Thermoelectric Effect

The thermoelectric effect is the direct conversion of temperature differences to electric voltage and vice versa via a thermocouple. Thermoelectric devices create a voltage when there is a different temperature on each side. Conversely, when a voltage is applied to it, heat is transferred from one side to the other, creating a temperature difference. At the atomic scale, an applied temperature gradient causes charge carriers in the material to diffuse from the hot side to the cold side.

This effect can be used to generate electricity, measure temperature or change the temperature of objects. Because the direction of heating and cooling is determined by the polarity of the applied voltage, thermoelectric devices can be used as temperature controllers.

The term "thermoelectric effect" encompasses three separately identified effects: the Seebeck effect, Peltier effect, and Thomson effect.

Seebeck Effect

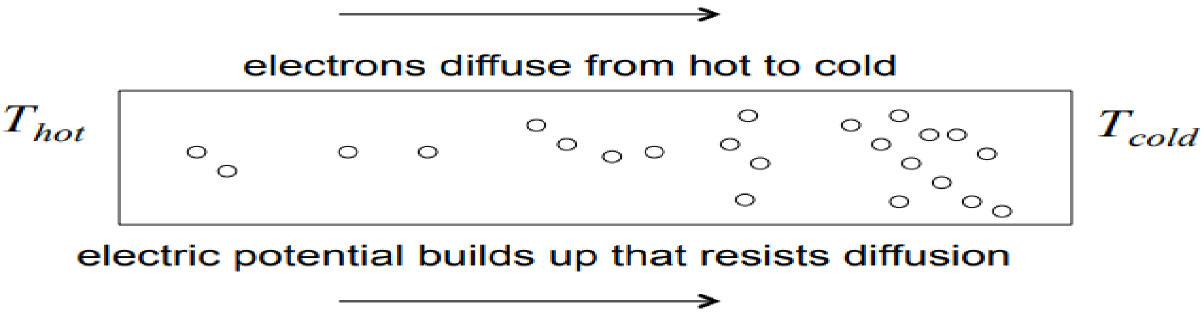
In 1821 Thomas Seebeck, a German physicist discovered that when two dissimilar metal (Seebeck used copper and bismuth) wires are joined at two ends to form a loop, a voltage is developed in the circuit if the two junctions are kept at different temperatures. The pair of metals forming the circuit is called a *thermocouple* . The effect is due to conversion of thermal energy to electrical energy.

- The Seebeck effect is a phenomenon in which a temperature difference between two dissimilar electrical conductors or semiconductors produces a voltage difference between the two substances.
- When heat is applied to one of the two conductors or semiconductors, heated electrons flow toward the cooler one. If the pair is connected through an electrical circuit, direct current (DC) flows through that circuit.
- The voltages produced by Seebeck effect are small, usually only a few microvolts (millionths of a volt) per kelvin of temperature difference at the junction.
- If the temperature difference is large enough, some Seebeck-effect devices can produce a few millivolts (thousandths of a volt). Numerous such devices can be connected in series to increase the output voltage or in parallel to increase the maximum deliverable current.
- Large arrays of Seebeck-effect devices can provide useful, small-scale electrical power if a large temperature difference is maintained across the junctions.

Explanation of Seebeck Effect

- The valence electrons in the warmer part of metal are solely responsible for that and the reason behind this is thermal energy.
- Also because of the kinetic energy of these electrons, these valence electrons migrate more rapidly towards the other (colder) end as compare to the colder part electrons migrate towards warmer part.

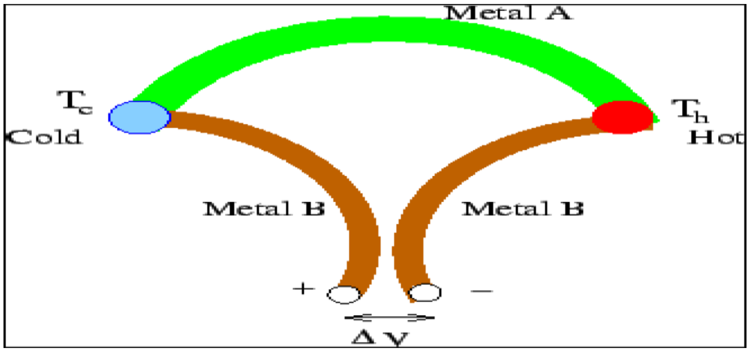
- At hot side Fermi distribution is soft i.e. the higher concentration of electrons above the Fermi energy but on cold side the Fermi distribution is sharp i.e. we have fewer electrons above Fermi energy.
- Electrons go where the energy is lower so therefore it will move from warmer end to the colder end which leads to the transporting energy and thus equilibrating temperature eventually



- In simple words we can come to conclusion that the electrons on a warmer end have a high average momentum as compared to the colder one. Therefore they will take energy with them (more in no.) as compared to the other one.
- This movement results in the more negative charge at colder part than warmer part, which Leads to the generation of electrical potential. If this pair is connected through an electrical circuit. It results in the generation of a DC.
- However the voltage produced is few microvolt (10-6) per Kelvin temperature difference. Now we all are aware of the fact that the voltage increase in series and current increase in parallel.
- So keeping this fact in mind if we can connect many such devices to increase the voltage (in case of series connection) or to increase the maximum deliverable current (in parallel). Keeping care of only one thing that a large temperature difference is required for this purpose.
- However one thing must keep in mind that we have to maintain constant, but different temperature and therefore the energy distribution at both the end will be different and hence it leads to the successful mentioned process.

The open circuit potential difference in the circuit whose junctions are maintained at temperatures T_h and $T_c (< T_h)$ is given by

$$\Delta V = S_{AB}(T_h - T_c)$$



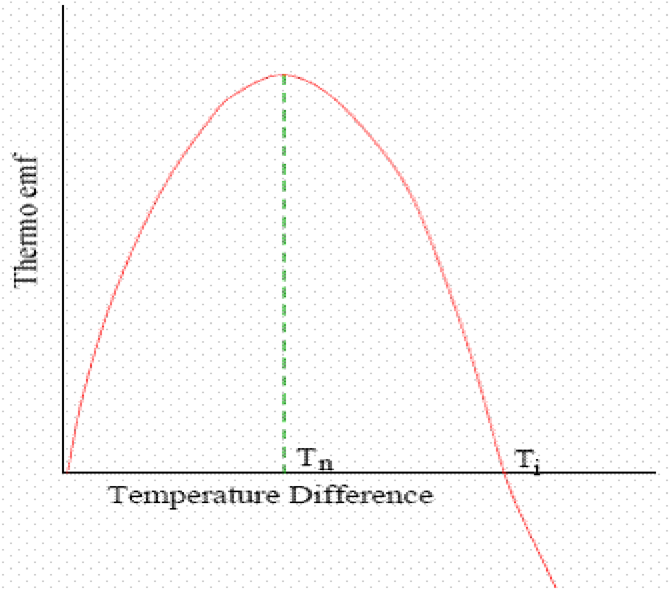
where the coefficient of proportionality is known as the **thermoelectric power** or the **Seebeck coefficient.** The term thermoelectric power is a misnomer because it does not measure any power and is measured in volt/ °K. **By convention, Seebeck coefficient's sign is the sign of the potential of the cold end with respect to the hot end.** Thus if S_{AB} is positive, convertional current flows from A to B at the hot junction. Seeback coefficient is not a constant but is dependant on temperature. The temperature dependence of a commercial thermocouple is usually expressed as a polynomial expansion in powers of temperature T. For instance, for a thermocouple with Platinum as one of the metals and an alloy of Pt-Rh (90:10) the open circuit voltage is given approximately by a quadratic

$$V = c + aT + bT^2$$

so that the thermoelectric power is given by

$$\frac{dV}{dT} = a + 2bT$$

The relationship between V and T is a parabola. The temp. $T_n = -a/2b$ at which the thermoelectric power is maximum is called the **neutral temperature** . The temperatures $T_i = T_0$ and $T_i = T_0 - a/b$ at which a small change in the difference of the junction temperatures leads to a change in the sign of emf is called the **inversion temperature**.



A complete understanding of Seebeck effect requires knowledge of behaviour of electron in a metal which is rather complicated. The Seebeck coefficient depends on factors like work functions of the two metals, electron densities of the two components, scattering mechanism within each solid etc. However, a simple minded picture is as follows.

Seebeck effect is a manifestation of the fact that if two points in a conductor (or a semiconductor) are maintained at different temperatures, the charged carriers (electrons or holes) in the hotter region, being more energetic (and, therefore, having higher velocities) will diffuse towards region of lower temperature. The diffusion stops when the electric field generated because of movement of charges has established a strong enough field to stop further movement of charges. For a metal, carriers being negatively charged electrons, the colder end would become negative so that Seebeck cofficient is negative. For a p-type semiconductor on the other hand, holes diffuse towards the lower temperature resulting in a positive Seebeck coefficient.

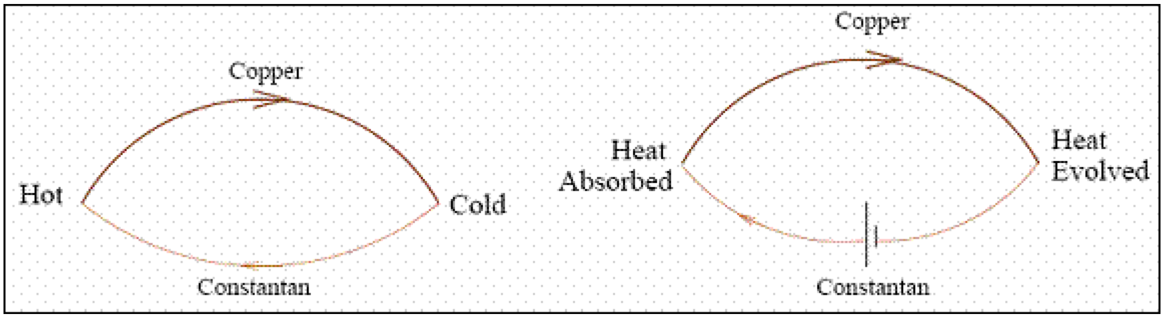
Performance of a thermocouple is determined by the Seebeck coefficient of the pair of metals forming the thermocouple. As it is impracticable to list the coefficient of all possible pairs, the Seebeck coefficients of metals are usually given with respect to Platinum as standard whose Seebeck coefficient is taken as zero. The following table gives the Seebeck coefficient (in mV/K) of some standard thermocouple material
at 0 $^{\circ}$ C.

Material	Seebeck coefficient	Material	Seeback coefficient	Material	Seebeck coefficient
Bismuth	-72	Lead	4	Iron	19
Constantan[1]	-35	Tantalum	4.5	Nichrome[2]	25
Nickel	-15	Rhodium	6	Antimony	47
Potassium	-9	Gold	6.5	Germanium	300
Sodium	-2	Silver	6.5	Silicon	440
Mercury	0.6	Copper	6.5	Tellurium	500
Carbon	3	Cadmium	7.5	Selenium	900
Aluminium	3.5	Tungsten	7.5		

Peltier Effect

In 1834 Jean Peltier, a french watch maker, discovered a second thermoelectric effect. If a current flows through a circuit containing junction of two dis-similar metals, it leads to an absorption or liberation of heat at the junctions. Heat is given out or absorbed depending on the pairs of metals and the direction of the current. The phenomenon of heat evolution is different from the Joule heat as Peltier effect is a reversible process while Joule loss is irreversible.

If the direction of the current at the junction is same as the direction of the Seebeck current, heat is liberated if the Seebeck junction is a hot junction or is absorbed if the junction is cold. Thus for a copper
- constantan thermocouple, if the current flow at the junction is from copper (+) to constantan (-), heat is absorbed. On changing the direction of the current, heat will be liberated at the same junction, showing that the phenomenon is reversible.



The amount of heat Q liberated to (or absorbed from) the surroundings in order that the junction may be kept at the same temperature is proportional to the current I passing through the junction

$$Q = \Pi_{AB} I$$

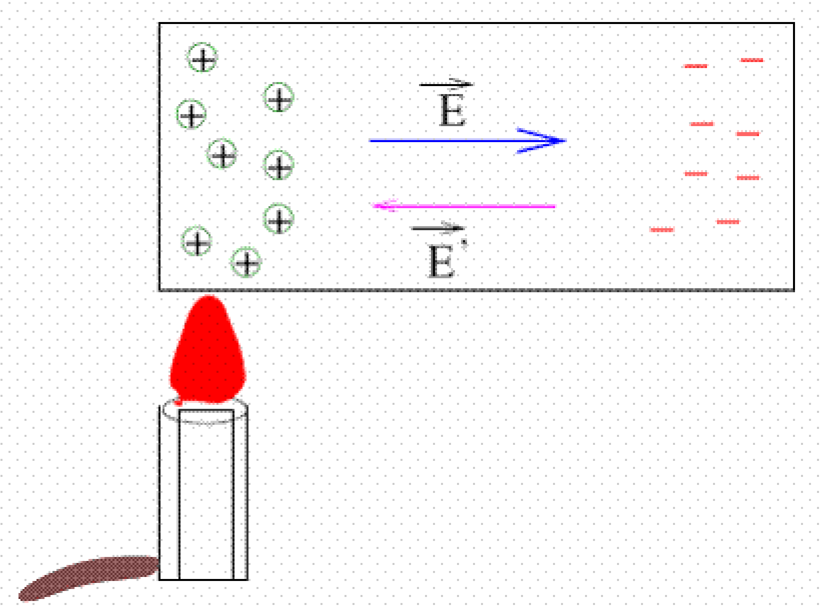
where the constant Π_{AB} is called the **Peltier coefficient** . The Peltier coefficient depends on the pair of materials A and B of the junction and also on the junction temperature.

Thomson Effect

William Thomson (later well known as Lord Kelvin) discovered a third thermoelectric effect which provides a link between Seebeck effect and Peltier effect.

Thomson found that when a current is passed through an wire of single homogeneous material along which a temperature gradient exists, heat must be exchanged with the surrounding in order that the original temperature gradient may be maintained along the wire. (The exchange of heat is required at all places of the circuit where a temperature gradient exists.)

Thomson effect may be understood by a simple picture. A conductor has free charge carriers, which are, electrons in metals, electrons and holes in semiconductors and ions in case of ionic conductors. Consider a section of such a conductor whose one end is hotter than the other end. Charge carriers at the hot end, being more energetic, will diffuse towards the colder end. The charge separation sets up an electric field $\vec{E}$. Diffusion of carriers would stop when the attractive force on the carriers due to this field $\vec{E}$ is strong enough to retard the motion of the carriers due to thermal effect.



We can represent the effect of the thermal gradient responsible for the diffusive motion of the carriers by an effective field $\vec{E'}$. This effective field is proportional to the thermal gradient and can be written as

$$E' = \sigma \frac{dT}{dx}$$

where σ is known as the **Thomson coefficient** for the material of the conductor. The Thomson electromotive force is $\mathcal{E}_{Th}$ given by

$$\mathcal{E}_{Th} = \int E' dx = \int_{T_1}^{T_2} \sigma dT$$

where T_1 and T_2 are the temperatures at the two ends of the rod.

Thomson effect is a manifestation of the Thomson emf described above. Clearly, one cannot demonstrate the existence of the emf by using it to drive a current in a close circuit. This is because if one uses a single metal with a temperature gradient, the integral σdT around a close loop is zero. For dis-similar metals, Peltier effect dominates over Thomson effect.
When a current I is passed through a homogeneous conductor with a temperature gradient, the rate of heat production per unit volume is given by

$$\dot{Q} = \rho I^2 - \sigma I \frac{dT}{dx}$$

where ρ is the resistivity of the sample. The first term is the irreversible Joule heat.
The second term is due to Thomson emf.

In metals such as copper and zinc, the hotter end is at a higher potential (as shown in the figure above). In such a situation if the current due to an external supply is in the same direction as the direction of decreasing potential, there is additional evolution of heat due to Thomson effect and the net heat produced is more than the Joule heat. If the direction of the current is reversed, heat energy is converted to electrical energy due to Thomson effect and the rate production of heat is reduced. This is known as **positive Thomson effect** .

An anomalous situation occurs in metals such as cobalt and iron. In these metals the hotter end is at a lower potential so that charge carriers move against the thermal gradient. The effect is opposite of what happens in case of positive Thomson effect. Such anomalous effect is known as **negative thomson effect** . Lead shows zero Thomson effect. The simple physical picture given above cannot explain the strange behaviour.