Free Electron Theory

A type of bonding between atoms of a material in which valance electrons of all atoms from an electron cloud around the positive ions, thus providing attractive forces which bond the atoms of the material together is known as **metallic bonding.**

The easily freed valence electrons thus freely move inside the conductor and act as charge carriers.

The free electron theory has been developed in three main stages:

1. The classical free electron theory (1900) of Drude and Lorentz, Which assumes that metals contain free electrons obeying the laws of classical mechanics.
2. The quantum free electron theory (1928) of Sommerfeld, in which the free electron obey quantum laws.
3. The Zone theory, proposed by Bloch in 1928 in which the electrons move in a periodic field provided by the lattice.

The important properties of metal are:

1. Metal have **high electric and thermal conductivities**.
2. In the steady state, metals obey Ohm's law according to which the current density J is proportional to the electric field strength E. Thus, for metals, $\mathbf{J \propto E}$, $\mathbf{J=\sigma E}$ Here σ, is the electrical conductivity
3. Metal obey **Widemann-Franz law** according to which the ratio of thermal and electrical conductivities at given temperature is the same for all metals and is proportional to the absolute temperature. Thus $\mathbf{K/\sigma \propto T}$, $\mathbf{K/\sigma T=}$ **const**. where K represents thermal conductivity.
4. They have a **positive temperature coefficient**, i.e., their resistance increases (or Conductivity decreases) with rise of temperature.

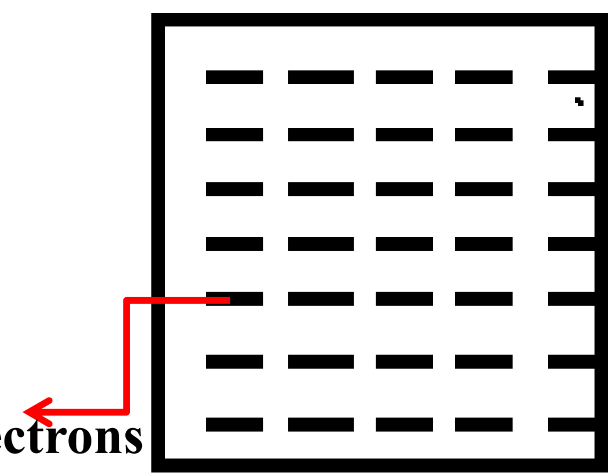
5. At low temperature, the resistivity is prepositional to the 5th power of the absolute temperature, i.e., **ρ=T^5**
6. The resistivity of metals at room temperature is of the order of **10^-7 ohm meter** and above Debye's temperature varies linearly with temperature; i.e., **ρ=T**
7. For most metals, resistivity is inversely proportional to the pressure; i.e., **ρ=1/P**
8. The resistivity of an impure specimen is given by Mathiessen's rule**, ρ=ρ(0) + ρ(T)** where $\rho(0)$ is a constant for the impure specimen and $\rho(T)$ is the temperature dependent resistivity of the pure specimen.
9. Near absolute zero, the resistivity of certain metals tends towards zero; i.e., exhibit the phenomena of **superconductivity.**
10. The conductivity varies in the presence of magnetic field. This effect is known as **magneto resistance.**

Classical Free Electron Theory (1900) (Drude – Lorentz model)

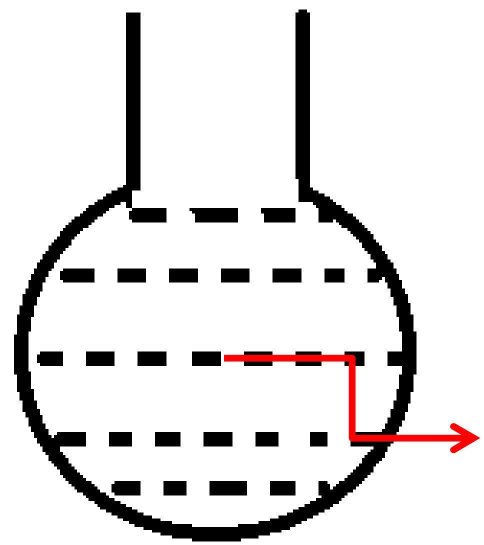
Metal obey Widemann Franz Law. This law is proved by Drude in 1900 on the basis of few assumption for free electrons.

To verify the behavior of free electrons and gas molecules are same in both the case.

1. Gas molecules in jar freely to move, randomly in different velocity and all possible direction. While in case of metal plate have same behavior of free electrons. i.e., metal behave like as molecules of perfect gas.
2. Maxwell studied the gas molecules speed with temperature. Temperature increases then speed of the gas molecules are increases with average kinetic energy 3/2 K_BT.



Metal Plate

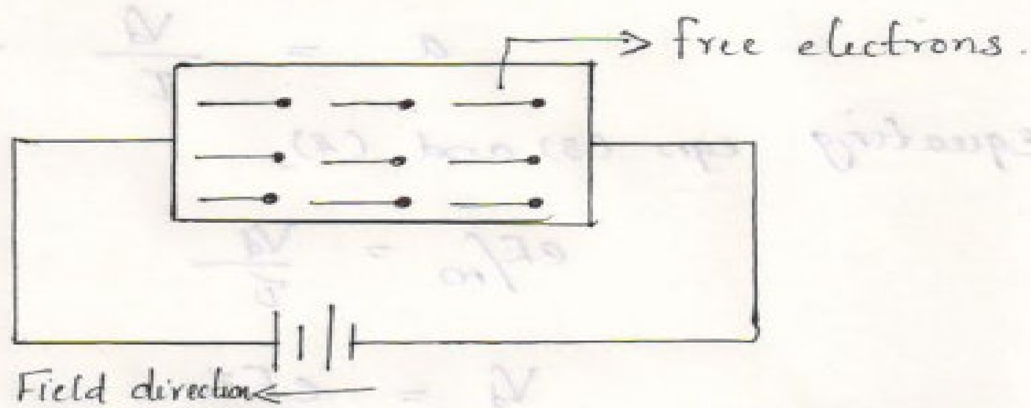


Jar

Drude studied same concept in metal, temperature increases then we will get the thermal conductivity.
i.e., electron move one end to other end with average kinetic energy. So Free electron speed depend on the temperature.

Derivation of Electrical Conductivity of a metal based on Drude & Lorentz theory.

Consider a metal piece of length 'l' and area of cross-section 'A'. An electric field 'E' is applied to the metal piece.



The electrons are accelerated with a drift velocity V_d in a direction opposite to that of the applied field. Due to this field, the force experienced by the electrons can be given as, $F = eE$ - - - - - - - - - (1)

where, $e \rightarrow$ charge of an electron

$E \rightarrow$ applied Electric field

From Newton's Second law of motion,

$$F = ma \quad \text{- - - - - - - - - (2)}$$

i.e. $a \Rightarrow$ acceleration

$m \rightarrow$ mass of the electron.

Equating (1) & (2),

$$eE = ma$$

$$\therefore a = eE/m \quad \text{- - - - - - - - - (3)}$$

We know, acceleration in terms of drift velocity and relaxation time is given as,

$$\text{acceleration} = \frac{\text{drift Velocity } V_d}{\text{relaxation time } \tau}$$

$$a = \frac{V_d}{\tau} \quad \text{-------- (4)}$$

equating eqn (3) and (4),

$$eE/m = \frac{V_d}{\tau}$$

$$V_d = \frac{eE\tau}{m} \quad \text{-------- (5)}$$

We know, Current density,

$$J = \sigma E \quad \text{-------- (6)}$$

Current density in terms of drift velocity is given as,

$$J = n e V_d \quad \text{-------} (7)$$

Substituting eqn (5) in eqn (7),

$$J = ne \frac{eE\tau}{m}$$

$$= \frac{ne^2 E\tau}{m}$$

$$J/E = \frac{ne^2\tau}{m} \quad \text{-------} (8)$$

We know the expression for electrical Conductivity

$$\sigma = J/E$$

$\therefore$ Eqn (8) is the equation for electrical Conductivity

$$\text{i.e.; } \sigma = \frac{ne^2\tau}{m}$$

from this equation, we can find that with increase of electron concentration 'n', the conductivity 'σ' increases. As 'm' increases, the motion of electron becomes slow and hence the conductivity 'σ' decreases.

$$\frac{1}{2}m(\bar{c})^2 = \frac{3}{2}k_B T$$

When an electric field is applied, the electron will acquire a drift velocity and the resulting acceleration is, $a = \dfrac{eE}{m}$. The drift velocity is small compared to the random velocity $\bar{c}$. Further the drift velocity is not retained after a collision with an atom because of the relatively large mass of the atom. Hence just after a collision the drift velocity is zero. If the mean free path is λ, then the time that elapses before the next collision takes place is $\dfrac{\lambda}{\bar{c}}$. Hence the drift velocity acquired before the next collision takes place is

$$u = \text{Acceleration} \times \text{Time interval}$$

$$= \left(\frac{eE}{m}\right)\left(\frac{\lambda}{\bar{c}}\right)$$

Thus the average drift velocity is

$$\frac{u}{2} = \frac{eE\lambda}{2m\bar{c}}$$

If n is the number of electrons per unit volume, then the current flowing through unit area for unit time is

$$\boxed{J_x = \frac{neu}{2} = \frac{ne^2E\lambda}{2m\bar{c}}}$$

or

$$\sigma = \frac{J_x}{E} = \frac{ne^2\lambda}{2m\bar{c}}, \text{ or } \rho = \frac{2m\bar{c}}{ne^2\lambda} \tag{6.16}$$

i.e.,

$$\boxed{\rho = 2 \times \sqrt{\frac{3mk_BT}{ne^2\lambda}}; \ \sigma = \frac{ne^2\lambda}{\sqrt{12mk_BT}}} \tag{6.17}$$

It was assumed by Drude and Lorentz that λ is independent of temperature and that is of the order of interatomic distance. Hence $\rho \propto \sqrt{T}$. This means that the specific resistance of an electric conductor is directly proportional to the square root of the absolute temperature. This is not in agreement with the experimental observation that $\sigma \propto T$. Apart from this discrepancy, it is also not correct to assume that the mean free path is independent of temperature and hence this classical theory is almost an unacceptable one. However, the Ohm's law is derived, since the conductivity in equation (6.16) is independent of the field.

Verification of Ohm's law:

We know that, the Current Density, $J = I/A$.

$$\therefore I = JA$$

$$= \sigma E A \qquad [\because J = \sigma E]$$

$$= \sigma (V/l) A \qquad [\because E = V/l]$$

$$= \left(\frac{\sigma A}{l}\right) V$$

$$= \left(\frac{A}{\rho l}\right) V \qquad \left[\because R = \frac{\rho l}{A}\right]$$

$$I = V/R$$

$$\therefore V = IR$$

$\therefore$ Ohm's law is Verified.

Derivation of Thermal Conductivity (k) :

Thermal conductivity of a metal is defined as the amount of heat (Q) conducted per unit time (t) through the material having unit area of cross section (A) maintaining at unit temperature gradient ($d\theta/dx$).

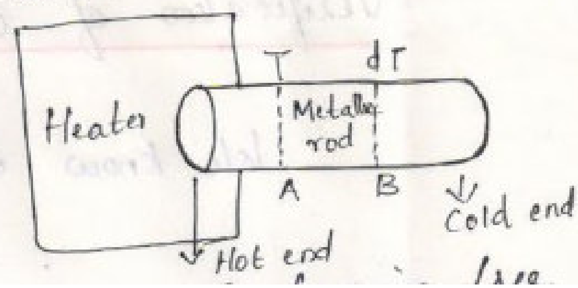
$$k = \frac{-Q}{d\theta/dx}$$

$$\therefore Q = -k \cdot d\theta/dx \quad W m^{-1} K^{-1}.$$

$k \rightarrow$ Thermal conductivity of material.

$Q \rightarrow$ Amount of heat energy.

$d\theta/dx \rightarrow$ temperature gradient.



Consider a uniform metallic rod containing free electrons. One end of the rod is heated using a heater. Let A and B be the two cross-sections of temperature T and (T - dT) seperated by a distance of mean free path (λ). Heat flows from hot end 'A' to the cold end 'B'.

During the collision, the electrons near A lose their kinetic energy and the electrons near B gain the energy.

At point A :

Average kinetic energy of electron = $\frac{1}{2} mv^2 = \frac{3}{2} kT$ ----- (1)

Where, $k \rightarrow$ Boltzmann's constant

$T \rightarrow$ Temperature at A.

At Point B :

Average kinetic energy of an electron $= \frac{3}{2} k (T - dT)$ .... (2)

Hence the Excess kinetic energy carried out by electron from A to B,

$$= \frac{3}{2} kT - \frac{3}{2} k(T - dT)$$

$$= \frac{3}{2} kT - \frac{3}{2} kT + \frac{3}{2} k\,dT$$

$$= \frac{3}{2} k\,dT \quad \text{.........} \ (3)$$

Let us assume that the electrons will flow in all 6 directions with equal probability. If 'n' is the free electron density and v is the thermal velocity, number of electrons carrying unit area per unit time from A to B $= \frac{1}{6} nv$ ...... (4)

Excess of energy carried from A to B for unit area in

unit time $= \frac{1}{6} n v \times \frac{3}{2} k dT$

$$= \frac{1}{4} n v k dT \quad \text{------} (5)$$

III^{ly}, the deficiency of energy carried from B to A for unit area in unit time $= -\frac{1}{4} n v k dT$ ....(6)

Hence, the net energy transferred from A to B per unit area per unit time, $Q = \frac{1}{4} n v k dT - \left[-\frac{1}{4} n v k dT\right]$.

$$\therefore \; Q = \frac{1}{2} n v k dT \quad \text{.......} (7)$$

We know, Thermal Conductivity, $Q = K\left[\frac{dT}{\lambda}\right]$ $\quad [\because dx = \lambda]$

$$\text{------} (8)$$

By comparing eqn (7) and eqn (8),

$$K\left[dT/\lambda\right] = \frac{1}{2} n v k dT$$

$$K = \frac{1}{2} n v k \lambda \quad \text{--------} (9)$$

For metals, relaxation time (τ) = Collision time (τ_c)

$$\therefore \tau = \tau_c = \lambda/v$$

$$\tau v = \lambda \quad \text{------------} \quad (10)$$

Substituting eqn. (10) in (9),

$$\therefore k = \frac{1}{2} n v k \tau v$$

$$k = \frac{1}{2} n v^2 k \tau \quad \text{----------} \quad (11)$$

Eqn (11) is the classical expression for thermal conductivity.

Wiedemann-Franz Law :

The ratio between the thermal conductivity and the electrical conductivity of a metal is directly proportional to the absolute temperature of the metal.

The ratio is constant for all metals in a given temp.

i; $K/\sigma \propto T$

or) $K/\sigma = LT \quad \ldots\ldots\ldots (1)$

Where,

$L \rightarrow$ Lorentz Number $(2.44 \times 10^{-8}\, W\Omega K^{-2}$ at $293K)$

$T \rightarrow$ absolute temperature

$k \rightarrow$ thermal conductivity

$\sigma \rightarrow$ electrical conductivity.

Derivation :

From classical theory, the electrical Conductivity.

$$\sigma = \frac{ne^2\tau}{m} \quad \text{-------- (2)}$$

III^{ly} thermal conductivity,

$$k = \frac{1}{2} n\bar{v}^2 k\bar{\tau} \quad \text{-------- (3)}$$

According to Wiedemann's Franz law,

$$\frac{\text{Thermal Conductivity}}{\text{Electrical conductivity}} = \frac{\frac{1}{2} nv^2 k\tau}{ne^2\tau/m}$$

$$K/\sigma = \frac{1}{2}\frac{mv^2 k}{e^2} \quad \text{------ (4)}$$

Kinetic energy of an electron,

$$\frac{1}{2} mv^2 = \frac{3}{2} kT \quad \text{-------- (5)}$$

Substituting eqn (5) in eqn (4),

$$\frac{k}{\sigma} = \frac{3}{2} kT \frac{k}{e^2}$$

$$= \frac{3}{2} \frac{k^2 T}{e^2}$$

$$= \frac{3}{2} \left(\frac{k}{e}\right)^2 T \quad \text{-------- (6)}$$

$$\frac{k}{\sigma} = LT \quad \text{-------- (7)}$$

Where, $L = \frac{3}{2}\left(\frac{k}{e}\right)^2$ is a Constant and it is known as Lorentz Number.

Lorentz - Number :

The ratio between the thermal conductivity (k) to the product of electrical conductivity (σ) and absolute temperature (T) of the metal is a constant. The constant value is known as Lorentz number.

$$\text{Lorentz Number } (L) = \frac{k}{\sigma T}$$

According to classical theory.

$$L = \frac{3}{2}\left(\frac{k}{e}\right)^2$$

Substituting, $k = 1.38 \times 10^{-23}\ J k^{-1}$, $e = 1.6021 \times 10^{-19}$ Coulomb

$$L = \frac{3}{2}\left[\frac{1.38 \times 10^{-23}}{1.6021 \times 10^{-19}}\right]^2$$

$$L = 1.112 \times 10^{-8}\ W\Omega K^{-2}.$$

Hence it was found that the classical value of Lorentz number is only half of the experimental value ie $L = 2.24 \times 10^{-8}\ W\Omega K^{-2}$. This discrepancy in the experimental and theoretical value of Lorentz number is the failure of classical theory.

This theory was developed by **Drude** and **Lorentz** during 1900 All the atoms are composed of and hence is also known as Drude-Lorentz theory. According to this theory, a metal consists of electrons which are free to move about in the crystal like molecules of a gas in a container. Mutual repulsion between electrons is ignored and hence potential energy is taken as zero. Therefore the total energy of the electron is equal to its kinetic energy.

Postulates of Classical free electron theory:

1. All the atoms are composed of atoms. Each atom have central nucleus around which there are revolving electrons.
2. The electrons are free to move in all possible directions about the whole volume of metals.
3. In the absence of an electric field the electrons move in random directions making collisions from time to time with positive ions which are fixed in the lattice or other free electrons. All the collisions are elastic i.e.; no loss of energy.
4. When an external field is applied the free electrons are slowly drifting towards the positive potential.
5. Since the electrons are assumed to be a perfect gas they obey classical kinetic theory of gasses.
6. Classical free electrons in the metal obey Maxwell-Boltzmann statistics.

Merits of Classical Free Eletron Theory:

•It is used to verify Ohm's law.

•The electrical and thermal conductivities of metals can be explained.

•It is used to derive Wiedemann- Franz law

Drawbacks of Classical Free Electron Theory:

• It is a macroscopic theory.

•It cannot explain the electrical conductivity of semiconductors and insulators properly.

•Dual nature is not explained.

•It cannot explain the Compton effect, Photo-electric effect.

•The theoretical and experimental values of specific heat are not matched.

•Atomic fine spectra could not be accounted.

•Different types of magnetisms could not be explained satisfactorily by this theory.

PROBLEMS

P-1 The following datas are given for copper

Density = 8.92×10^3 kgm^{-3}

Resistivity = 1.73×10^8 Ω m

Atomic weight = 63.5 kg

Calculate the mobility and the average time collision of electrons in copper obeying classical laws

P-2 A uniform silver wire has a resistivity of 1.54×10^{-8} Ωm at room temperature. For an electric field along the wire of 1 volt cm^{-1}, compute the average drift velocity of electron assuming that there is 5.8×10^{28} conduction electrons /m^3. Also calculate the mobility.

P-3 The density of silver 10.5×10^3 kg^{-3} assuming that each silver atom provides one conduction electron. The conductivity of silver at 20°C is 6.8×10^7 Ω^{-1} m^{-1}. Calculate the density and mobility of electron in silver with atomic weight 107.9×10^{-3} kg m^{-2}.

P-4 Calculate the drift velocity of electrons in copper and current density in wire of diameter 0.16 cm which carries a steady current of 10 A. Given $n = 8.46 \times 10^{28}$ m^{-3}.

P-5 The resistivity of a piece of silver at room temperature 1.6×10^{-8} Ωm. Estimate the mean free path of the conduction electrons. Calculate the electronic relaxation time and the electronic drift velocity in a field of 100 Vm^{-1}. The density of silver is 1.05×10^4 kgm^{-3} .

P-6 A conducting rod contains 8.5×10^{28} electrons/m^3. Calculate its resistivity at room temperature and also the mobility of electrons if the collision time for electron scattering is 2×10^{-14} sec.

P-7 Calculate the drift velocity of the free electrons (with a mobility of 3.5×10^{-3} m^2 V^{-1} s^{-1}) in copper for an electric field strength of 0.5 V m^{-1}.

P-8 Copper has electrical conductivity at 300 K as 6.40×10^7 Ω^{-1} m^{-1}. Calculate the thermal conductivity of copper.(Lorentz number is 2.44×10^{-8} W Ωk^{-2}).

P-9 The thermal and electrical conductivities of copper at 20°C are 380 Wm^{-1} K^{-1} and 5.67×10^{7} $^{-1}$ m^{-1} respectively. Calculate the Lorentz number.

P-10 **The mobility of electrons in copper $3\times10^{3} m^2V^{-1}s^{-1}$ assuming $e=1.6\times10^{-19}C$ and $m_e=9.1\times10^{-31}$ kg. Calculate the mean collision time.**

P-11 **The thermal conductivity of a metal is 123.92 $Wm^{-1}K^{-1}$. Find the electrical conductivity and Lorentz number when the metal posses relaxation time 10^{-14} sec at 300 K. (Density of electron = 6×10^{28} per m^3)**

P-12 **Find the velocity of copper wire whose cross-sectional area is 1 mm when the wire carries a current of 10 A. Assume that each copper atom contributes one election to the electron gas. (n= 8.5 x 10^28 per m^3)**