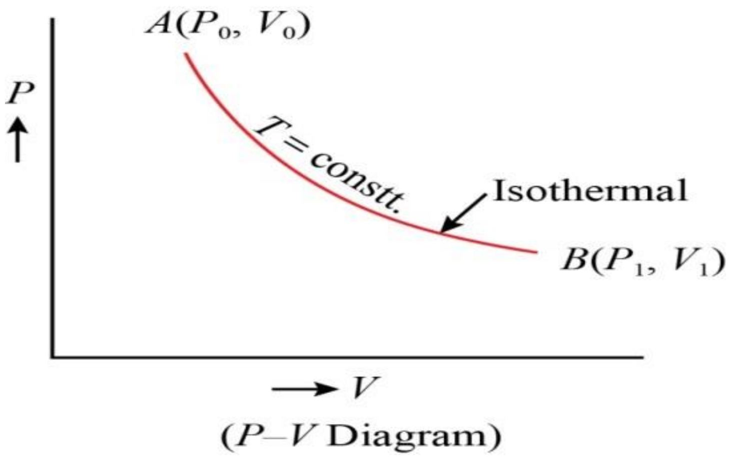

Fig. 2.3. PV Curve

Adiabatic Process

The process, during which the heat content of the system remains constant, is an **adiabatic process**. During this process heat neither enters the system nor leaves the system.

For an adiabatic process,

$$\Delta Q = 0$$

Then according to the first law of thermodynamics,

$$\Delta U + \Delta W = \Delta Q = 0$$

Where, Q is the heat supplied to the system and W is the work done by the system and U is the internal energy of the system.

Quasi-Static Process

When a process is which system remains close to an equilibrium state at each time, such process will be termed as the quasi-static process or quasi-equilibrium process.

For example, if a person is coming down from roof to ground floor with the help of ladder steps then it is a quasi-static process. But if he jumps from roof to ground floor then it will not be a quasi-static process.

Laws of Thermodynamics

Zeroth Law (Ralph H. Fowler)

When a body ‘A’ is in thermal equilibrium with another body ‘B’, and also separately in thermal equilibrium with a body ‘C’, then body ‘B’ and ‘C’ will also be in thermal equilibrium with each other. This statement defines the zeroth law of thermodynamics. The law is based on temperature measurement.

The zeroth law of thermodynamics frames an idea of temperature as an indicator of thermal equilibrium.

“Systems that are in thermal equilibrium exist at the same temperature”.

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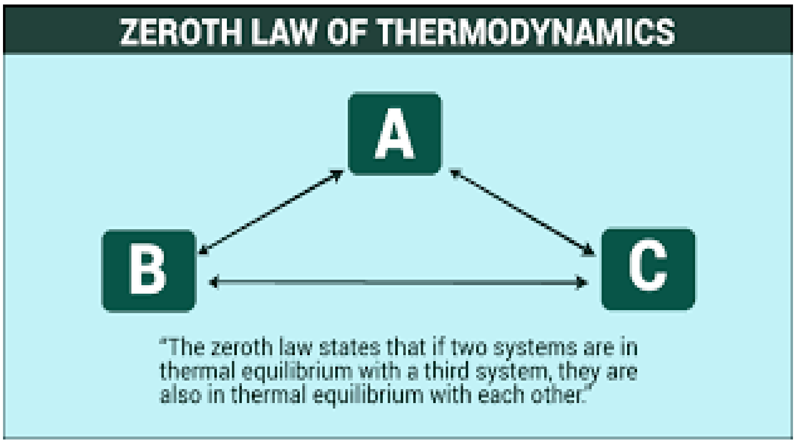


“The zeroth law states that if two systems are in thermal equilibrium with a third system, they are also in thermal equilibrium with each other.”

Fig. 2. 4. Zeroth Law

First Law of Thermodynamics (Rudolf Clausius-in 1850)

According to this law, some of the heat given to system is used to change the internal energy while the rest in doing work by the system. Mathematically,

$$\mathbf{\Delta Q=\Delta U+\Delta W}$$

ΔQ = Heat supplied to the system

ΔW= Work done by the system.

ΔU = Change in the internal energy of the system.

If Q is positive, then there is a net heat transfer into the system, if W is positive, then there is work done by the system. So positive Q adds energy to the system and positive W takes energy from the system. It can also be represented as $\mathbf{\Delta U=\Delta Q-W}$

We can say that internal energy tends to increase when heat is given to the system and vice versa.

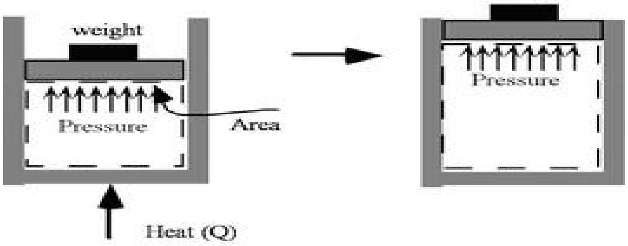


Fig. 2.5 First Law

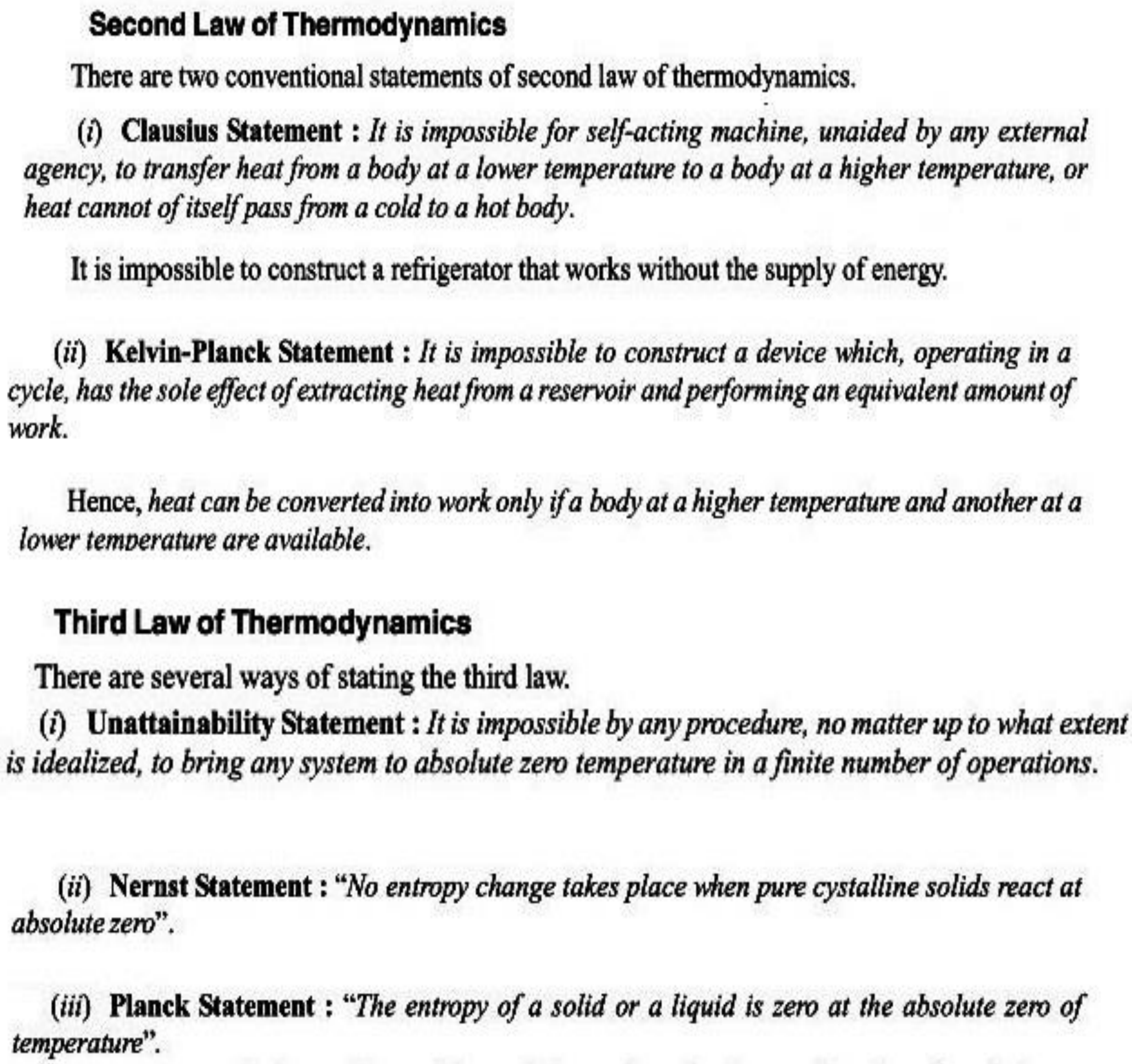
Limitations of First Law of Thermodynamics

The limitation of the first law of thermodynamics is that

- It does not say anything about the direction of flow of heat.
- It does not say anything whether the process is a spontaneous process or not.
- The reverse process is not possible.

For Example

In actual practice, the heat doesn't convert completely into work. If it would have been possible to convert the whole heat into work, then we could drive ships across the ocean by extracting heat from the water of the ocean.



Second Law of Thermodynamics

There are two conventional statements of second law of thermodynamics.

(*i*) **Clausius Statement :** *It is impossible for self-acting machine, unaided by any external agency, to transfer heat from a body at a lower temperature to a body at a higher temperature, or heat cannot of itself pass from a cold to a hot body.*

It is impossible to construct a refrigerator that works without the supply of energy.

(*ii*) **Kelvin-Planck Statement :** *It is impossible to construct a device which, operating in a cycle, has the sole effect of extracting heat from a reservoir and performing an equivalent amount of work.*

Hence, *heat can be converted into work only if a body at a higher temperature and another at a lower temperature are available.*

Third Law of Thermodynamics

There are several ways of stating the third law.

(*i*) **Unattainability Statement :** *It is impossible by any procedure, no matter up to what extent it is idealized, to bring any system to absolute zero temperature in a finite number of operations.*

(*ii*) **Nernst Statement :** "*No entropy change takes place when pure cystalline solids react at absolute zero*".

(*iii*) **Planck Statement :** "*The entropy of a solid or a liquid is zero at the absolute zero of temperature*".

Entropy

- **Entropy (S),** the measure of a system’s thermal energy per unit temperature that is unavailable for doing useful work. (S = Q/T).
- Because work is obtained from ordered molecular motion, the amount of entropy is a **measure of the molecular disorder**, **or randomness**, of a system.
- The concept of entropy provides deep insight into the direction of spontaneous change for many everyday phenomena.

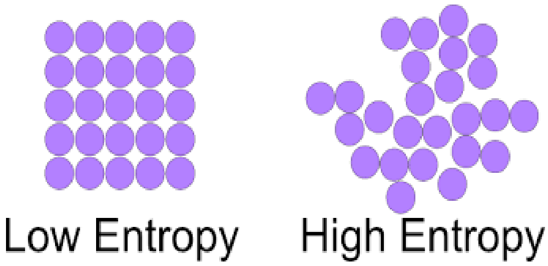


Fig. 2. 6

Applications of Entropy

- Wherever **heat transfer** takes place entropy of the universe increases. And it continuously increases until whole system comes in thermal equilibrium which leads to heat death.

- Whatever we do in the universe it leads to increase in entropy, like :

breaking a piece of glass, breaking an egg, even when we eat, tear a page from our notebooks, breathe or do any work that leads to increase in entropy because every work is irreversible and irreversible work leads to increase in entropy.

Reversible Process

A thermodynamic process is reversible if the process can return back in such both the system and the surroundings return to their original states, with no other change anywhere else in the universe. It means both system and surroundings are returned to their initial states .

Examples of Reversible Process

- Here, we have listed a few examples of Reversible Process:
- extension of springs
- slow adiabatic compression or expansion of gases
- electrolysis (with no resistance in the electrolyte)
- the frictionless motion of solids

- slow isothermal compression or expansion of gases

Irreversible Processes

- An irreversible process can be defined as a process in which the system and the surroundings do not return to their original condition once the process is initiated.
- Taking an example of an automobile engine, that has travelled a distance with the aid of fuel equal to an amount ‘x’. During the process, the fuel burns to provide energy to the engine, converting itself into smoke and heat energy. We cannot retrieve the energy lost by the fuel and cannot get back the original form. There are many factors due to which the irreversibility of a process occurs, namely:
- The friction that converts the energy of the fuel to heat energy
- Mixing of two different substances which cannot be separated as the process of intermixing is again spontaneous in nature, the reverse of which is not feasible.

Examples of Irreversible Processes

- Relative motion with friction ,
- Throttling ,
- Heat transfer,
- Diffusion ,
- Electricity flow through a resistance

Change of entropy in a reversible process (Carnot's cycle)

Consider a reversible Carnot cycle *ABCD* (Fig. 2.12).

(*i*) In the isothermal expansion from A to B, the working substance absorbs an amount of heat Q_1 at a constant temperature T_1.

$$\left.\begin{matrix}\text{Increase in entropy of working} \\ \text{substance from } A \text{ to } B\end{matrix}\right\} = \frac{Q_1}{T_1}.$$

(*ii*) During the adiabatic expansion from B to C, there is no change in entropy.

(*iii*) During the isothermal compression from C to D, the working substance gives out a quantity of heat Q_2 at a constant temperature T_2.

Decrease in entropy of working substance from C to $D = \frac{Q_2}{T_2}$.

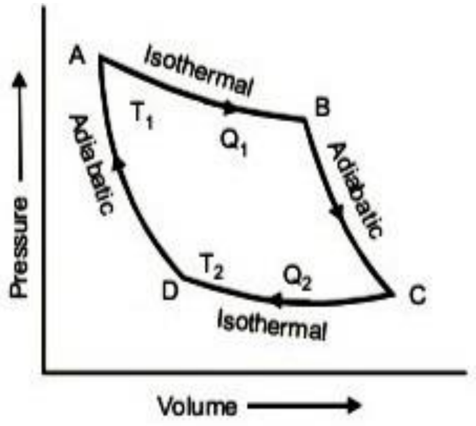


Fig 2.7. Carnot cycle

(*iv*) During the adiabatic compression from D to A, there is no change in entropy.

$$\therefore \quad \left.\begin{array}{r}\text{The net change in entropy of the working}\\ \text{substance during the cycle } ABCD\end{array}\right\} = \frac{Q_1}{T_1} - \frac{Q_2}{T_2}.$$

For a reversible cycle,

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$$

$$\therefore \quad \frac{Q_1}{T_1} - \frac{Q_2}{T_2} = 0$$

Thus, the total change of entropy is zero during a Carnot's cycle.

Entropy change in a reversible cycle is zero.

Change in entropy in an irreversible process

Consider an irreversible process like conduction or radiation of heat. Suppose a body at a higher temperature T_1 conducts away a small quantity of heat dQ to another body at a lower temperature T_2. Then,

$$\text{decrease in entropy of the hot body} = \frac{dQ}{T_1}$$

$$\text{increase in entropy of the cold body} = \frac{dQ}{T_2}$$

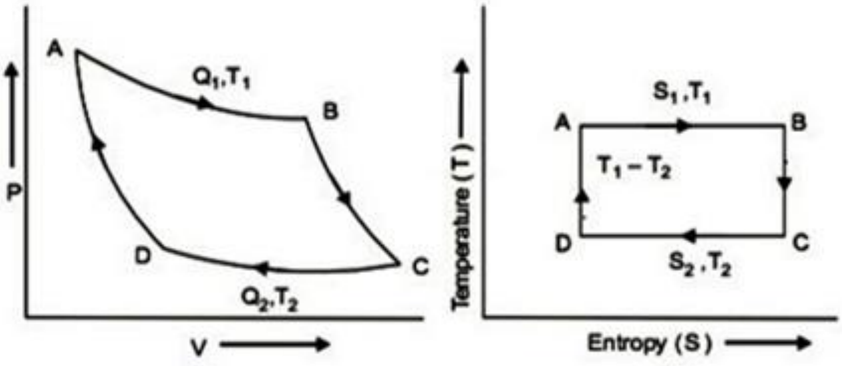
$$\therefore \quad \text{the net increase in the entropy of the system} = dS = \frac{dQ}{T_2} - \frac{dQ}{T_1}$$

dS is always positive since $T_1 > T_2$. Hence there is an increase of entropy. Similarly, there is an increase of entropy during the loss of heat by radiation. Therefore, generally, *the entropy of a system increases in all irreversible processes.* This is called the *law of increase of entropy*.

Temperature-entropy diagram

The state of a substance may be represented by points plotted with temperature as ordinates and entropies as abscissae. This is the *TS* diagram. Here the isothermals are horizontal straight lines (parallel to *S*-axis). The adiabatics are vertical straight lines (parallel to *T*-axis).

Consider the Carnot cycle *ABCD* (Fig. 2. 8).



(*a*) (*b*)

Fig. 2. 8

(*i*) From *A* to *B*, heat energy Q_1 is absorbed at temperature T_1. The increase in entropy S_1 takes place from *A* to *B*

$$S_1 = \frac{Q}{T_1} \qquad \text{...(1)}$$

Features of Entropy

Entropy is an **extensive** properly and a state function. Thermodynamic properties are divided into two broad types: Intensive properties and extensive properties.

An extensive property is any property that depends on the size (or extent) of the system under consideration. Volume is an example.

(2) It's value depends upon mass of substance present in the system

(3) $dS = S_{final} - S_{initial}$

(4) At equilibrium dS = Zero

(5) For a cyclic process dS = Zero

(6) For natural process dS > Zero i.e Increasing.

(7) For a adiabatic process dS is Zero

OTTO Engine

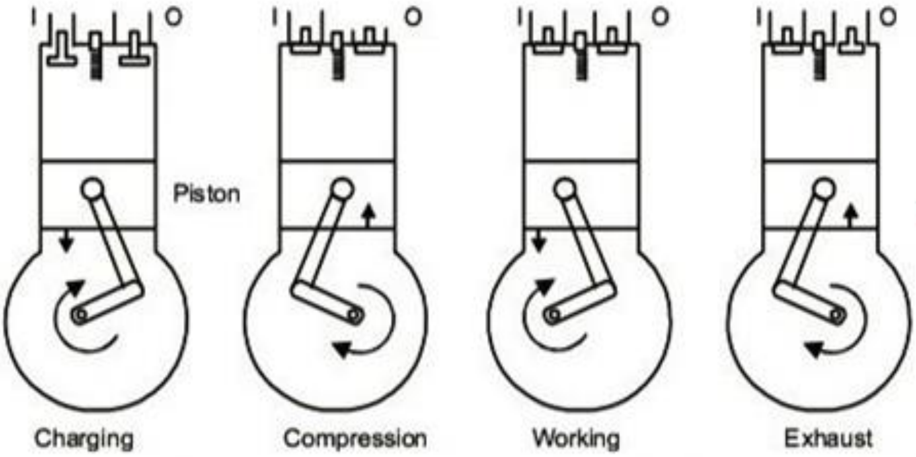


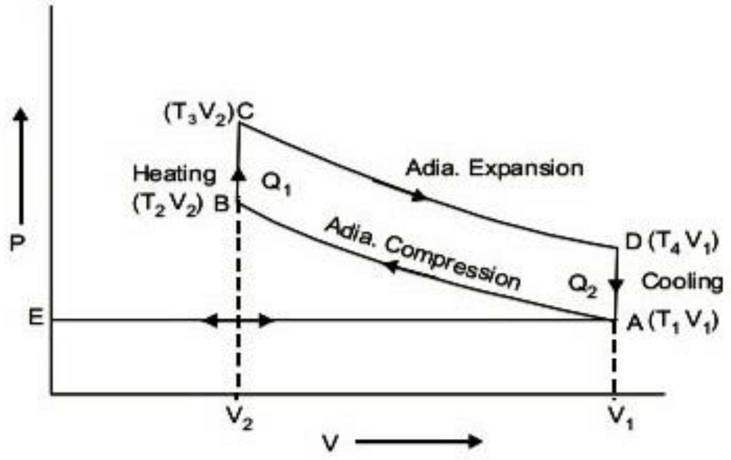
Fig. 2.9

Construction. It consists of a cylinder fitted with a piston (Fig. 2 9).The working substance is air. The cylinder has an inlet valve *I* to allow air and vapour in and an outlet valve *O* for throwing out the burnt mixture. These valves are operated by the movement of piston.

Working. There are *four strokes* in each cycle of operation.

1. Charging stroke. The inlet valve *I* opens. The mixture of petrol vapour and air enters into the cylinder at atmospheric pressure. This is represented by *EA* (Fig.2.10). The final volume is V_1 at temperature T_1.

2. Compression stroke. (*i*) Both the inlet and outlet valves are closed and the mixture is compressed adiabatically. The volume decreases to V_2 and temperature increases to T_2. This is represented by *AB*.



(*ii*) At the end of compression stroke, an electric spark is produced. The mixture of air and petrol vapour is ignited. The temperature rises to T_3. A quantity of heat Q_1 at a higher temperature is absorbed from *B* to *C*.

3. Working stroke. *C* to *D* represents the *working stroke.* The gas expands adiabatically and the engine works. The volume changes from V_2 to V_1. Temperature decreases from T_3 to T_4.

4. Exhaust stroke. (*i*) At *D*, exhaust valve opens. *D* to *A* represents the change of pressure to the atmospheric pressure and the temperature changes from T_4 to T_1.

A quantity of heat Q_2 is rejected at a lower temperature from *D* to *A*.

(*ii*) The exhaust gases are completely discharged from the cylinder. Thus, the initial condition of the engine is restored. This is represented by *AE*.

Efficiency

Quantity of heat absorbed from B to C at a higher temperature is

$$Q_1 = m\,C_V(T_3 - T_2) \qquad ...(1)$$

Here, m = The mass of the mixture of air and petrol,

C_V = Specific heat capacity of the mixture at constant volume.

Quantity of heat rejected at a lower temperature from D to A is

$$Q_2 = m\,C_V\,(T_4 - T_1) \qquad ...(2)$$

Heat converted into useful work = $Q_1 - Q_2$

$$\text{Efficiency } \eta = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1}$$

$$\eta = 1 - \frac{(T_4 - T_1)}{(T_3 - T_2)} \qquad ...(3)$$

The points A and B lie on the same adiabatic.

$$\therefore \qquad T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1} \qquad ...(4)$$

The points D and C lie on the same adiabatic.

$$\therefore \qquad T_4 V_1^{\gamma-1} = T_3 V_2^{\gamma-1} \qquad ...(5)$$

Subtracting (4) from (5),

$$(T_4 - T_1)V_1^{\gamma-1} = (T_3 - T_2)V_2^{\gamma-1}$$

or

$$\left(\frac{T_4 - T_1}{T_3 - T_2}\right) = \left(\frac{V_2}{V_1}\right)^{\gamma-1} \qquad ...(6)$$

Substituting this value in Eq. (3),

$$\eta = 1 - \left(\frac{V_2}{V_1}\right)^{\gamma-1} = 1 - \left[\frac{1}{(V_1/V_2)}\right]^{\gamma-1}$$

$$\frac{V_1}{V_2} = \rho = \text{adiabatic compression ratio.}$$

$$\therefore \qquad \eta = 1 - \left(\frac{1}{\rho}\right)^{\gamma-1} \qquad ...(7)$$

Diesel engine

Construction. It consists of a cylinder fitted with a piston (Fig. 2.9a). There are separate inlet valves for air (I) and diesel (I_1). There is an exhaust valve (O) for throwing out the burnt mixture of gases. The working substance is the mixture of diesel vapour and air. The diesel engine works on the four-stroke principle. The cycle is called '*Diesel cycle*'.

Working

1. Charging stroke. The inlet valve is opened. Pure air is sucked into the cylinder at atmospheric pressure. E to A (Fig. 2.9b) represents the intake of air. V_1 is the volume of air at A.

2. Compression stroke. (*i*) A to B represents the *compression stroke*. Air is compressed adiabatically. The temperature changes from T_1 to T_2. The volume changes from V_1 to V_2.

(*ii*) **Injection of oil.** Diesel is sprayed into the cylinder. The diesel burns due to high temperature. The pressure is maintained constant. The temperature changes from T_2 to T_3. The volume changes from V_2 to V_3. This is represented by the line BC in the P-V diagram.

Q_1 is the quantity of heat absorbed at constant pressure.

3. Working stroke. C to D represents the *working stroke*. The mixture of air and diesel oil vapour expand adiabatically. The piston is moved forward and work is done by the working substance.

4. Exhaust stroke. (*i*) As the point D is reached, the exhaust valve opens and the pressure drops to the point A. The volume remains constant, but temperature and pressure decrease. This is represented by the line DA.

Q_2 is the quantity of heat rejected to the sink.

(*ii*) The burnt mixture is forced out. This is represented by AE.

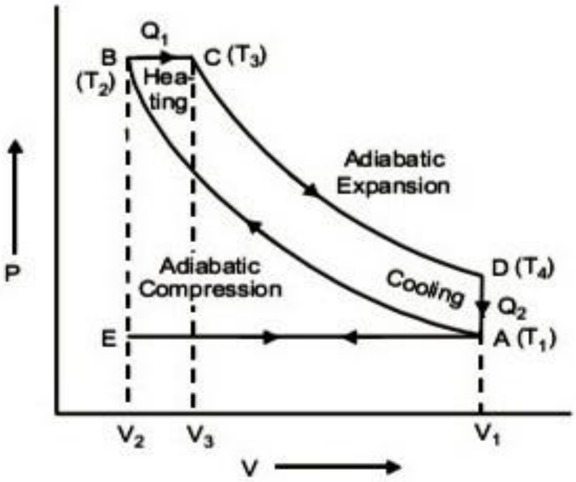


Fig. 2.11. PV Curve of diesel engine

Efficiency

Heat absorbed by the working substance at constant pressure during BC is

$$Q_1 = m\,C_P(T_3 - T_2) \qquad \text{...(1)}$$

Here, m = mass of the working substance

C_P = specific heat capacity at constant pressure.

From D to A the volume remains constant.

The quantity of heat rejected,

$$Q_2 = m\,C_V(T_4 - T_1) \qquad \text{...(2)}$$

Here, C_V = specific heat capacity at constant volume.

Efficiency $\eta = 1 - \frac{Q_2}{Q_1} = 1 - \frac{C_V}{C_P}\left(\frac{T_4 - T_1}{T_3 - T_2}\right)$

$$\eta = 1 - \frac{1}{\gamma}\left(\frac{T_4 - T_1}{T_3 - T_2}\right) \qquad \text{...(3)}$$

To evaluate $\left(\frac{T_4 - T_1}{T_3 - T_2}\right)$, all the temperatures are expressed in terms of T_2.

Let $\frac{V_1}{V_2} = \rho$ (adiabatic compression ratio), $\frac{V_1}{V_3} = r$ (adiabatic expansion ratio) and $\frac{\rho}{r} = k$.

$$\therefore \qquad k = \frac{V_1/V_2}{V_1/V_3} = \frac{V_3}{V_2}.$$

(1) The points A and B are on the same adiabatic.

$$\therefore \qquad T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$$

$$T_1 = T_2\left(\frac{V_2}{V_1}\right)^{\gamma-1} = T_2\left[\frac{1}{\rho}\right]^{\gamma-1} \qquad \text{...(4)}$$

(2) The points B and C are at the same pressure.

$$\therefore \qquad \frac{T_3}{V_3} = \frac{T_2}{V_2}$$

or

$$T_3 = T_2\left[\frac{V_3}{V_2}\right] = T_2\,(k)$$

(3) The points C and D are on the same adiabatic.

$$\therefore \quad T_4 V_1^{\gamma-1} = T_3 V_3^{\gamma-1} \qquad \text{...(5)}$$

$$T_4 = T_3\left[\frac{V_3}{V_1}\right]^{\gamma-1} = T_3\left[\frac{V_3}{V_2}\times\frac{V_2}{V_1}\right]^{\gamma-1}$$

$$= T_3\left[\frac{k}{\rho}\right]^{\gamma-1} = T_2\, k\left[\frac{k}{\rho}\right]^{\gamma-1}$$

or

$$T_4 = T_2\, k^{\gamma}\left[\frac{1}{\rho}\right]^{\gamma-1} \qquad \text{...(6)}$$

$$\eta = 1-\frac{1}{\gamma}\left[\frac{T_4 - T_1}{T_3 - T_2}\right]$$

$$= 1-\frac{1}{\gamma}\left[\frac{T_2\, k^{\gamma}\left[\frac{1}{\rho}\right]^{\gamma-1} - T_2\left(\frac{1}{\rho}\right)^{\gamma-1}}{T_2\,(k) - T_2}\right]$$

$$\therefore \quad \eta = 1-\frac{1}{\gamma}\left(\frac{1}{\rho}\right)^{\gamma-1}\left[\frac{k^{\gamma}-1}{k-1}\right] \qquad \text{...(7)}$$

The following table shows the differences between the *Otto* and *Diesel engines*.

The Otto engine	***The Diesel engine***
1. The fuel vapours are introduced into the cylinder, *along with air.*	The fuel vapours are introduced into the cylinder *after the air has first been sufficiently compressed.*
2. Heat is taken in by the air *at constant volume.*	Heat is taken in by the air *at constant pressure.*
3. The *adiabatic compression ratio is low.*	The *adiabatic compression ratio is high.*
4. Its efficiency is *not high.*	Its efficiency is *comparatively higher.*

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DEPARTMENT OF PHYSICS

Thermal Physics – SPH1211

III. Low Temperature Physics

Introduction

Low-temperature physics, science concerned with the production and maintenance of temperatures much below normal, down to almost absolute zero, and with various phenomena that occur only at such temperatures. The temperature scale used in low-temperature physics is the Kelvin temperature scale, or absolute temperature scale, which is based on the behavior of an idealized gas.

Low-temperature physics is also known as cryogenics, from the Greek meaning "producing cold”. Low temperatures are achieved by removing energy from a substance. This may be done in various ways. The simplest way to cool a substance is to bring it into contact with another substance that is already at a low temperature. Ordinary ice, dry ice (solid carbon dioxide), and liquid air may be used successively to cool a substance down to about 80°K; (about −190°C).

The heat is removed by conduction, passing from the substance to be cooled to the colder substance in contact with it. If the colder substance is a liquefied gas, considerable heat can be removed as the liquid reverts to its gaseous state, since it will absorb its latent heat of vaporization during the transition. Various liquefied gases can be used in this manner to cool a substance to as low as 4.2°K;, the boiling point of liquid helium. If the vapor over the liquid helium is continually pumped away, even lower temperatures, down to less than 1°K;, can be achieved because more helium must evaporate to maintain the proper vapor pressure of the liquid helium. Most processes used to reduce the temperature below this level involve the heat energy that is associated with magnetization.

Successive magnetization and demagnetization under the proper combination of conditions can lower the temperature to only about a millionth of a degree above absolute zero. Reaching such low temperatures becomes increasingly difficult, as each temperature drop requires finding some kind of energy within the substance and then devising a means of removing this energy. Moreover, according to the third law of thermodynamics, it is theoretically impossible to reduce a substance to absolute zero by any finite number of processes.

Joule – Thomson's Effect

Statement

If a gas initially at constant high pressure is allowed to suffer throttle expansion through the porous plug of silk, wool or cotton wool having a number of fine pores, to a region of constant low pressure adiabatically, a change in temperature of gas (either cooling or heating) is observed. This effect is called as Joule –Thomson or Joule-Kelvin effect.

Porous Plug experiment

Joule in collaboration with Thomson [Lord Kelvin] devised a very sensitive technique known as Porous Plug experiment. The experiment set up of porous plug experiment to study the Joule-Thomson effect is shown in Fig.2.1. It consists of the following main parts:

(a) A Porous plug having two perforated -brass discs D & D1.
(b) The space between D & D1 is placed with cotton wool or silk fibers.
(c) The porous plug is fitted ina cylindrical box-wood W which is surrounded by a vessel containing cotton wool. This is to avoid loss or gain of heat from the surroundings.
(d) T1 &T2 are two sensitive platinum resistance thermometers and they measure the temperatures of the incoming and outgoing gas.
(e) The gas is compressed to a high pressure with the help of piston P and it is placed through a spiral tube immersed in water bath maintained at a constant temperature. If there is any heating of the gas due to compression, this heat is absorbed by the circulating water in the water bath.

Experimental Procedure

The experimental gas is compressed by Pump P and is passed slowly and uniformly through the porous plug keeping the high pressure constant read by pressure gauge. During the passage through the porous plug, the gas is throttled. The separation between the molecules increases.

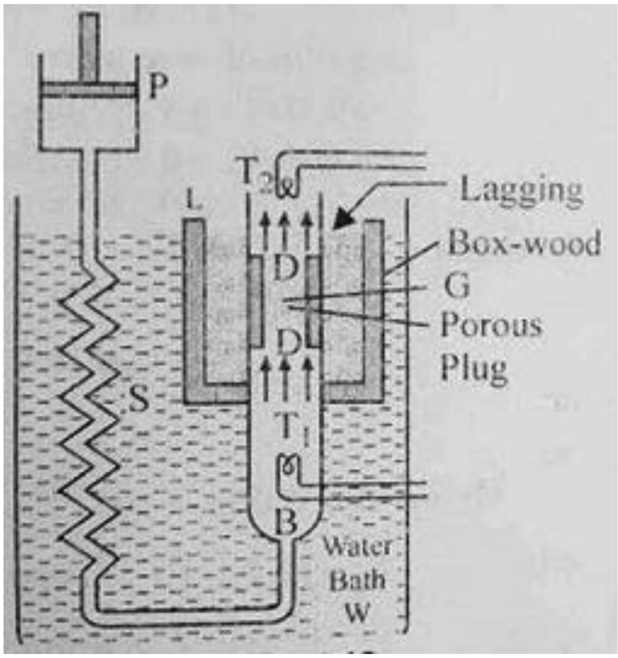


Fig. 3.1. Porous plug Experiment setup.

On passing through the porous plug, the volume of the gas increases against the atmospheric pressure. As there is no loss or gain of heat during the whole process, the expansion of the gas takes place adiabatically. The initial and final temperatures are noted by platinum resistance thermometers T1 & T2.

Experimental Results

A simple arrangement of porous plug experiment is shown in Fig.3.1 .The behavior of large number of gases was studied at various inlet temperatures of the gas and the results are as follows:

(1) At sufficiently low temperatures, all gases show a cooling effect.
(2) At ordinary temperatures, all gases except hydrogen and helium show cooling effect. Hydrogen and Helium show heating effect.
(3) The fall in temperature is directly proportional to the difference in pressure on the two sides of porous plug.
(4) The fall in temperature for a given difference with rise in the initial temperature of the gas. It was found that the cooling effect decreased with the increase of initial

temperature and becomes zero at a certain temperature and at a temperature higher than the temperature instead of cooling heating was observed. This particular temperature at which the Joule –Thomson effect changes sign is called temperature of inversion.

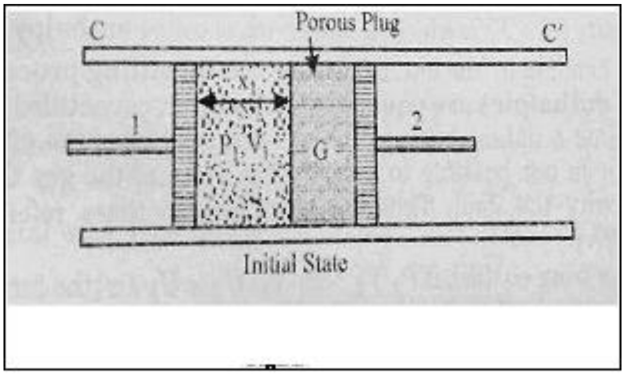


Fig. 3.2. Porous plug

Theory of Porous Plug experiment

The gas is passed through the porous plug from the high pressure side to the low pressure side. Consider one mole of the gas. Let P_1, V_1 and P_2 ,V_2 represent the pressure and volume of the two sides of the porous plug.

Let dx be the distance through which each piston moves to the right.

The work done on the gas by the piston A = $P_1A_1dx = P_1V_1$

The work done by the gas on the piston B = $P_2A_2dx = P_2V_2$

Net external work done by the gas = $P_2V_2 – P_1V_1$

Let w be the work done by the gas in separating the molecules against their inter-molecular attraction.

Total amount of work done by the gas = $(P_2V_2 – P_1V_1) + w$

There are three cases depending upon the initial temperature of gas.

(i) Below the Boyle temperature: $P_2V_2 < P_1V_1$

$P_2V_2 – P_1V_1$ is +ve and w must be either positive or zero. Thus, a net +ve work is done by the gas.

Hence, there must be a cooling effect.

(ii) At the Boyle temperature: $P_2V_2 = P_1V_1$ $P_2V_2 - P_1V_1 = 0$.

The total work done by the gas in this case is w. Therefore, cooling effect at this temperature is only due to the work done by the gas in overcoming inter-molecular attraction.

(iii) Above the Boyle temperature: $P_2V_2 > P_1V_1$ $P_2V_2 - P_1V_1$ is –ve.

Thus, the observed effect will depend upon whether ($P_2V_2 - P_1V_1$) is greater than or less than w.

If w > ($P_2V_2 - P_1V_{1,}$), cooling will be observed.
If w < ($P_2V_2 - P_1V_{1,}$), heating will be observed.
Thus, the cooling or heating of a gas depends on the deviation from Boyle's law and work done in overcoming inter-molecular attraction.

Definition of temperature of inversion: The temperature at which the Joule-Thomson effect change sign (ie. The cooling effect becomes the heating effect) is called the temperature of inversion. (T_i). At this temperature (T_i), there is neither cooling nor heating.

Relation between temperature of inversion (T_i) and critical temperature (T_c).

Let (T_i) be the critical temperature of a gas.
Then, its temperature of inversion $\mathbf{T_i}$ is = 6.75 T_c
Thus, the temperature of inversion of a gas is much higher than its critical temperature.

Liquefaction of Gases

Introduction

A gas goes into liquid and solid forms as the temperature is reduced. Thus the processes of liquefaction of gases and solidification of liquids are involved in the production of low temperatures. Andrews's experiment showed that if a gas is to be liquefied by merely applying pressure on it, it has to be cooled below its critical temperature. Since the critical temperatures of carbon dioxide and sulphur dioxide and ammonia are higher than room temperature, these gases can be liquefied at room temperature without precooking simply by increasing the pressure. Joule Thomson experiment is a very important technique to liquefy gases. The cooling produced depends on the difference of pressure on the two sides of the porous plug and the initial temperature.

Linde’s process

Linde’s process is known as adiabatic expansion of compressed gas.

Principle

The process is based upon Joule – Thomson Effect, which states, “When a gas under high pressure is allowed to expand adiabatically through a fine hole into a region of low pressure, it is accompanied by cooling.

The term ‘adiabatically’ means that apparatus is perfectly insulated so that no heat is lost to or gained from the surroundings. An obvious reason for the cooling is that when the gas expands from a region of high pressure to the region of low pressure, the intermolecular distance increases. Some work is to be done for increasing intermolecular distances. This is done on the cost of Kinetic energy of the gas. Thus, the Kinetic energy of the gas decreases and therefore the temperature falls.

Procedure

The process based upon the above principle is known as ***Linde’s Process***. The apparatus used is shown in figure on side with names of different parts. This apparatus was used by **Linde** to liquefy air.

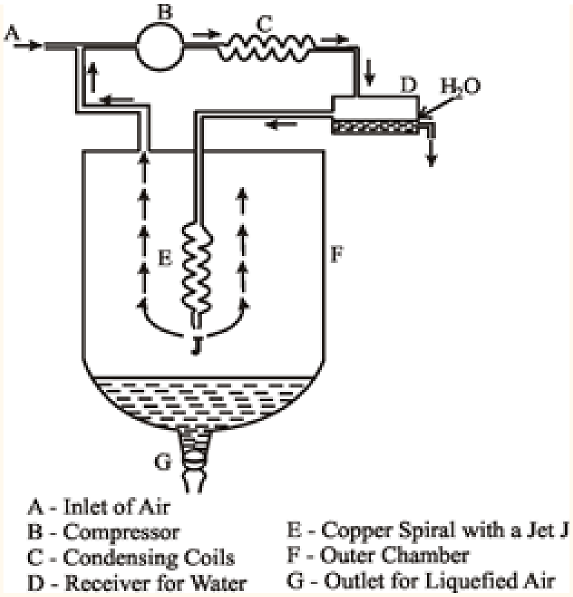


Fig. 3.3. Linde Liquifier

The air is first compressed to about 200 atmospheres in the compressor and then passed through the condensing coils. As a result, the air is cooled and the water vapours present condense to form the water which is removed from receiver. The dry air is then passed through the spiral copper tube which terminates into a jet .The air expands through the jet into the chamber where pressure is about 50 atmospheres. Thus, as a result of *Joule-Thomson effect*, the air is cooled. As this cooled air moves up, it further cools the incoming air. The cooled air is sent to the compressor again and the process is repeated a number of times till ultimately the air is cooled to such an extent that it liquefies. The liquefied air gets collected at the bottom of the outer chamber and can be drawn off. Any uncondensed air is re-circulated.

Applications of Liquefaction

- Liquefaction processes are used for scientific, industrial and commercial purposes. Many gases can be put into a liquid state at normal atmospheric pressure by simple cooling;
- A few, such as carbon dioxide, require pressurization as well. Liquefaction is used for analyzing the fundamental properties of gas molecules (intermolecular forces), or
- For the storage of gases, for example: In **refrigeration** and **air conditioning**. There the gas is liquefied in the ***condenser***, where the **heat of vaporization** is released, and

evaporated in the ***evaporator***, where the heat of vaporization is absorbed.

- Ammonia was the first such refrigerant, and is still in widespread use in industrial refrigeration.
- But it has largely been replaced by compounds derived from petroleum and halogens in residential and commercial applications.
- Liquid oxygen is provided to hospitals for conversion to gas for patients with breathing problems, and
- Liquid nitrogen is used in the medical field for cryosurgery, to preserve samples.
- Liquefied chlorine is transported for eventual solution in water, after which it is used for water purification, sanitation of industrial waste, sewage and swimming pools, bleaching of pulp and textiles and manufacture of carbon tetrachloride, glycol .
- Liquefaction of helium (^{4}He) with the pre-cooled Hampson–Linde cycle led to a Nobel Prize for Heike Kamerlingh Onnes in 1913. At ambient pressure the boiling point of liquefied helium is 4.22 K (−268.95 °C). Below 2.17 K liquid ^{4}He becomes a superfluid (Nobel Prize 1978, Pyotr Kapitsa) and shows characteristic properties such as heat conduction through second sound, zero viscosity and the fountain effect among others.
- The liquefaction of air is used to obtain nitrogen, oxygen, and argon and other atmospheric noble gases by separating the air components by fractional distillation in a cryogenic air separation unit.

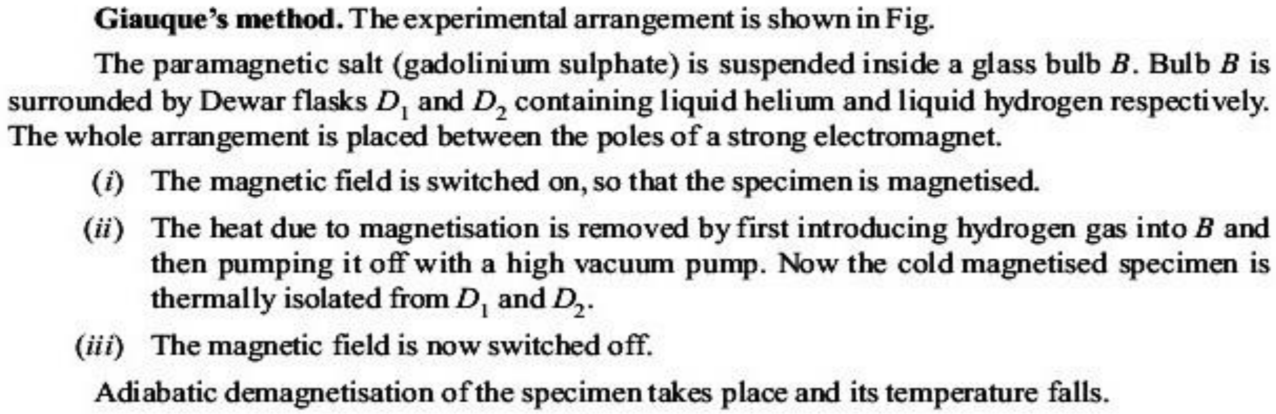
Adiabatic process

An adiabatic process is a process in which change in volume and pressure of a given gas takes place in completer thermal isolation. During an adiabatic process, no heat enters or leaves the system, but the temperature changes.

Adiabatic demagnetisation

Generally, the method used to reach the very low temperature of about 10^{-4} K is adiabatic demagnetisation. In this method the paramagnetic samples such as Gadolinium sulphate is placed surrounding the gas sample and cooled to about 1K along with the gas in any one of the cooling methods. The paramagnetic sample used in this method is suddenly magnetised by the application of strong magnetic field. This magnetisation (ordering of molecular magnets) occurs while the sample surrounds the cooled gas and has thermal contact with the walls of the container. When the magnetic field is suddenly removed, demagnetisation occurs which brings in a disordered state of the molecular magnets. To reach this state thermal energy is taken away from the cooled air such that its temperature gets further lowered. By this technique, temperature as low as zero Kelvin can be reached.

Giauque's Method



Giauque's method. The experimental arrangement is shown in Fig.

The paramagnetic salt (gadolinium sulphate) is suspended inside a glass bulb B. Bulb B is surrounded by Dewar flasks D_1 and D_2 containing liquid helium and liquid hydrogen respectively. The whole arrangement is placed between the poles of a strong electromagnet.

(*i*) The magnetic field is switched on, so that the specimen is magnetised.

(*ii*) The heat due to magnetisation is removed by first introducing hydrogen gas into B and then pumping it off with a high vacuum pump. Now the cold magnetised specimen is thermally isolated from D_1 and D_2.

(*iii*) The magnetic field is now switched off.

Adiabatic demagnetisation of the specimen takes place and its temperature falls.

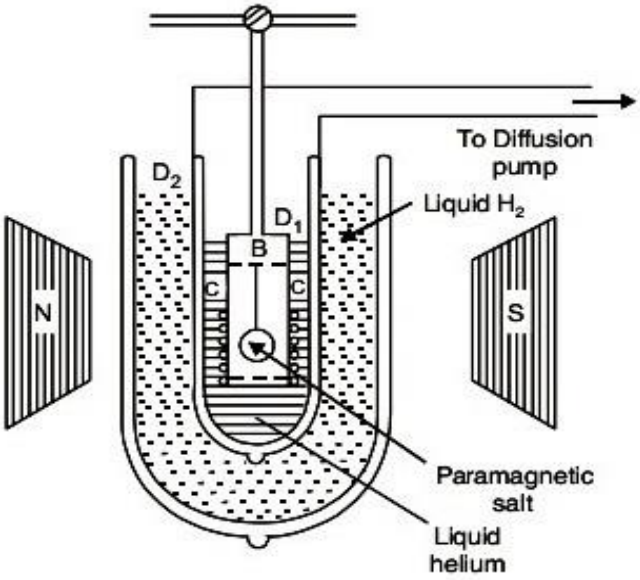


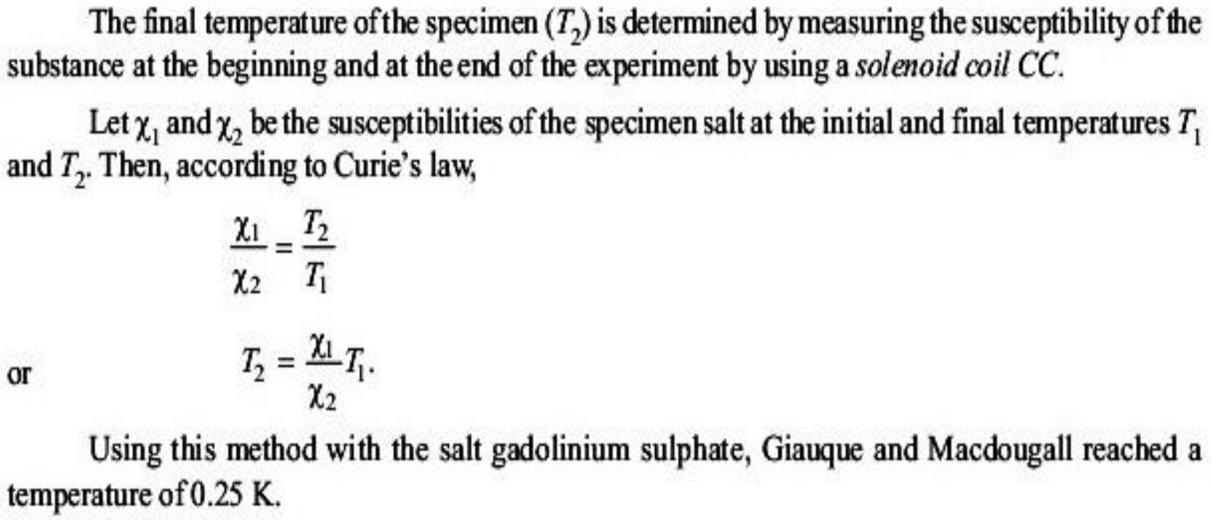
Fig. 3.4. Giauque's Method

Procedure

- First, the sample to be cooled is allowed to touch a cold He reservoir (which has a constant temperature of around 3-5 K)
- Allow the sample to attain thermal equilibrium with the cold reservoir(say 5K).
- A magnetic field is induced in the region of the sample.(With the help of N & S Pole) and the magnetic field strength is increased (Magnetized).
- This causes the entropy of the sample to decrease, because the system becomes more ordered as the particles align with the magnetic field. The temperature of the sample is still the same as that of the cold reservoir at this point.
- Then the sample is isolated from the cold reservoir, and the magnetic field strength is reduced (Demagnetized).
- Its temperature drops in reaction to the reduction in the magnetic field strength. If the sample was already at a fairly low temperature, this temperature decrease can be ten-fold or greater.
- This process can be repeated, permitting the sample to be cooled to very low temperatures (0.25K).

Later on, Hass and Weirsma obtained still lower temperature of 0.0034K using Potash chrome alum in the place of gadolinium sulphate. Also just for your information, though this method is reliable, safe and eco-friendly but this isn't the only way to achieve such low temperatures. Much low temperatures can be attained by an analogous means called adiabatic nuclear demagnetization. This process relies on aligning nuclear dipoles (arising from nuclear spins), which are at least 1,000 times smaller than those of atoms. With this process, temperature of the ordered nuclei as low as 16 micro-degrees (0.000016 degree) absolute have been reached.

Temperature Determination



The final temperature of the specimen (T_2) is determined by measuring the susceptibility of the substance at the beginning and at the end of the experiment by using a *solenoid coil CC*.

Let χ_1 and χ_2 be the susceptibilities of the specimen salt at the initial and final temperatures T_1 and T_2. Then, according to Curie's law,

$$\frac{\chi_1}{\chi_2} = \frac{T_2}{T_1}$$

or

$$T_2 = \frac{\chi_1}{\chi_2} T_1.$$

Using this method with the salt gadolinium sulphate, Giauque and Macdougall reached a temperature of 0.25 K.

$$dT = \Delta T = -CVBi^2/C_B 2Ti$$

Where,

C – Curie constant

C_B –Spec.heat at constant field

T_i – Initial Temperature

V – volume

B_i – initial magnetic field

Negative sign indicates the fall in temperature.

Practical applications of low temperatures Applications in pure sciences

(a) Separation of the constituents of air
(b) Production of high vacuum
(c) Calorimetric work
(d) Study of properties of the upper atmosphere
(e) Study of properties of substances at low temperatures
(f) Applications in pure sciences

Applications in Industry

(a) Liquid oxygen stored in cylinders are used In hospitals for artificial respiration.
(b) Liquid oxygen is used in the manufacture of explosives.
(c) Argon is used in ‘gas filled’ electric lamps.
(d) Neon is employed in discharge tube required for illumination and advertising sign boards.
(e) Liquid air is importance in separation and purification o gases.
(f) The most important application of liquefied gases is in the working of refrigerating and air conditioning machines.

Refrigerating mechanism

Definition

Refrigeration is defined as the production of temperature lower than that of the surroundings and maintains that temperature within the boundary of s given space.

Electrolux refrigerator

Principle

The principle used in the production of low temperature is by the evaporation of a suitable liquid under reduced pressure. The liquid ammonia is made to evaporate under reduced pressure in an atmosphere of hydrogen. Fig.2.7 shows the schematic diagram of an Electrolux refrigerator

Construction and Working:

It consists of four essential parts

(a) **Generator:** Ammonia gas is generated by heating the strong aqueous solution of ammonia in it by means of a heater H.
(b) **Condenser**: It is cooled by water circulating round it. So the gaseous ammonia condenses to the liquid form
(c) **Evaporator:** The evaporator is inside the space desired to be cooled. Here the liquid ammonia gets evaporated.
(d) **Absorber**: The absorber is surrounded by a cold water jacket. Here, the gaseous

ammonia from the evaporator gets absorbed by the weak aqueous solution from the generator.

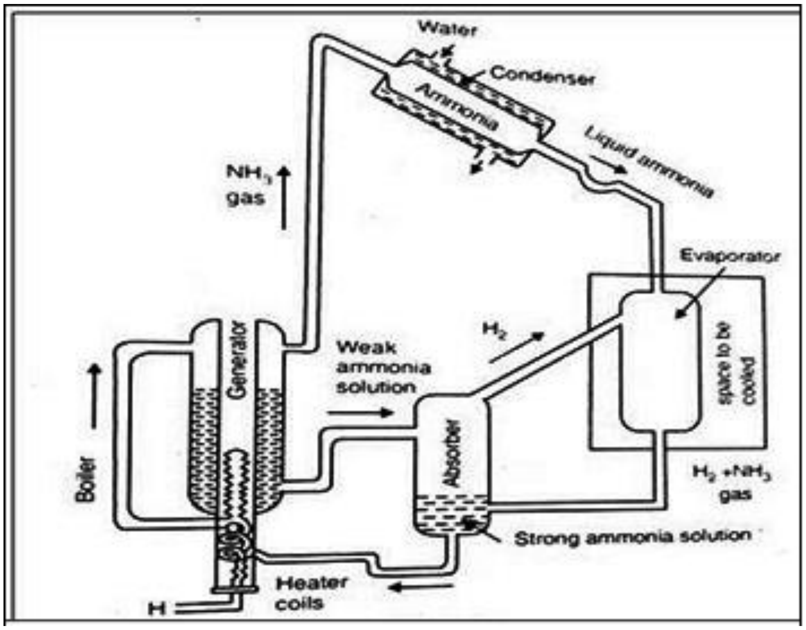


Fig. 3.5. Electrolux refrigerator

Working:

The weak ammonia solution is forced into absorber. The strong ammonia solution goes into boiler. The gaseous ammonia enters the condenser and it is cooled and condensed. Liquid ammonia enter the evaporator and is mixed with hydrogen. Hydrogen reduces the partial pressure of ammonia below its saturation point and causes evaporation. The evaporator is surrounded by the compartment to be cooled. When ammonia evaporates under reduced pressure, the latent heat of vapourisation is taken from surrounding compartment. In this way, the compressor is cooled. Hydrogen and gaseous ammonia leave the evaporator and enters the absorber. The ammonia gas is dissolved and hydrogen gas rises through the absorber and enters the evaporator. The strong ammonia solution is forced up into the boiler again. The process continues and a sufficiently low temperature is produced in the compartment to be cooled.

Advantages: No compressor is required and the circulation of liquid and gas is automatic.

Air conditioning

Definition

Air conditioning may be defined as a method of controlling the weather conditions within the limited space of a room, or a hall, so that one may have the maximum comfort.

Air conditioner

Air conditioner cools the air, removes the dust and controls the humidity of the atmosphere. The important actions involved in the operation of air conditioning system are: (a) Temperature control (b) Humidity control (c) Air filtering, cleaning and purification. (d) Air movement and circulation.

Window air conditioner (room air conditioner)

This is suitable for cooling rooms in summer. It consists of three parts.
It consists of two units (1) indoor unit (2) outdoor unit.[Fig.2.9] An indoor unit consists of an evaporator, fan, air filter, control panel, trays etc. The outdoor unit consists of a motor driven compressor, condenser, fan, trays, etc.

Working:

The condenser and evaporator are connected through capillary tube. The liquid refrigerant collects in the lower half of the condenser and from there flows via capillary tube into the evaporator. Pressure inside the evaporator is very low. So, the liquid refrigerant evaporates rapidly by picking up hear fro evaporator surface which is consequently cooled. The motor driven fan F2 draws air from inside the room through a suitable filter and force it to flow over the evaporator. The air so cooled goes back to the room. An adjustable thermostat mounted on the control panel provides the necessary temperature control. The low pressure refrigerant is sucked back into the compressor. From the compressor, the refrigerant is forced into the conditioner to be cooled and condensed into a liquid. The cycle is repeated. Compressor and condenser are connected to fan F1 that drives air in from outside, circulates it over the condenser where it is heated up and hen discharge it so outside, the moisture which collects on the evaporator is drained into a drip pan kept under the evaporator.

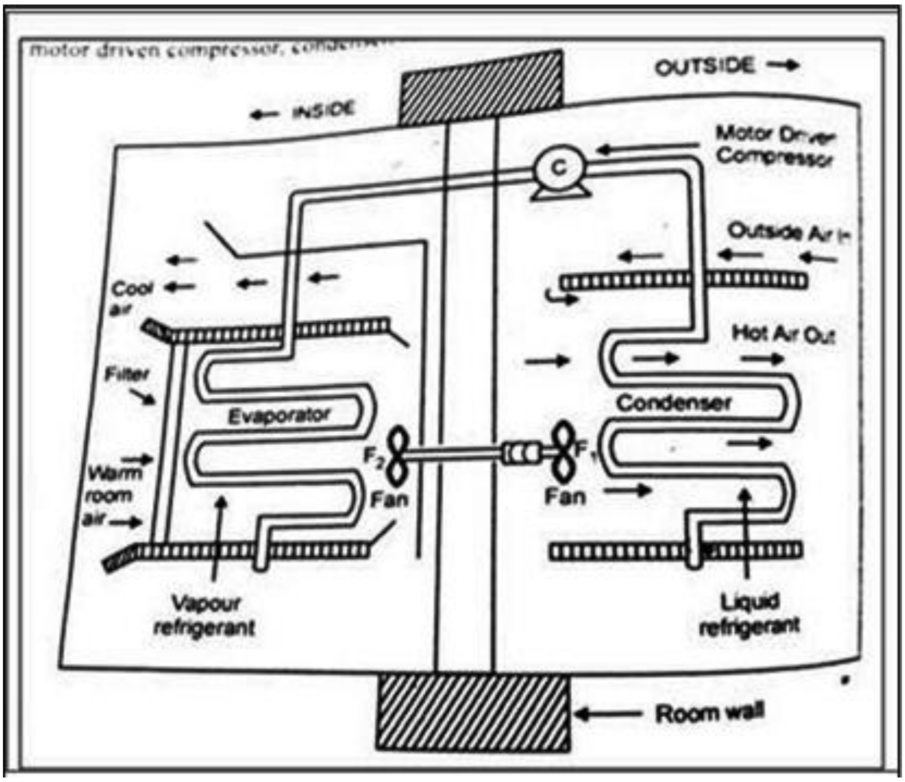


Fig. 3.6. Window air conditioner

Difference between AC and Refrigerator

1. Design of AC and Refrigerator

- Refrigerators are designed with condenser, compressor, and evaporator in one set unit, and as they push away the heat the outer surface of refrigerator is getting warm.
- In AC the compressor and condenser are in separate unit from the evaporator.

2. Purpose of AC and Refrigerator

- AC is used for maintaining the temperature and humidity of the air; cooling or heating.
- Refrigerators are used in cooling and freezing of products (mostly food).

The ozone layer

- The ozone layer is a concentration of ozone molecules in the stratosphere.
- The region of the atmosphere above the troposphere. The stratosphere extends from about 10km to about 50km in altitude.

- Commercial airlines fly in the lower stratosphere. The stratosphere gets warmer at higher altitudes.
- In fact, this warming is caused by ozone absorbing ultraviolet radiation. Warm air remains in the upper stratosphere, and cool air remains lower.

- Stratospheric ozone is a naturally occurring gas that filters the sun's ultraviolet radiation.
- A diminished ozone layer allows more UV radiation to reach the Earth's surface.
- For people, overexposure to UV rays can lead to skin cancer, cataracts, and weakened immune systems.
- Increased UV can also lead to reduced crop yield and disruptions in the marine food chain.

Freon

Chlorofluorocarbons or CFCs (also well-known as Freon) are non-toxic, non-flammable and non-carcinogenic (not cause cancer).

- They mainly contain fluorine atoms, carbon atoms and chlorine atoms.
- The 5 main CFCs include:

  CFC-11 (trichlorofluoromethane - CFCl3),
  CFC-12 (dichloro-difluoromethane - CF2Cl2),
  CFC-113 (trichloro-trifluoroethane - C2F3Cl3),
  CFC-114 (dichloro-tetrfluoroethane - C2F4Cl2), and
  CFC-115 (chloropentafluoroethane - C2F5Cl).

The lifetime of CFCs in the atmosphere is about **20 to 100 years**, and **one chlorine atom may destroy more than 100,000 ozone molecules before it is transformed into a non-reactive species.** Although the emissions of CFCs around the developed world have largely controlled due to international conformity, the damage to the **stratospheric ozone layers** are still not stopped.

Effects of $CF_2\,Cl_2$ on ozone layer

In the atmosphere, about 50 km above the surface of the earth, the ozone molecules (O_3) form an umbrella. It prevents the penetration of harmful ultra violet radiation from the sun and thus protects the life on the earth. It is now feared that there is danger of holes appearing on the ozone umbrella. This is caused by the use of *freons* and other *chlorine-fluorine-carbons* as refrigerents in domestic refrigerators and other cold storage facilities. They destroy ozone molecules as a result of photochemical reactions (Fig. 3.16). Fig. 3.16 shows how breakdown products of CFCs attack atmospheric ozone molecules.

The compound $CF_2\,Cl_2$, which is widely used as refrigerant, decomposes to form chlorine atoms when exposed to UV radiation at 200 *nm*.

$$CF_2\,Cl_2(g) \rightarrow CF_2\,Cl(g) + Cl(g)$$

Chlorine atom strips an atom from the molecule of ozone turning it into ordinary oxygen.

$$Cl + O_3 \rightarrow ClO + O_2$$

The chlorine goes on to repeat the process, and in this way one CFC molecule can destroy thousands of molecules of ozone.

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DEPARTMENT OF PHYSICS

Thermal Physics – SPH1211

IV. Conduction and Radiation

Introduction

In conduction process, heat is transmitted from one point to the other through the substance without the actual motion of the particles. When one end of a brass rod is heated in flame the other end gets heated in course of time. In this case the molecules at the hot end vibrate with higher amplitude (K.E) and transmit the heat energy from one particle to the next and so on. Heat is said to be conducted through the rod. However, particles in the body remain in their position and so not move. Thus conduction is the transference of heat from the hotter part of a body to the colder part without the motion of the particles in the body.

Metals are good conductors of heat and wood, glass, brick, cotton, wool, rubber are bad conductors of heat. For example 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. Also 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 (higher temperature) to the blade to low temperature. Therefore it appears colder. Since wood is a bad conductor of heat, does not allow heat to flow to the handle.

Convection is the process in which heat is transmitted from one place to another by the actual movement of the heated particles. It is prominent in the case of liquids and gases. Land and sea breezes and trade winds are formed due to convection. Suppose water in a container is heated from below. The layer of water in the bottom gets heated, its density decreases and it comes up transferring heat. In this case, the transference of heat from the bottom of the vessel to the top of the vessel is by convection.

Radiation is the process in which heat in transmitted from one place to the other directly without the necessity of the intervening medium. We get heat radiations directly from the sun without affecting the intervening medium. Heat radiation can pass through vacuum. Also it forms a part of electromagnetic spectrum.

Thermal conductivity

Thermal conductivity or heat conductivity is the property of a material to conduct heat.

Examples of metals are iron, copper etc. Examples of non-metals are aluminium oxide, diamond.

Co-efficient of thermal conductivity:

Consider a slab of material of length x and area of cross section A [Fig. 4.1]. The opposite faces of the slab are maintained at temperatures θ_1 and θ_2 where $\theta_1 > \theta_2$. Assume that no heat is lost from the sides of the slab.

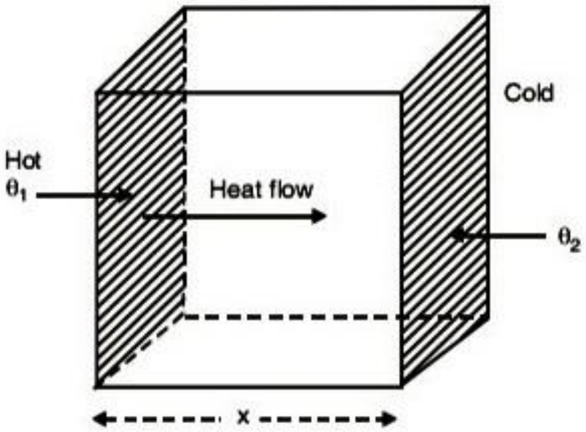


Fig. 4.1

The quantity of heat Q conducted from one face to the other is

(*i*) *directly proportional to the area of cross-section A.*

(*ii*) *directly proportional to the difference of temperature between the ends* $(\theta_1 - \theta_2)$,

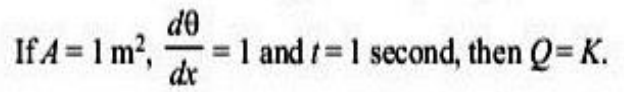
(*iii*) *directly proportional to the time of conduction t, and*

(*iv*) *inversely proportional to the length x.*

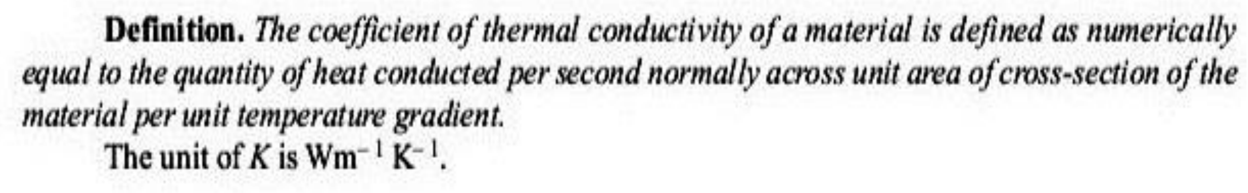
$$\text{or} \quad Q \propto \frac{A(\theta_1 - \theta_2)t}{x} \quad \text{or} \quad Q = KA\left(\frac{\theta_1 - \theta_2}{x}\right)t$$

Here K is a constant called the *coefficient of thermal conductivity* of the material of the slab.

The quantity $(\theta_1 - \theta_2)/x$ represents the rate of fall of temperature with respect to distance. It is called the *temperature gradient*. Consider a slab of infinitesimal thickness dx, across which there is a temperature difference $d\theta$. Then the temperature gradient is $\frac{d\theta}{dx}$.

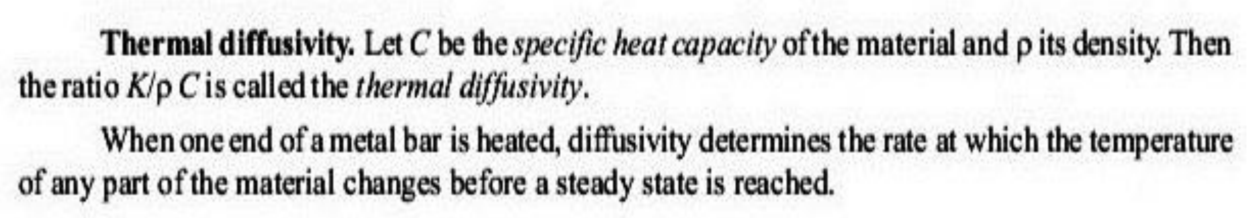


If $A = 1\ \text{m}^2$, $\dfrac{d\theta}{dx} = 1$ and $t = 1$ second, then $Q = K$.



Definition. *The coefficient of thermal conductivity of a material is defined as numerically equal to the quantity of heat conducted per second normally across unit area of cross-section of the material per unit temperature gradient.*

The unit of K is $\text{Wm}^{-1}\ \text{K}^{-1}$.



Thermal diffusivity. Let C be the *specific heat capacity* of the material and ρ its density. Then the ratio $K/\rho C$ is called the *thermal diffusivity*.

When one end of a metal bar is heated, diffusivity determines the rate at which the temperature of any part of the material changes before a steady state is reached.

Thermal Conduction-Kinetic exchange of energy

- Thermal conduction: is the kinetic exchange of energy between two objects in physical contact.
- In this scenario, one object has a higher temperature than the other.
- Heat Energy will diffuse from the hotter object to the cooler object until thermal equilibrium is reached as described in the second law of thermodynamics.
- This conduction will continue until a state of thermal equilibrium is reached between the object and its surroundings. At this point, the object is no longer "cold."

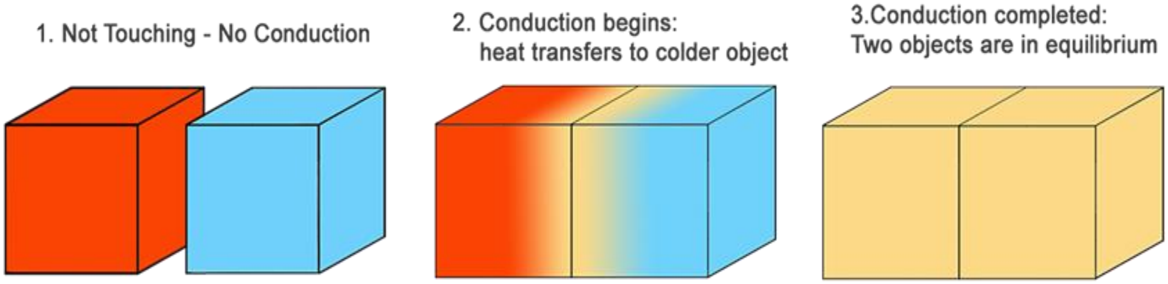


Fig. 4.2. Kinetic exchange of energy

Thermal Conductivity of a bad conductor – Lee’s Disc Method

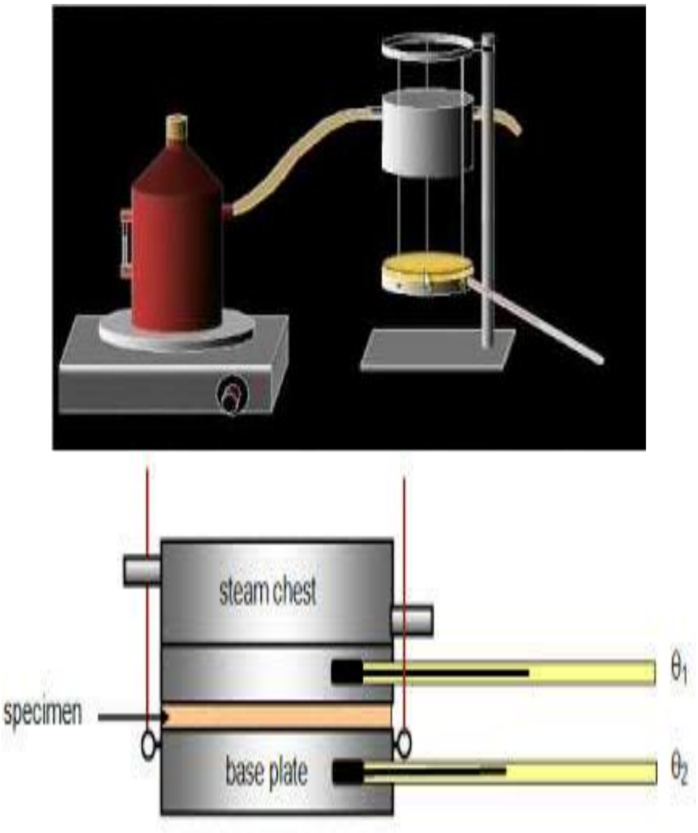


Fig. 4.3 Experimental setup of Lee’s Disc method

The given **bad conductor (B)** is placed in between the **steam chamber (S)** and the **metallic Lee’s disc (C),** provided the bad conductor, steam chamber and the Lee’s disc should be of same diameter. Holes are provided in the steam chamber and the metallic Lee’s disc in which the thermometers are inserted to measure the temperatures. The total arrangement is hanged over the stand as shown in fig.

Working

- Steam is passed through the steam chamber till the **steady state is reached** i.e., the thermometer show constant temperature.
- Let the temperature of the steam chamber (hot end) and the metallic disc (cold end) be θ_1 and θ_2 respectively.

- Let ‘**t**’ be the thickness of the bad conductor, ‘**m**’ be the mass, ‘**S**’ be the specific heat capacity, ‘**r**’ is the radius and ‘**h**’ be the height of the metallic **Lee’s disc** then,

  Amount of heat conducted by the bad conductor *per second* =

$$\frac{K\,A\,(\theta_1-\theta_2)}{t}$$

$$= \boxed{\frac{K\,\pi r^2\,(\theta_1-\theta_2)}{t} \quad \dashrightarrow (1)}$$

- The amount of heat lost by the disc *per second*

$$= m \times S \times \text{Rate of cooling} = m \times S \times R_c \text{ ------(2)}$$

Under steady state,

We can write eqn. (1) = eqn. (2)

$$\frac{K\,\pi r^2\,(\theta_1-\theta_2)}{t} = m\,S\,Rc$$

$$\boxed{K = \frac{m\,S\,t\,Rc}{\pi r^2\,(\theta_1-\theta_2)} \quad \dashrightarrow (3)}$$

To find the rate of cooling

- The bad conductor is removed and the steam chamber is directly placed over the disc and heated.
- When the temperature of the disc attains 5°C higher than θ_2, the steam chamber is removed.
- The disc is allowed to cool, as shown in the fig.
- Note time taken for the fall in temperature

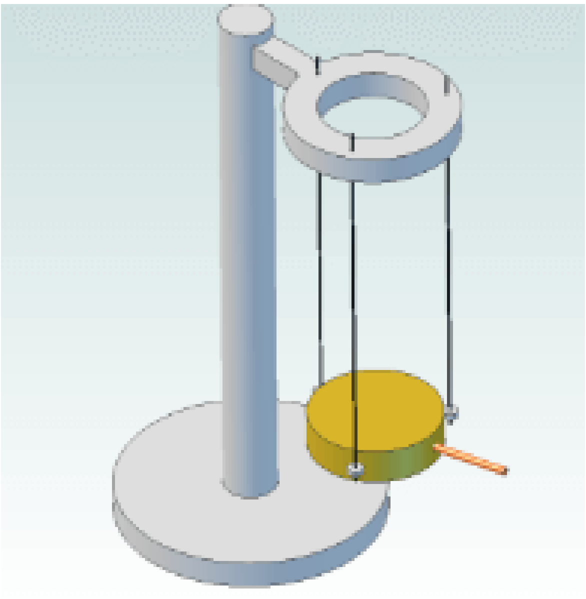


Fig. 4.4. Rate of Cooling

- A graph is plotted taking time along ‘x’ axis and temperature along ‘y’ axis.
- The rate of cooling $\frac{d\theta}{dt}$ for the disc is found from the graph.
- The rate of cooling is directly proportional to the surface area exposed.

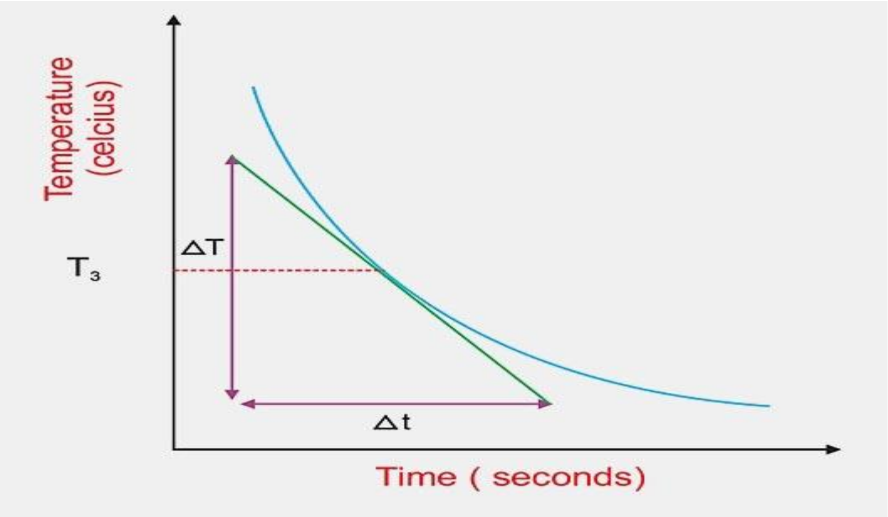


Fig. 4.5. Cooling Curve

Case (i):

When Steam chamber and bad conductor are placed over Lee's disc, the heat lose takes place from the bottom surface of the disc of area (πr^2) and the sides of area ($2 \pi r h$).

$$\therefore R_c = \pi r^2 + 2\pi r h$$

$$R_c = \pi r (r + 2h) \qquad \text{-----------} \quad (4)$$

Case (ii):

When the Lee's disc is alone, heat is lost from the bottom of area (πr^2), top surface of the disc of area (πr^2) and also through the sides of the disc area ($2 \pi r h$).

$$\left(\frac{d\theta}{dt}\right)_{\theta_2} = \pi r^2 + \pi r^2 + 2 \pi r h$$

$$= 2 \pi r (r + h) \dashrightarrow \quad (5)$$

From eqns (4) and (5),

$$\frac{R_c}{\left(\frac{d\theta}{dt}\right)_{\theta_2}} = \frac{\pi r (r + 2h)}{2 \pi r (r + h)}$$

$$R_c = \frac{(r + 2h)}{2 (r + h)} \left(\frac{d\theta}{dt}\right)_{\theta_2} \dashrightarrow (6)$$

Substituting eqn. (6) in eqn. (3),

$$\boxed{K = \frac{m\, s\, t \left(\frac{d\theta}{dt}\right)_{\theta_2} (r + 2h)}{\pi r^2 (\theta_1 - \theta_2)\, 2\, (r + h)} W\, m^{-1} K^{-1} \qquad \dashrightarrow (7)}$$

Thermal conductivity of the given bad conductor can be determined from the above formula.

Blackbody radiation

"Blackbody radiation" or "cavity radiation" refers to an object or system which absorbs **all radiation** incident upon it and re-radiates energy which is characteristic of this radiating system only, not dependent upon the type of radiation which is incident upon it.

The radiated energy can be considered to be produced by **standing wave or resonant modes** of the cavity which is radiating.

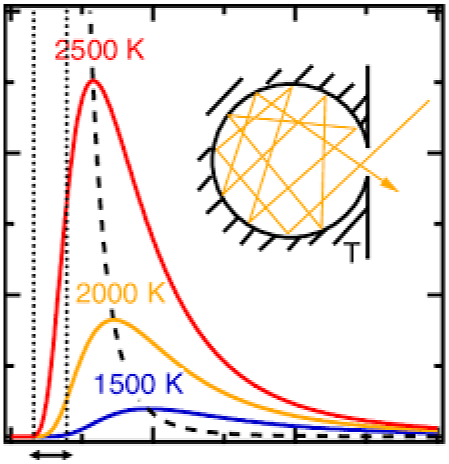


Fig. 4.6. Black body radiation

- All normal matter at temperatures above absolute zero **emits** electromagnetic radiation,
- which represents a conversion of a body's internal thermal energy into electromagnetic energy, and is therefore called *thermal radiation*.
- Conversely, all normal matter ***absorbs*** electromagnetic radiation to some degree.
- **An object that absorbs ALL radiation falling on it, at all wavelengths, is called a blackbody**.

When a blackbody is at a uniform temperature, its emission has a characteristic frequency distribution that depends on the temperature. This emission is called ***blackbody radiation***.

- A room temperature blackbody appears black,
- as most of the energy it radiates is **infra-red** and cannot be perceived by the human eye.

- Because the human eye cannot perceive light waves at lower frequencies, a black body, viewed in the dark at the lowest just faintly visible temperature, subjectively appears **grey**, even though its objective physical spectrum peaks in the infrared range.
- When it becomes a **little hotter**, it appears **dull red**. As its **temperature increase**s further it becomes **yellow, white**, and ultimately **blue-white**.
- When heated, all objects emit electromagnetic radiation whose wavelength (and color) depends on the temperature of the object.
- A relatively **low-temperature object**, such as a horseshoe forged by a blacksmith, **appears red**, whereas a **higher-temperature object**, such as the surface of the sun, appears **yellow or white**.
- Blackbody radiation has a characteristic, continuous frequency spectrum that experimentally depends only on the body's temperature.

A body emits radiation at a given temperature and frequency *exactly* as well as it absorbs the same radiation.

Perfect black body

A perfect black body is one which absorbs and emits in all the radiations (corresponding to all wavelengths) that fall on it. The radiation given out by a perfect black body is called Black body radiation.

Construction of Black body

- Anybody at any temperature above absolute zero will radiate to some extent, the intensity and frequency distribution of the radiation depending on the detailed structure of the body. To begin analyzing heat radiation, we need to be specific about the body doing the radiating: *the simplest possible case is an idealized body which is a perfect absorber, and therefore also (from the above argument) a perfect emitter.*
- In 1859 Kirchhoff had a good idea: a small hole in the side of a large box is an **excellent absorber**, since any radiation that goes through the hole bounces around inside, a lot getting absorbed on each bounce, and has little chance of ever getting out again.

- So, we can do this *in reverse*: have an oven with a tiny hole in the side, and presumably the radiation coming out the hole is as good a representation of a **perfect emitter** as we're going to find Figure.

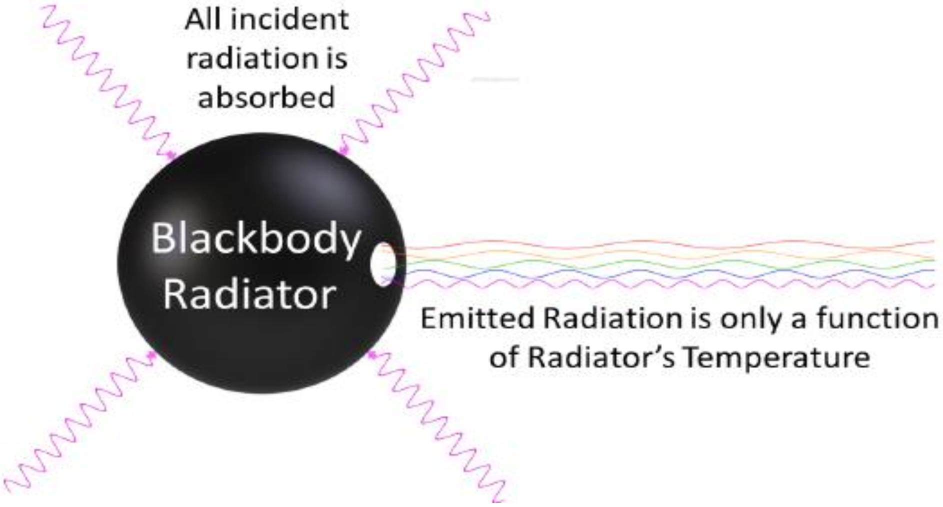


Fig. 4.7. Blackbody radiator

Black body radiation sources

- All objects are black body radiators, the amount of radiation and position in the spectrum depends on the object temperature as well its emissivity.
- Some examples of blackbody radiators that emit visible light or whose radiation is used for other processes include the electric heaters, incandescent light bulbs, stoves, the sun, the stars, night vision equipment, burglar alarms, warm-blooded animals, etc.

Selecting a black body radiation source

- The blackbody radiators for commercial applications almost approach an ideal blackbody and are used for a variety of applications. The choice of the blackbody radiation sources depends on the temperature, type of the application and environment.

The major factors considered include;

- Temperature
- Emissivity
- Size of Emissive area
- Warm-up time
- Cooling time
- Regulation stability

The temperature depends on the object under test. For example, a low-temperature blackbody is suitable for applications such as calibrating IR sensor that looks at buildings, vehicles, or human bodies.

Applications

- The blackbodies are used for lighting, heating, security, thermal imaging, as well as testing and measurement applications.
- Since the intensity of the energy at any temperature and wavelength and can be determined using the Planck Law of radiation.
- A blackbody radiation source with a known temperature, or, whose temperature can be measured, is usually used for calibrating and testing the radiation thermometers.

Energy density

- Energy density is the amount of energy stored in a given system (or region of space)per unit volume. It may also be used for energy per unit mass, though the accurate term for this is **specific energy**.
- **In SI base units:** $kg \cdot m^{-1} s^{-2}$
- **SI unit:** J/m^3

Spectral energy Density

At a certain temperature the average energy density between wavelength λ and $\lambda + d\lambda$ is given by $u_\lambda d\lambda$. where $u - \lambda$ is called spectral energy density. the relation between u and u_λ is

$$U = \int_0^\infty u_\lambda d\lambda \tag{4}$$

One can use u_ν instead of u_λ . Which is defined between frequency range ν and $\nu + d\nu$.

Emissive Power

Total radiation energy emitted by unit surface area of the blackbody at a certain temperature is called Emmisive power of the blackbody. It is denoted by E.

Spectral Emissive Power

Total radiated energy between λ and $\lambda + d\lambda$ range emitted by unit surface area of blackbody at certain temperature is given by

$$E_\lambda d\lambda$$

Where E_λ is called spectral emissive power of blackbody. It is clear from the definition that

$$E = \int_0^\infty E_\lambda d\lambda \tag{5}$$

If we know E_λ at a certain temperature we can find u_λ by the following relation

$$U = \frac{4}{c} E_\lambda \tag{6}$$

Where c is the speed of light.

Characteristics of Black Body Radiation

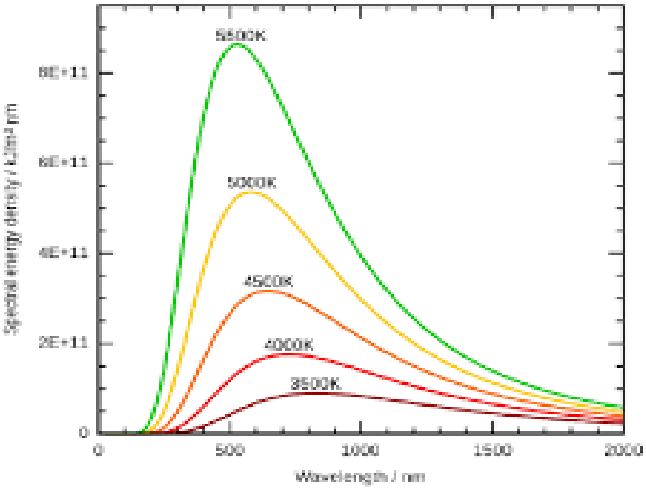


Fig. 4.8. Characteristics Curve of Black Body Radiation

1. As it is clear from the figure the graph is continuous which means that at every temperature radiation for all wavelengths emitted but the spectral emissive power is different for different wavelength.
2. Spectral energy density $E\lambda$ for each λ increases with temperature.
3. At a particular temperature at first $E\lambda$ increases with λ but after reaching a

certain highest value it goes on decreasing. That highest value is denoted by E_{λ_m} and the wavelength at which E_λ is maximum is denoted by λ_m

4. Wien's Displacement Law-

   As we see from the graph λ_m (corresponding wavelength for maximum emission) decreases with temperature. It was Wien who first discovered mathematically that

$$\lambda_m \propto \frac{1}{T}$$

   or

$$\lambda_m = \frac{b}{T} \tag{7}$$

   Where b is called Wien's constant its value is $b = 2.898 * 10^{-3} meter Kelvin$ The above law is known as Wien's displacement law. This is very important law as it law helps us to find the temperature of stars(hot bodies).

   Wien's displacement law may be expressed in terms of frequency as

$$\nu_m = \frac{cT}{b} \tag{8}$$

5. We also see that the peak of graph increases rapidly with temperature. It is found that

$$E\lambda_m \propto T^5$$

6. Stephan Boltzmann's Law- At a particular temperature the area under the curve is given by

$$\int_0^\infty E_\lambda d\lambda$$

   Which is the total emissive power of blackbody. Hence the area of the curve represents the total emissive power. It is found to be proportional $to T^4$ i.e.

$$E \propto T^4$$

   or

$$E = \sigma T^4 \tag{9}$$

   Where σ is known as Stephan's constant having value

$$\sigma = 5.67 * 10^{-8} \texttt{ watt}/m^2/K^4$$

   This law is known as Stephan Boltzmann's law.

Laws of black body radiation

The Stefan-Boltzmann Law

- First quantitative conjecture based on experimental observations was the **Stefan-Boltzmann Law (1879)**
- Law states the total power radiated from one square meter of black surface goes as the ***fourth power*** of the absolute temperature $E = \sigma T^4$,

Where

- E is the total amount of radiation emitted by an object per square meter Wm^{-2}
- **σ** is a constant called the Stefan-Boltzmann constant ($5.67\times10^{-8} Wm^{-2}K^{-4}$).
- T is the absolute temperature of the object (in K)

The law applies only to **blackbodies**, theoretical surfaces that absorb all incident heat radiation.

The **Stefan-Boltzmann's Law** is observed as the increase in the emission amplitude with increasing temperature.

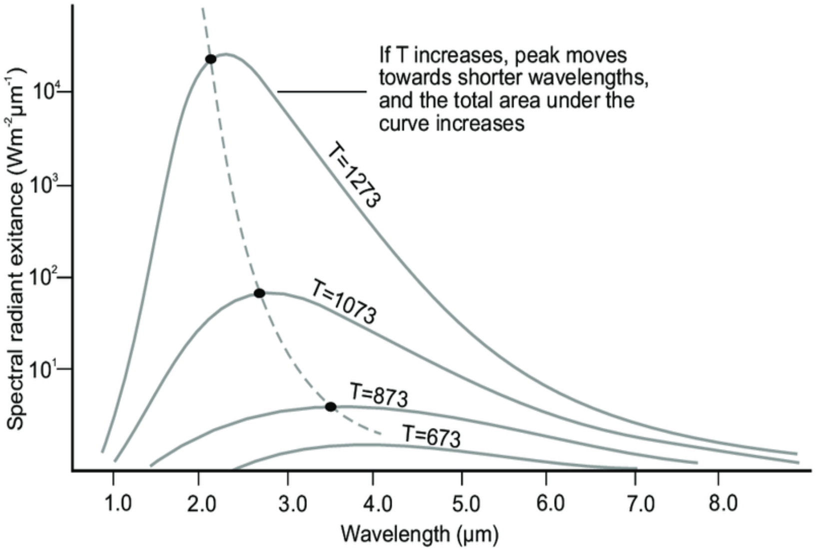


Fig. 4.9. Characteristics curve of Stefan-Boltzmann's Law

Wien's displacement law:

This law states that the product of wavelength (λ_m) corresponding to maximum energy of radiation and absolute temperature of the black body (T) is a constant. i.e.,

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

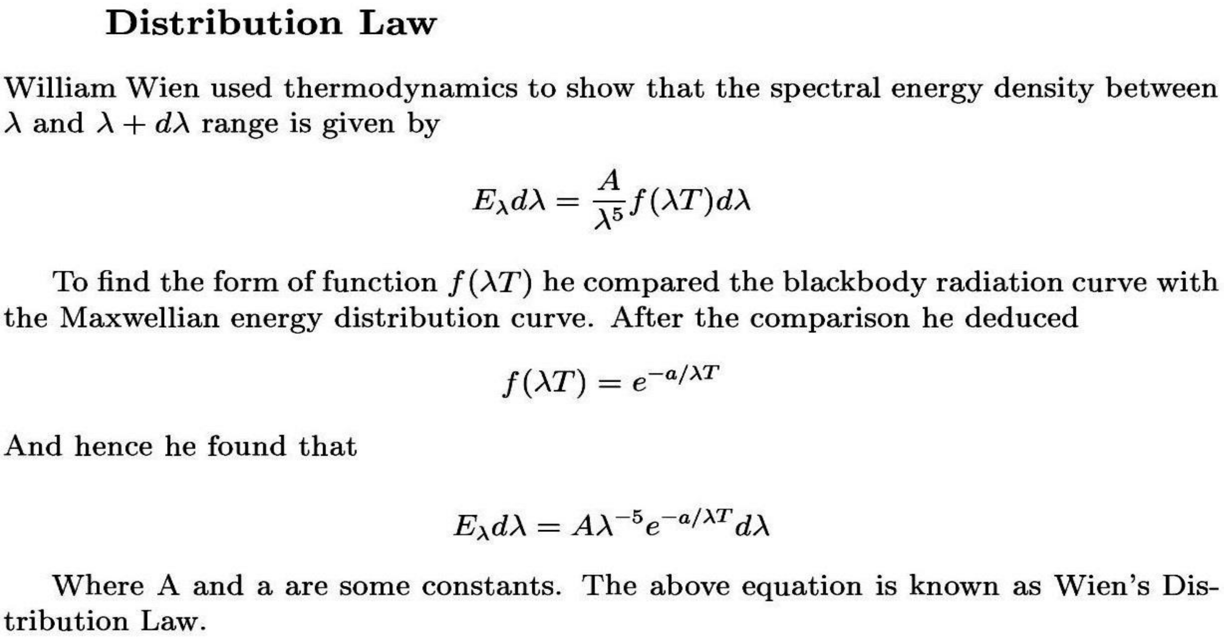
$$\lambda_m = \frac{constant}{T}$$

$$\boldsymbol{\lambda_m \propto \frac{1}{T}}$$

b = constant = **2.898×10^{3}mK**

This law shows that, as the temperature increases, the wavelength corresponding to maximum energy decreases. This law is used to find the Temperature of Stars –hot bodies.

This law holds well only **for shorter wavelength** regions and not for longer wavelengths.



Distribution Law

William Wien used thermodynamics to show that the spectral energy density between λ and $\lambda + d\lambda$ range is given by

$$E_\lambda d\lambda = \frac{A}{\lambda^5} f(\lambda T) d\lambda$$

To find the form of function $f(\lambda T)$ he compared the blackbody radiation curve with the Maxwellian energy distribution curve. After the comparison he deduced

$$f(\lambda T) = e^{-a/\lambda T}$$

And hence he found that

$$E_\lambda d\lambda = A\lambda^{-5} e^{-a/\lambda T} d\lambda$$

Where A and a are some constants. The above equation is known as Wien's Distribution Law.

Raleigh Jeans law:

According to this law, the energy distribution is directly proportional to the absolute temperature and is inversely proportional to the fourth power of the wavelength. It is governed by the equation,

$$\mathrm{E}_\lambda \propto T \text{ and } \qquad \mathrm{E}_\lambda \propto \frac{1}{\lambda^4}$$

$$\mathrm{E}_\lambda \propto \frac{T}{\lambda^4}$$

$$\mathbf{E}_\lambda = \frac{\boldsymbol{8\pi K_B T}}{\boldsymbol{\lambda^4}}$$

Where, $\mathbf{K_B}$ is Boltzmann Constant.

This law holds well only **for longer wavelength** regions and not for shorter wavelengths.

Planck's law

Planck's radiation law, a mathematical relationship formulated in 1900 by German physicist Max Planck to explain the spectral-energy distribution of radiation emitted by a blackbody.

The energy E_λ radiated per unit volume by a cavity of a black body in the wavelength interval λ to λ + Δλ can be written as

$$E_\lambda = \frac{8\pi hc}{\lambda^5} \times \frac{1}{\exp(hc/kT\lambda) - 1}.$$

Where, h is the Planck's constant, c is the speed of light, K is the Boltzmann constant and T is the absolute temperature.

Experimental Verification of Stefan's Law

Lummer and Pringsheim experimentally verified Stefan's law over a wide range of temperature (100 °C to 1,300 °C).

Apparatus. The apparatus is shown in Fig. 4.10

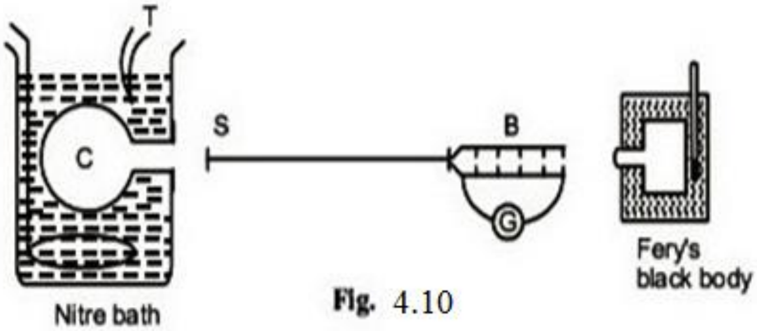


Fig. 4.10

The black body for the range 200 to 600 °C consists of a hollow copper sphere *C* coated with platinum black. It is placed in a bath containing a mixture of fused sodium and potassium nitrates. The bath can be maintained at any temperature between 200 °C to 600 °C. The temperature can be measured by a thermocouple *T*.

For higher temperatures, the copper sphere is replaced by an iron cylinder enclosed in a double-walled gas furnace. The radiation coming out of the opening *O* is measured by the bolometer *B* designed by Lummer and Kurlbaum. The radiation could be stopped when required by a water-cooled shutter *S*.

Experiment. The bolometer is calibrated by means of a Fery's black body kept at 100 °C. The bolometer is kept at different distances from this black body and the deflections are observed. The deflections are found to be inversely proportional to the square of the distances. From this it is concluded that the deflection of the galvanometer in the bolometer circuit is directly proportional to the quantity of radiation received by it.

The black body *C* is next heated to any desired temperature and the water-cooled shutter is removed. The radiation is allowed to fall on the receiving face of the bolometer. The steady deflection of the galvanometer is noted. Keeping the bolometer at a particular distance, the deflection θ in the galvanometer is found for various steady temperatures of the black body.

Calculation. Let T be the temperature of the black body and T_0, the temperature of the shutter. Then

$$\theta = a\left(T^4 - T_0^4\right).$$

The coefficient a is found to be constant. This verifies the law.

Note. The constant a is not the Stefan's constant σ. a is some other constant which depends on the calibration of the bolometer.

Solar constant

- **The total radiation energy received from the Sun per unit of time per unit of area on a theoretical surface on earth perpendicular to the Sun's rays.**
- The theoretical surface is at Earth's mean distance from the Sun.
- It is most accurately measured from satellites where atmospheric effects are absent. The value of the constant is approximately **1.366 kilowatts per square metre.**
- The "constant" is fairly constant, increasing by only 0.2 percent at the peak of each 11-year solar cycle. In the past **400 years it has varied less than 0.2 percent**. Billions of years ago, it was significantly lower.

Angstrom pyrheliometer

- Solar Pyrheliometer is an instrument used to measure the quantity of heat radiation and solar constant.
- Pyrheliometer designed by Angstrom is the **simplest and most accurate.**
- Angstrom's pyrheliometer consists of two identical strips S_1 and S_2 of area A. One junction of a thermocouple is connected to S_1 and the other junction is connected to S_2. A sensitive galvanometer is connected to the thermo couple.

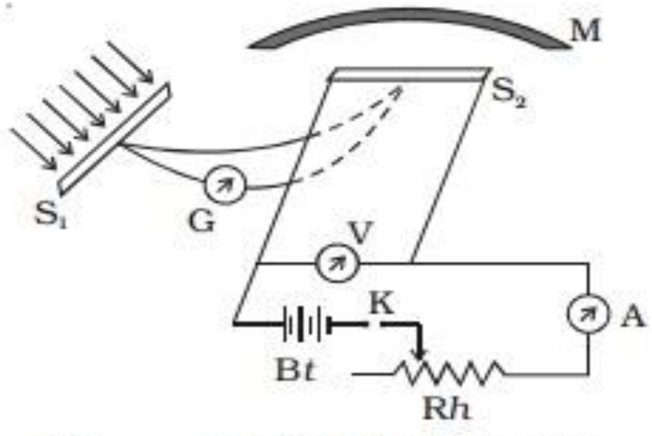


Fig. 4.11. Angstrom Pyrheliometer

Working

- Strip S2 is connected to an external electrical circuit as shown in Fig.
- When both the strips S1 and S2 are shielded from the solar radiation, galvanometer shows no deflection as both the junctions are at the same temperature.
- Now strip S1 is exposed to the solar radiation and S2 is shielded with a cover M.
- As strip S1 receives heat radiations from the sun, its temperature rises and hence the galvanometer shows deflection. Now current is allowed to pass through the strip S_2 and it is adjusted so that galvanometer shows no deflection. Now, the strips S_1 and S_2 are again at the same temperature.
- If the quantity of heat radiation that is incident on unit area **A** in unit time on strip S_1 is **S** and ***a*** its absorption co-efficient.
- Then the amount of heat radiations absorbed by the strip S_1 in unit time is

$$S\,A\,a.$$

- Also, heat produced in unit time in the strip S_2 is given by ***VI***, where ***V*** is the potential difference and **I** is the current flowing through it.

As heat absorbed = heat produced

$$S\,A\,a = VI \quad (or)$$

$$S = VI/A\,a$$

Knowing the values of *V*, *I*, *A* and *a*, *Q* can be calculated.

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SCHOOL OF SCIENCE AND HUMANITIES

DEPARTMENT OF PHYSICS

Thermal Physics – SPH1211

V. Statistical Physics

Statistical mechanics is the art of turning the microscopic laws of physics into a description of Nature on a macroscopic scale. Suppose you've got theoretical physics cracked. Suppose you know all the fundamental laws of Nature, the properties of the elementary particles and the forces at play between them. How can you turn this knowledge into an understanding of the world around us?

For centuries — from the 1600s to the 1900s — scientists were discovering "laws of physics" that govern different substances. There are many hundreds of these laws, mostly named after their discovers. Boyle's law and Charles's law relate pressure, volume and temperature of gases (they are usually combined into the ideal gas law); the Stefan-Boltzmann law tells you how much energy a hot object emits; Wien's displacement law tells you the colour of that hot object; the Dulong-Petit law tells you how much energy it takes to heat up a lump of stuff; Curie's law tells you how a magnet loses its magic if you put it over a flame; and so on and so on. Yet we now know that these laws aren't fundamental.

In some cases they follow simply from Newtonian mechanics and a dose of statistical thinking. In other cases, we need to throw quantum mechanics into the mix as well. But in all cases, we're going to see how derive them from first principles.

- Thermodynamics is a phenomenological theory of equilibrium states and transition among them.
- Statistical mechanics is concerned with deducing the thermodynamics properties of a macroscopic system from its microscopic system,
- Kinetic theory aims at a microscopic description of the transition process between equilibrium states.

- **Ideal Gas:-** A ideal gas is one which has a zero size of molecule and zero force of interaction between its molecules.
- **Ideal Gas Equation:-** A relation between the pressure, volume and temperature of an ideal gas is called ideal gas equation.

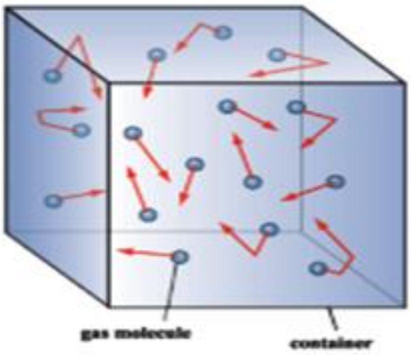


Fig. 5.1

PV/T = Constant or $PV = nRT$

Here, n is the number of moles and R is the universal gas constant.

- **Gas Constant:-**

(a) Universal gas constant (R):-

Kinetic molecular theory

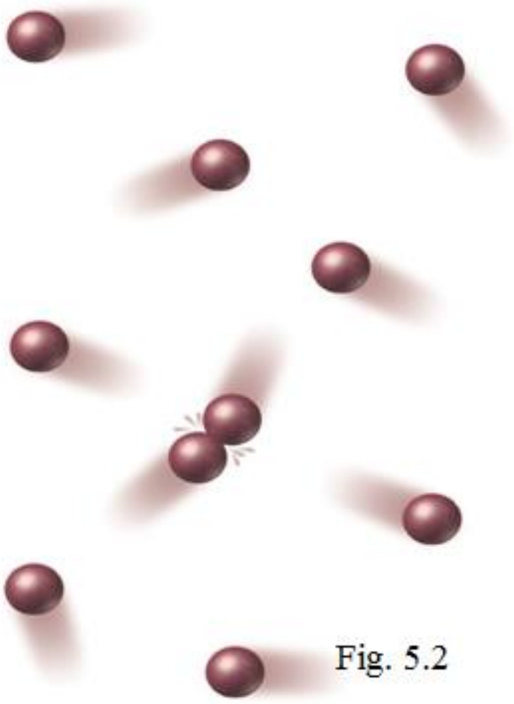


Fig. 5.2

1 Collection of particles in constant motion

2 No attractions or repulsions between particles; collisions like billiard ball collisions

3 A lot of space between the particles compared to the size of the particles themselves

4 The speed that the particles move increases with increasing temperature

Statistical Distribution-Types

1. Identical particles that are sufficiently far apart to be distinguishable.
   Example: molecules of a gas.
   Negligible overlapping of ψ
   Maxwell-Boltzmann Statistics
2. Indistinguishable identical particles of ‘0’ or integral spin.
   Example: Bosons (don’t obey the exclusion principle)
   Overlapping of ψ
   Bose-Einstein Statistics
3. Indistinguishable identical particles with odd-half integral spin (1/2, 3/2, 5/2 ..).
   Example: Fermions (obey the exclusion principle)
   Fermi-Dirac Statistics

What is the Maxwell-Boltzmann distribution?

The air molecules surrounding us are not all traveling at the same speed, even if the air is all at a single temperature. Some of the air molecules will be moving extremely fast, some will be moving with moderate speeds, and some of the air molecules will hardly be moving at all. Because of this, we can't ask questions like "What is the speed of an air molecule in a gas?" since a molecule in a gas could have any one of a huge number of possible speeds.

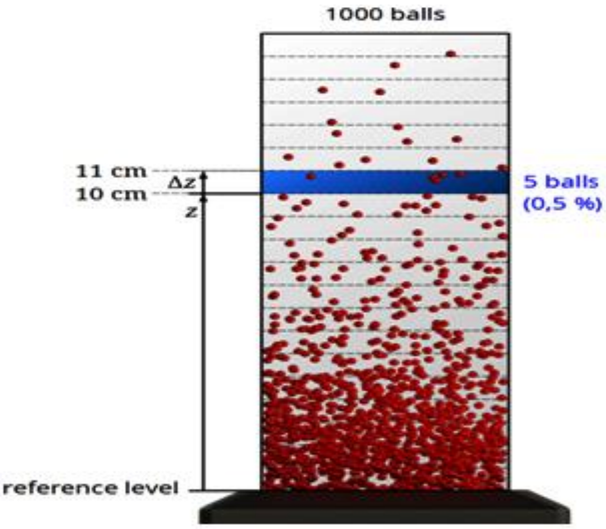


Fig. 5.3

What does root-mean-square speed mean?

You might think that the speed located directly under the peak of the Maxwell-Boltzmann graph is the average speed of a molecule in the gas, but that's not true. The speed located directly under the peak is the most probable speed v_p, since it is the speed that is most likely to be found for a molecule in a gas.

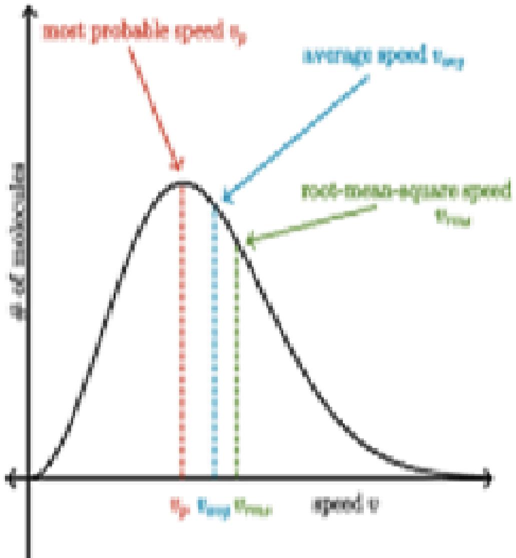


Fig. 5.4

The average speed v_{avg} of a molecule in the gas is actually located a bit to the right of the peak. The reason the average speed is located to the right of the peak is due to the longer "tail" on the right side of the Maxwell-Boltzmann distribution graph. This longer tail pulls the average speed slightly to the right of the peak of the graph.

Another useful quantity is known as the root-mean-square speed v_{rms}. This quantity is interesting because the definition is hidden in the name itself. The *root-mean-square* speed is the *square root* of the *mean* of the *squares* of the velocities. *Mean* is just another word for *average* here. We can write the root-mean-square speed mathematically as,

$$v_{rms} = \sqrt{\frac{1}{N}(v_1^2 + v_2^2 + v_3^2 + \ldots)}$$

What does the area under a Maxwell-Boltzmann distribution represent?

The y-axis of the Maxwell-Boltzmann distribution graph gives the **number of molecules** per unit speed. The total area under the entire curve is equal to the total number of molecules in the gas.

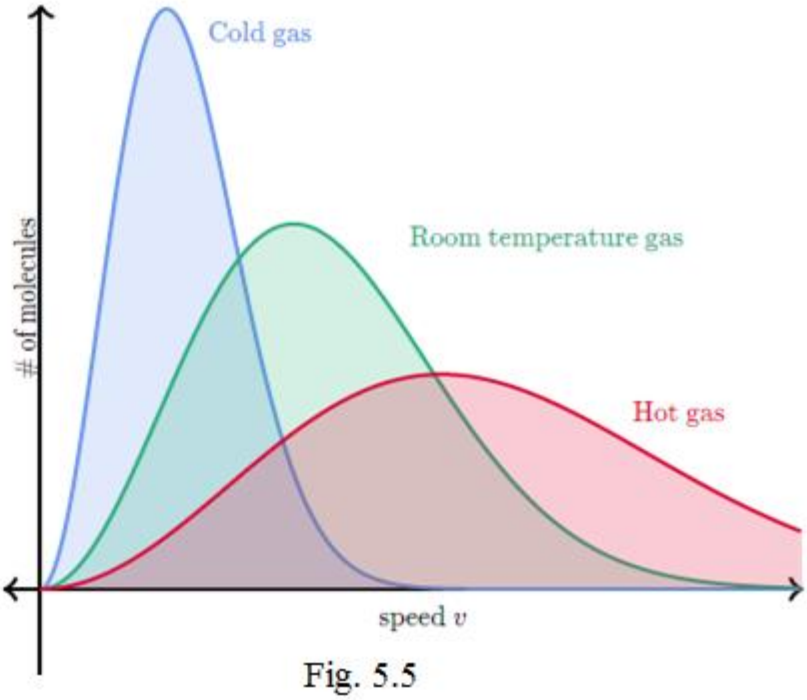


Fig. 5.5

If we heat the gas to a higher temperature, the peak of the graph will shift to the right (since the average molecular speed will increase). As the graph shifts to the right, the height of the graph has to decrease in order to maintain the same total area under the curve. Similarly, as a gas cools to a lower temperature, the peak of the graph shifts to the left. As the graph shifts to the left, the height of the graph has to increase in order to maintain the same area under the curve. This can be seen in the curves below which represent a sample of gas (with a constant amount of molecules) at different temperatures.

As the gas gets colder, the graph becomes taller and more narrow. Similarly, as the gas gets hotter the graph becomes shorter and wider. This is required for the area under the curve (i.e. total number of molecules) to stay constant.

If molecules enter the sample, the total area under the curve would increase. Similarly, if molecules were to leave the sample, the total area under the curve would decrease.

M-B Distribution Curve

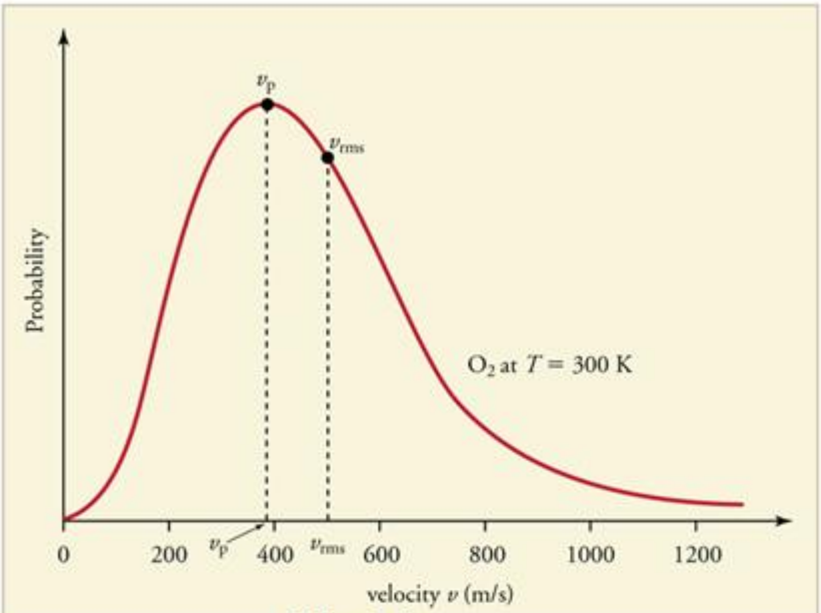


Fig. 5.6

Maxwell-Boltzmann Statistics

(Classical Approach)

According to this law number of identical and distinguishable particles in a system at temperature, T having energy ϵ is

n(ϵ) = (No. of states of energy ϵ).(average no. of particles in a state of energy ϵ)

$$n(\varepsilon) = g(\varepsilon).Ae^{-\varepsilon/kT} \qquad \text{(i)}$$

Here A is a constant and $f_{M.B.}(\varepsilon) = Ae^{-\varepsilon/kT}$

Equation (i) represents the Maxwell-Boltzmann Distribution Law

This law cannot explain the behavior of photons (Black body radiation) or of electrons in metals (specific heat, conductivity)

Applications of M.B. Statistics

(i) Molecular energies in ideal gas

No. of molecules having energies between ϵ and ϵ + dϵ is given by

$$n(\varepsilon)d\varepsilon = \{g(\varepsilon)d\varepsilon\}\{f(\varepsilon)\}$$

$$n(\varepsilon) = Ag(\varepsilon)e^{-\varepsilon/kT}d\varepsilon \qquad \text{(i)}$$

The momentum of a molecule having energy ϵ is given by

$$p = \sqrt{2m\varepsilon} \qquad \Rightarrow dp = \frac{md\varepsilon}{\sqrt{2m\varepsilon}}$$

No. of states in momentum space having momentum between p and p + dp is proportional to the volume element i.e.

$$\alpha\iiint dp_x dp_y dp_z$$

$$\alpha \quad \frac{4}{3}\pi(p+dp)^3 - \frac{4}{3}\pi p^3$$

$$\alpha \quad 4\pi p^2 dp$$

$$g(p)dp \quad \alpha \quad 4\pi p^2 dp$$

$$g(p)dp = Bp^2 dp$$ B is a constant

Each momentum corresponds to a single ϵ

$$g(\varepsilon)d\varepsilon = Bp^2 dp$$

$$g(\varepsilon)d\varepsilon = B.2m\varepsilon.\frac{md\varepsilon}{\sqrt{2m\varepsilon}}$$

$$g(\varepsilon)d\varepsilon = 2m^{3/2}B\sqrt{\varepsilon}d\varepsilon$$

Put in (i)

No. of molecules with energy between ϵ and ϵ + dϵ

$$n(\varepsilon)d\varepsilon = 2m^{3/2}BA\sqrt{\varepsilon}e^{-\varepsilon/kT}$$

$$n(\varepsilon)d\varepsilon = C\sqrt{\varepsilon}e^{-\varepsilon/kT} \qquad \text{(ii)}$$

Total No. of molecules is N

$$N = \int_0^\infty n(\varepsilon)d\varepsilon = C\int_0^\infty \sqrt{\varepsilon}e^{-\varepsilon/kT}d\varepsilon$$

Using identity $\int_0^{\infty} x^{1/2} e^{-ax} dx = \frac{1}{2a}\sqrt{\frac{\pi}{a}}$

$$C = \frac{2\pi N}{(\pi kT)^{3/2}}$$

Put value of C in equation (ii)

$$n(\varepsilon)d\varepsilon = \frac{2\pi N}{(\pi kT)^{3/2}}\sqrt{\varepsilon}e^{-\varepsilon/kT}d\varepsilon$$

This equation gives the number of molecules with energies between ϵ and ϵ + dϵ in a sample of an ideal gas that contains N molecules and whose absolute temperature is T. It is called molecular energy distribution equation.

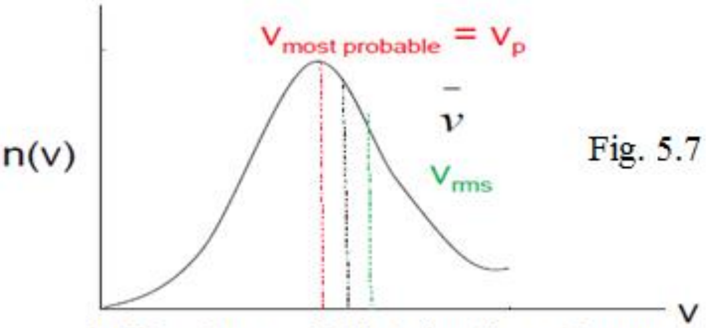


Fig. 5.7

M.B. Speed Distribution Curve

(i) Speed distribution is not symmetrical

(ii) $v_p < \bar{v} < v_{rms}$

$$\sqrt{\frac{2kT}{m}} < \sqrt{\frac{8kT}{\pi m}} < \sqrt{\frac{3kT}{m}}$$

Maxwell–Boltzmann Statistics: This is sometimes called the classical case. In this case the particles are distinguishable so let's label them A and B. Let's call the 2 single particle states 1 and 2. For Maxwell–Boltzmann statistics any number of particles can be in any state. So let's enumerate the states of the system:

Single Particle State	1	2
	AB	
		AB
	A	B
	B	A

We get a total of 4 states of the system as a whole. Half of the states have the particles bunched in the same state and half have them in separate states.

Bose–Einstein Statistics: This is a quantum mechanical case. This means that the particles are indistinguishable. Both particles are labelled A. Recall that bosons have integer spin: 0, 1, 2, etc. For Bose statistics any number of particles can be in one state. So let's again enumerate the states of the system:

Single Particle State	1	2
	AA	
		AA
	A	A

We get a total of 3 states of the system as a whole. 2/3 of the states have the particles bunched in the same state and 1/3 of the states have them in separate states.

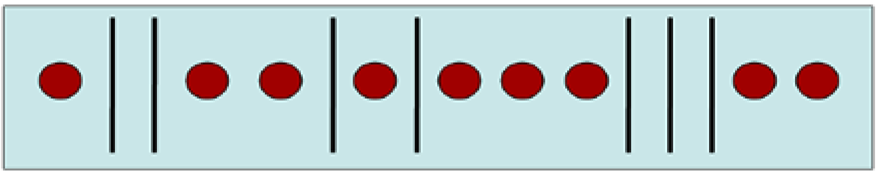
Fermi Statistics: This is another quantum mechanical case. Again the particles are indistinguishable. Both particles are labelled A. Recall that fermions have half–integer spin: 1/2, 3/2, etc. According to the Pauli exclusion principle, no more than one particle can be in any one single particle state. So let's again enumerate the states of the system:

Single Particle State	1	2
	A	A

We get a total of 1 state of the system as a whole. None of the states have the particles bunched up; the Pauli exclusion principle forbids that. 100% of the states have the particles in separate states.

Bose –Einstein Distribution

Consider an energy level ε_i with degeneracy g_i, containing n_i bosons. The states may be represented by $g_i - 1$ lines, and the bosons by n_i circles; distinguishable microstates correspond to different orderings of the lines and circles. For example, with 9 particles in 8 states corresponding to a particular energy, a particular microstate might be:



The number of *distinct* orderings of lines and circles is:

$$t_i = \frac{(n_i + g_i - 1)!}{n_i!(g_i - 1)!}. \qquad (1)$$

A particular distribution has a specified number of particles n_i within each of the possible energy levels ε_i. The total number of microstates for a given distribution is therefore:

$$t(\{n_i\}) = \prod_i \frac{(n_i + g_i - 1)!}{n_i!(g_i - 1)!}. \qquad (2)$$

Let us assume that each state has a high degeneracy, i.e. $g_i \gg 1$. Then we can make the approximation:

$$t(\{n_i\}) \approx \prod_i \frac{(n_i + g_i)!}{n_i!g_i!}. \qquad (3)$$

To find the most probable distribution, we follow the same procedure as for the Boltzmann and the Fermi-Dirac distributions. That is, we maximise (9):

$$t\left(\{n_i\}\right) = \prod_i \frac{(n_i + g_i)!}{n_i! g_i!},$$

subject to the constraint on the total number of particles:

$$\sum_i n_i = N, \tag{4}$$

and the constraint on the total energy:

$$\sum_i \varepsilon_i n_i = U. \tag{5}$$

As usual, rather than maximise t directly, we maximise $\ln t$. If we assume that both g_i and n_i are large enough for Stirling's approximation to hold for $\ln g_i!$ and $\ln n_i!$, we find that $\ln t$ is given by:

$$\ln t \approx \sum_i \left[(n_i + g_i) \ln (n_i + g_i) - g_i \ln g_i - n_i \ln n_i\right]. \tag{6}$$

The change in $\ln t$ resulting from changes dn_i in each of the populations n_i is then:

$$d \ln t \approx \sum_i \left[\ln (n_i + g_i)\, dn_i - \ln n_i\, dn_i\right]. \tag{7}$$

From the constraints (10) and (11), we find:

$$\sum_i dn_i = 0, \quad \sum_i \varepsilon_i dn_i = 0. \tag{8}$$

Combining (13) and (14) with Lagrange multipliers α and β, we have:

$$d \ln t \approx \sum_i \left[\ln\left(\frac{n_i + g_i}{n_i}\right) + \alpha + \beta\varepsilon_i\right] dn_i. \tag{9}$$

For appropriate values of α and β, equation (15) is true for all dn_i, hence:

$$\ln\left(\frac{n_i + g_i}{n_i}\right) + \alpha + \beta\varepsilon_i = 0. \tag{10}$$

We then find that the most probable distribution can be written:

$$n_i = \frac{g_i}{e^{-\alpha-\beta\varepsilon_i} - 1}. \qquad (11)$$

Equation (11) is the Bose-Einstein disbribution. It gives the population of an energy level that has energy ε_i and degeneracy g_i. The constants α and β are determined from the constraints eqn, (4) and (5) on the total number of particles and the total energy. β can, as usual, be related to the thermodynamic temperature, so that the Bose-Einstein distribution takes the form:

$$n_i = \frac{g_i}{Be^{\frac{\varepsilon_i}{kT}} - 1}. \qquad (12)$$

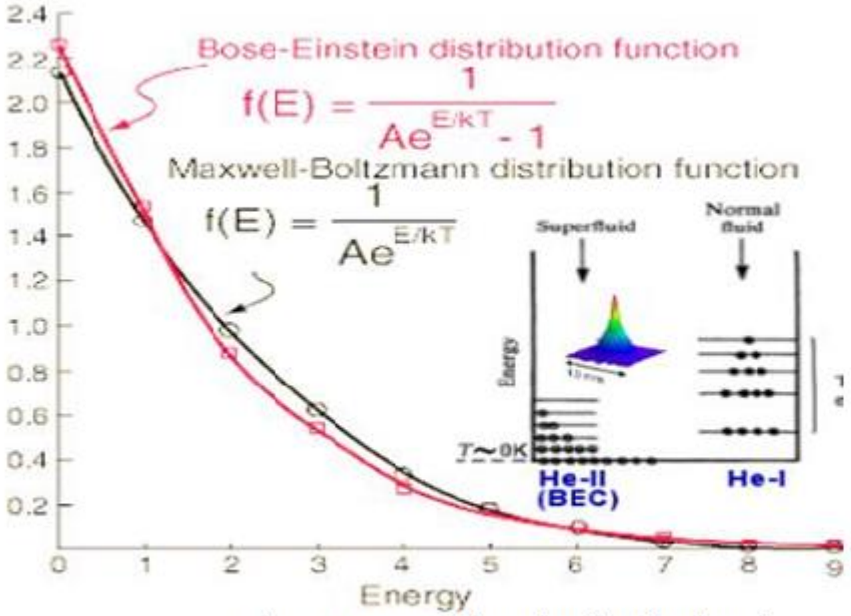


Fig. 5.8 Bose-Einstein distribution fn

Fermi-Dirac Distribution

- Fermions are particles that are identical and indistinguishable.
- Fermions include particles such as electrons, positrons, protons, neutrons, etc. They all have half-integer spin.
- Fermions obey the Pauli exclusion principle, i.e. each quantum state can only accept one particle.
- Therefore, for fermions N_j cannot be larger than g_j.
- FD statistic is useful in characterizing free electrons in semi-conductors and metals.

The number of possible ways - called configurations - to fit $g_i f_i$ electrons in g_i states, given the restriction that only one electron can occupy each state, equals:

$$W_i = \frac{g_i!}{(g_i - g_i f_i)! g_i f_i!} \qquad (1)$$

The number of possible ways to fit the electrons in the number of available states is called the multiplicity function.

The multiplicity function for the whole system is the product of the multiplicity functions for each energy E_i:

$$W = \prod_i W_i = \prod_i \frac{g_i!}{(g_i - g_i f_i)! g_i f_i!} \qquad (2)$$

Using Stirling's approximation[#], one can eliminate the factorial signs, yielding:

$$\ln W = \sum_i \ln W_i = \sum_i \left[g_i \ln g_i - g_i (1 - f_i) \ln (g_i - g_i f_i) - g_i f_i \ln g_i f_i \right] \qquad (3)$$

The total number of electrons in the system equals N and the total energy of those N electrons equals U. These system parameters are related to the number of states at each energy, g_i, and the probability of occupancy of each state, f_i, by:

$$N = \sum_i g_i f_i \qquad (4)$$

and

$$U = \sum_i E_i g_i f_i \qquad (5)$$

probability in thermal equilibrium is therefore obtained by finding the maximum of the multiplicity function, W, while keeping the total energy and the number of electrons constant.

For convenience, we maximize the logarithm of the multiplicity function instead of the multiplicity function itself. According to the Lagrange method of undetermined multipliers, we must maximize the following function:

$$\ln W - a\sum_j g_j f_j - b\sum_j E_j g_j f_j \tag{6}$$

where a and b need to be determined. The maximum of the multiplicity function, W, is obtained from:

$$\frac{\partial}{\partial(g_i f_i)}\left[\ln W - a\sum_j g_j f_j - b\sum_j E_j g_j f_j\right] = 0 \tag{7}$$

which can be solved, yielding:

$$\ln \frac{g_i - g_i f_i}{g_i f_i} - a - bE_i = 0 \tag{8}$$

$$f_i = f_{FD}(E_i) = \frac{1}{1 + \exp(a + bE_i)} \tag{9}$$

which can be written in the following form

$$f_{FD}(E_i) = \frac{1}{1 + \exp(\frac{E_i - E_F}{\beta})} \tag{10}$$

with $\beta = 1/b$ and $E_F = -a/b$. The symbol E_F was chosen since this constant has units of energy and will be the constant associated with this probability distribution.

Three Distributions

We have now completed our collection of three distributions. First, a collection of distinguishable particles follows the Boltzmann distribution:

$$n_j = \frac{N}{Z} e^{-\frac{\varepsilon_j}{kT}}.$$

Note that j indexes particle *states*, not energy levels.

Then, for a collection of indistinguishable fermions, we found the Fermi-Dirac distribution:

$$n_i = \frac{g_i}{e^{\frac{\varepsilon_i - \mu}{kT}} + 1}.$$

In this case, i indexes energy *levels*, not individual states.

Finally, we found the Bose-Einstein distribution for a collection of indistinguishable bosons

$$n_i = \frac{g_i}{Be^{\frac{\varepsilon_i}{kT}} - 1}.$$

Fermions & Bosons

The formulas for the Fermi-Dirac distribution (20):

$$n_i = \frac{g_i}{e^{\frac{\varepsilon_i - \mu}{kT}} + 1}$$

and the Bose-Einstein distribution (18):

$$n_i = \frac{g_i}{Be^{\frac{\varepsilon_i}{kT}} - 1}.$$

appear very similar. However, the difference in sign in the denominator is critical. Since $e^x > 0$ for all x, for the Fermi-Dirac distribution, we always have $n_i < g_i$; in other words, fermions always obey the Pauli exclusion principle.

Quantum Statistics (Indistinguishable identical particles)

Bosons	**Fermions**
1. ‘0’ or integral spin	1. Odd half integral spin
2. Do not obey exclusion principle	2. Obey exclusion principle
3. Symmetric wave function	3. Anti-symmetric wave function
4. Any number of bosons can exist in the same quantum state of the system	4. Only one fermion can exist in a particular quantum state of the system