

\* WIEDEMANN - FRANZ LAW : EMPIRICAL LAW :

Relation between the Thermal Conductivity and Electrical Conductivity

STATEMENT : " The ratio of the thermal Conductivity to electrical Conductivity at a Particular temperature is the same for all metals."

Lorenz extended the law and showed that this ratio is proportional to the absolute temperature.

That is :

$\frac{k}{\sigma} = \text{a Constant (Wiedemann-Franz law) at Constant temperature.}$

$\frac{k}{\sigma} \propto T$  [extension to the law due to Lorenz]

or  $\frac{k}{\sigma} = (\text{Constant}) T$  or  $\frac{k}{\sigma T} = (\text{Constant})$

This law implies that good thermal conductors are also good electrical conductors.

\* DEDUCTION OF THE LAW : Drude's Theory

Drude attempted to explain this law by assuming that free electrons are responsible for both the thermal and the electrical conduction in metals. He further assumed that the free

Electrons inside the metal behave like gas molecules (Perfect gas)

The Thermal conductivity ( $K$ ) for the electron-gas Expressed in Calories is:

$$K = \frac{1}{3} n \bar{c} \lambda \frac{d\bar{E}}{dT} = \frac{1}{3} \frac{n \bar{c} \lambda}{J} \frac{d}{dT} \left( \frac{3}{2} kT \right)$$

$\bar{E} = \frac{3}{2} kT$ , if the electron is assumed to possess only the translational energy and no rotational or internal energy in equation (1):

$n \rightarrow$  density of gas molecules (molecular density)

$\bar{c} \rightarrow$  mean molecular velocity of the gas.

$\lambda \rightarrow$  mean free path of the gas.

$\bar{E} \rightarrow$  average energy of the each molecule at temperature  $T$

Now, let us come for the electrical conduction through the metallic conductor.

$m \rightarrow$  mass of the electron;  $e \rightarrow$  electronic charge.

$B \rightarrow$  Electrical intensity along the wire.

$B \cdot e \rightarrow$  Force on each electron.

$B \cdot e / m \rightarrow$  Acceleration of the electron.

The electron is accelerated between two collisions but parts with its acquired kinetic energy (velocity) on collision with the atom. Thus

The velocity at the beginning of the path is 0

The velocity at the end of the path  $\frac{\lambda}{c} \cdot \frac{Be}{m}$

(Using  $v = u + at$ ; the time of travel through the space between collisions is  $\lambda/c$ )

where  $\lambda$  and  $\bar{v}$  be the mean free path and the mean velocity of the electrons corresponding to temperature  $T$

Hence the average velocity of electrons through the metal (called Average drift velocity) may be put as:

$$u = \frac{1}{2} \cdot \frac{\lambda}{c} \cdot \frac{Be}{m}$$

The current per unit area = electronic charge  $\times$  number of electrons crossing unit area per second

or  $I = e(nu)$  where  $n$  being the number of free electrons per unit volume

$$= e \left( n \cdot \frac{1}{2} \cdot \frac{\lambda}{c} \cdot \frac{Be}{m} \right) \quad (\text{current per unit area is called current den})$$

Now  $i = \sigma B$  where  $\sigma \rightarrow$  electrical conductivity

So the electrical conductivity ( $\sigma$ ) of unit length and unit cross section area is

$$\sigma = \frac{i}{B} = \frac{1}{B} e \left( n \cdot \frac{1}{2} \cdot \frac{\lambda}{c} \cdot \frac{Be}{m} \right) = \frac{ne^2 \lambda}{2m^2 c}$$

$$= \frac{ne^2 l}{2(3kT)} \cdot \bar{v} = \frac{ne^2 l \bar{c}}{6kT} \quad \text{--- 2}$$

(because  $mc^2 = 3kT$ )

(Provided we neglect the difference between the mean velocity and the square root of the mean square velocity and take the validity of the equipartition law)

1/2 provided

$$\frac{\kappa}{\sigma} = \frac{3}{J} \left( \frac{\kappa}{e} \right)^2 T$$

$$\text{or } \frac{\kappa}{\sigma T} = \frac{3}{J} \left( \frac{\kappa}{e} \right)^2 = \text{Constant.}$$

Equation (3) gives the laws of both Wiedemann and Franz and of Lorenz. The results however show that at ordinary temperatures equation (3) is satisfied for pure metals but at lower temperatures the ratio falls off. The experiments of Meissner and of Onner and Holst also support the view that the value of  $\kappa/\sigma T$  falls with the fall of temperature.

Now at low temperatures both the thermal and electrical conductivities are found to increase. Hence it follows that the thermal and the electrical conductivity do not increase in the same ratio as the temperature falls, the electrical conductivity increasing much more faster (rapidly). Truly speaking, the latter appears to become infinite for pure metals at the absolute zero but for impure metals

it attains a certain limiting value ( $\sigma \times$ ) independent of temperature. A part of the variation of  $k/\sigma T$  with temperature has also been attributed to the fact that the thermal conductivity of metals is not entirely due to electrons but takes place by pro-cess similar to heat conduction in insulators.

In equation (3)  $I$  is in calories  $\text{cm}^{-1}$  degree $^{-1}$  and  $\sigma$  in absolute e.m units we have

$$\frac{k}{\sigma T} = \frac{3}{4.2 \times 10^7} \left[ \frac{1.37 \times 10^{-16}}{1.89 \times 10^{-20}} \right]^2 = 5.3$$

If however  $k$  be expressed in watts/ $\text{cm}^2$  X degree and  $\sigma$  in reciprocal ohms then

$$\frac{k}{\sigma T} = 5.3 \times 4.2 \times 10^{-9} = 2.2 \times 10^{-8}$$