

Module 4 : THERMOELECTRICITY

Lecture 21 : Seebeck Effect

Objectives

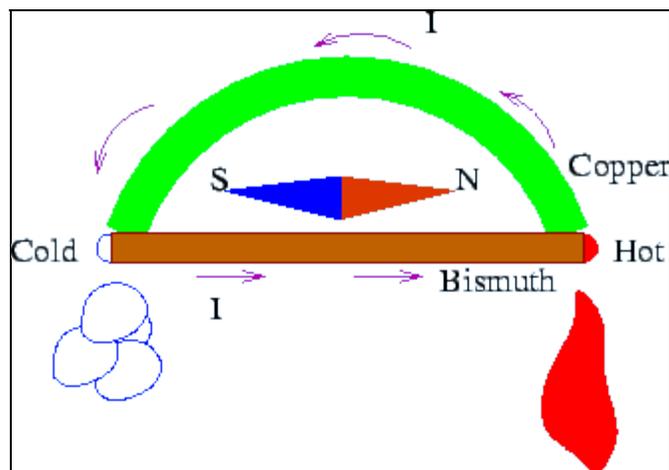
In this lecture you will learn the following

- Seebeck effect and thermo-emf.
- Thermoelectric series of metals which can be used to form thermocouples.
- Peltier effect, i.e. absorption or evolution of heat at junctions of dissimilar metals if a current exists in the circuit.
- Thomson effect of heat exchange in a circuit of a single metal in which a temperature gradient exists.

Seebeck Effect :

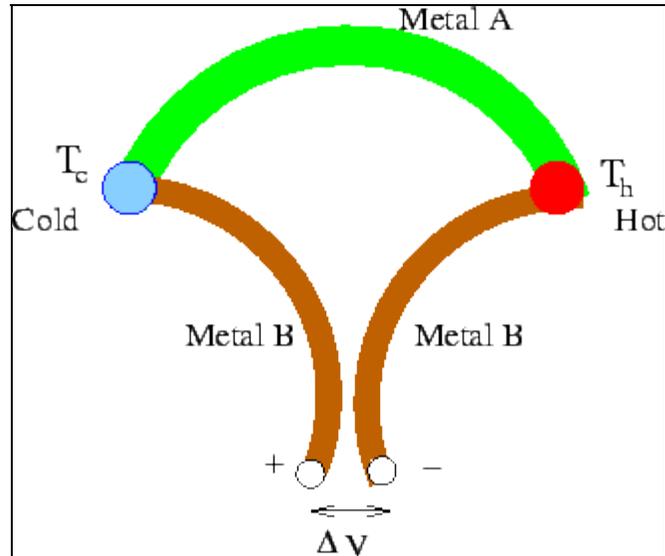
In 1821 Thomas Seebeck, a German physicist discovered that when two dissimilar metal (Seebeck used copper and bismuth) wires are joined at two ends to form a loop, a voltage is developed in the circuit if the two junctions are kept at different temperatures. The pair of metals forming the circuit is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

- The existence of current in the closed circuit may be confirmed by
- the deflection of a magnetic needle caused by the magnetic field of the current
- Joule heating produced in the wires
- closing the circuit with a capacitor to accumulate measurable charge
- placing a sensitive ammeter or a galvanometer in the circuit
- measuring the amount of chemical deposit at the electrodes of an electrochemical cell.



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Thermoelectric Power



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

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

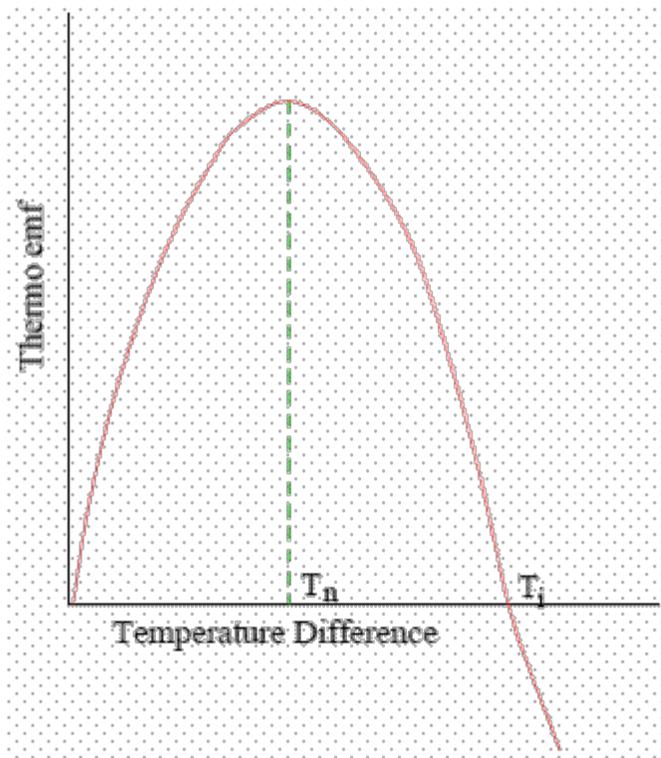
where the coefficient of proportionality is known as the **thermoelectric power** or the **Seebeck coefficient**. The term thermoelectric power is a misnomer because it does not measure any power and is measured in volt/°K. **By convention, Seebeck coefficient's sign is the sign of the potential of the cold end with respect to the hot end.** Thus if S_{AB} is positive, conventional current flows from A to B at the hot junction. Seebeck 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 temperature $T_n = -a/2b$ 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 coefficient 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 ° C.

Material	Seebeck coefficient	Material	Seebeck coefficient	Material	Seebeck coefficient
Bismuth	-72	Lead	4	Iron	19
Constantan ¹	-35	Tantalum	4.5	Nichrome ²	25
Nickel		Rhodium	6	Antimony	47

	-15				
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		

¹ An alloy of copper (60%) and nickel (40%)

² An alloy of Ni-Cr-Fe-Si

Example -1

Seebeck voltage for Copper- Constantan (Cn) thermocouple is given by the linear relation $V = a + bT$, where T is the absolute temperature of the hot junction and a and b are constants given by

- Cu : $a = 0.6$ mV $b = 0.008$ mV/K
- Cn : $a = -20$ mV $b = -0.056$ mV/K

Calculate the thermoelectric power when the hot junction is at 100°C .

Solution

$$\begin{aligned}
 V_{\text{Cu-Cn}} &= (a + bT)_{\text{Cu}} - (a + bT)_{\text{Cn}} \\
 &= 0.6 + 0.008T + 20 + 0.056T \\
 &= 20.6 + 0.064T
 \end{aligned}$$

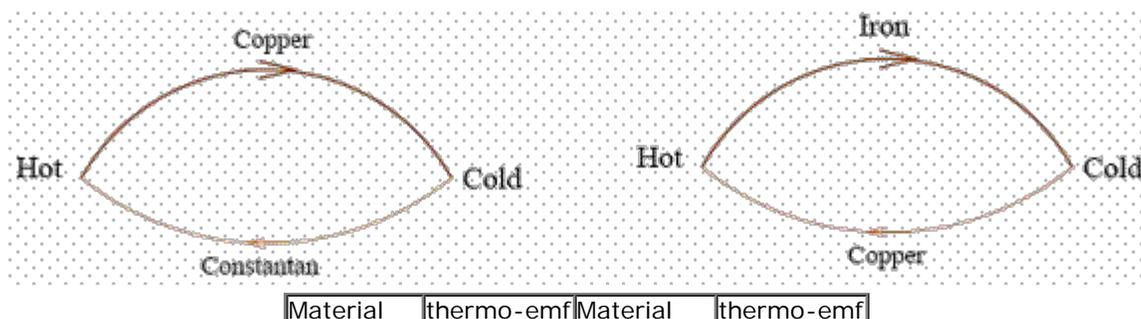
The thermoelectric power

$$\alpha = \frac{dV}{dT} = 0.064 \text{ mV/K}$$

Thermoelectric Series

A thermoelectric series is an ordering of thermocouple elements in such a way that when any pair of materials in the series is used to form a thermocouple, Seebeck current at the cold junction flows from the member occurring earlier in the series to that occurring later. One should be careful in using the series as the opposite convention is sometimes used. As one uses pairs of members which are closer in the series, the thermoelectric yield goes down when one reduces the temperature difference. The following table gives the thermal emf (in μV) with respect to Platinum when the cold junction is at 0°C while

the hot junction is at 100°C .



Chromel ¹	2810	Rh	700
Fe	1980	Pb	440
W	1120	Al	420
Cd	900	Ta	330
Au	780	Alumel ²	— 1290
Cu	760	Ni	— 1480
Zn	760	Constantan	— 3510
Ag	740	Bi	— 7340

¹ An alloy of Ni-Cr-Mn

² An alloy of Ni-Al-Mn

If the temperatures of the two junctions are kept fixed at T_1 and $T_2 (> T_1)$, then the emf of a circuit consisting of a pair of metals A and B is equal to the difference between the emfs of two circuits, one consisting of the pair A-C and the other of the pair B-C, i.e.

$$\mathcal{E}_{AB} = \mathcal{E}_{AC} - \mathcal{E}_{BC}$$

In view of this, it is convenient to measure the thermo-emf with respect to a reference metal C. Platinum is taken to be such a reference.

Example-2

Compute the thermo-emf of a copper-constantan thermocouple with its junctions at 0° C and 100° C.

Solution

From the table above we have $\mathcal{E}_{Cu-Pt} = +760 \mu V$ and $\mathcal{E}_{Cn-Pt} = -3510 \mu V$. Thus

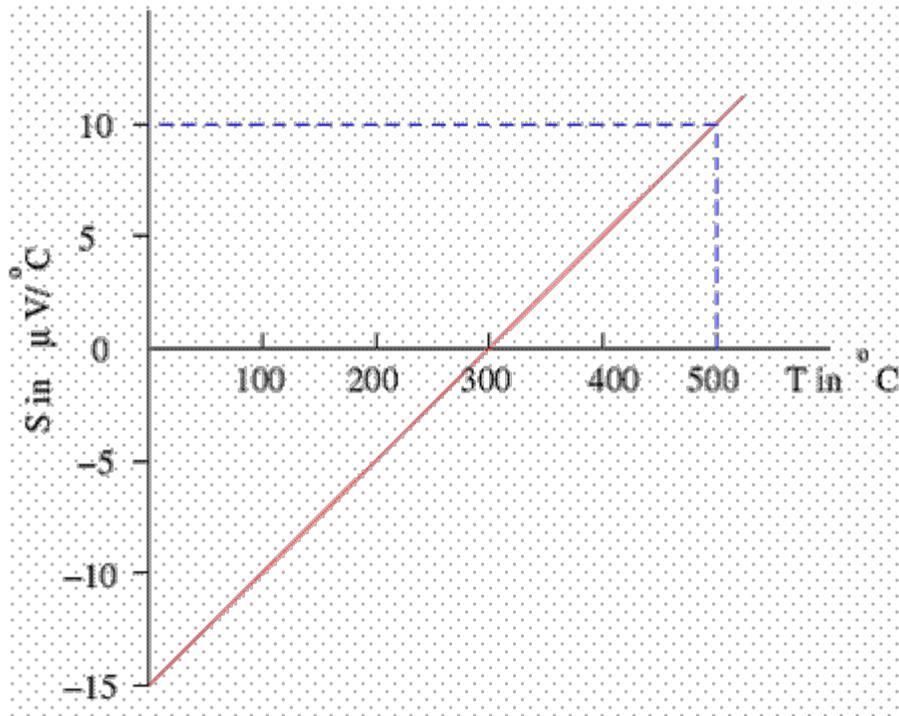
$$\begin{aligned} \mathcal{E}_{Cu-Cn} &= \mathcal{E}_{Cu-Pt} - \mathcal{E}_{Cn-Pt} \\ &= 760 - (-3510) = 4270 \mu V \end{aligned}$$

Thus the emf yield of a copper-constantan thermocouple is 4.27 mV.

Exercise

The thermoelectric power of a thermocouple whose cold junction is maintained at 0° C and the hot junction at t° C is given by the following graph.

- (1) Sketch the thermo-emf with temperature.
- (2) Determine the neutral temperature and the temperature of inversion. How will these two temperatures change if the cold junction were maintained at 50° C ?



(Ans. (ii) 300°C , 600°C ; No change, 550°C)

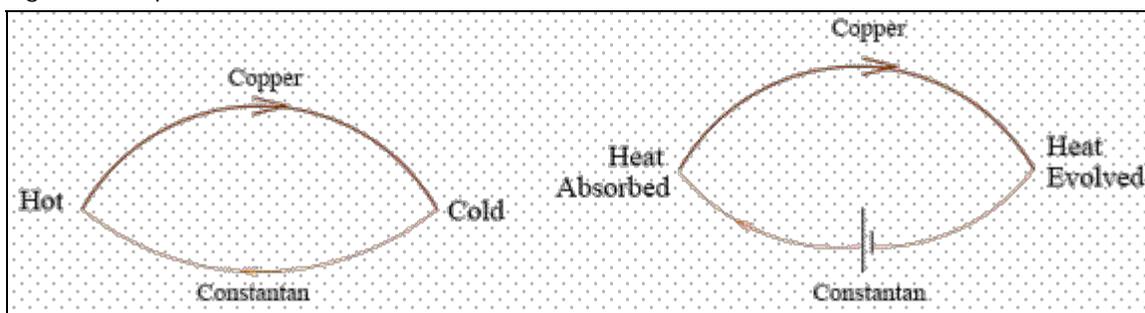
Exercise

A chromel-constantan thermocouple with the cold junction at 0°C has a linear variation of the open circuit voltage for temperatures of the hot junction between 0°C and 200°C . Calculate the thermoelectric emf when the hot junction is maintained at 150°C . [Hint : Emf is zero when both the junctions are at the same temperature] (Ans. 9.5 mV)

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

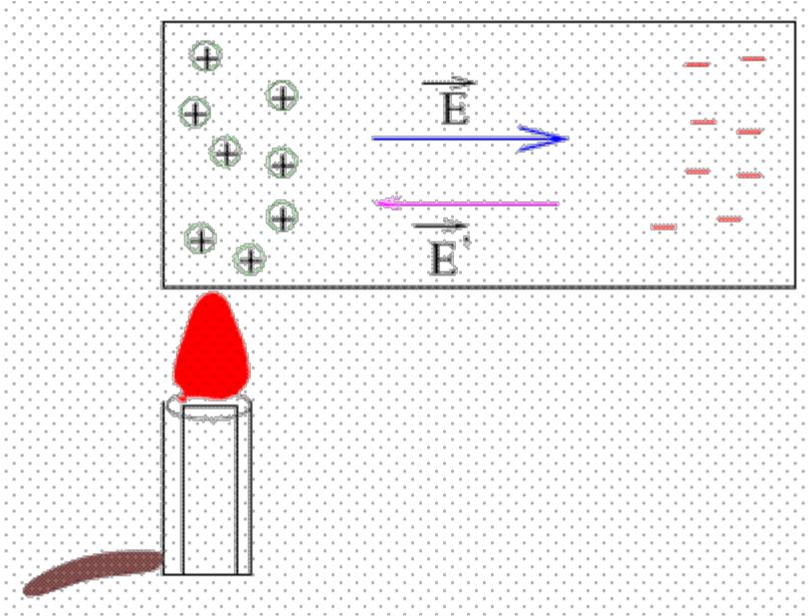
of materials A and B of the junction and also on the junction temperature.

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 \mathcal{E}_{Th} is 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

ρ

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.

Recap

In this course you have learnt the following

- A current flows in a circuit of two dissimilar metals, when the two junctions are kept at different temperatures. The junction circuit is called thermocouple.
- The magnitude and sign of the thermo-emf developed depends on the material of the two metals and the temperatures of the two junctions. The metals can be arranged in an order called the thermoelectric series such that in a thermocouple made with two metals in the series, the current in the hot junction is from the metal preceding in the series to the one occurring later.
- The inverse effect in which heat is evolved or absorbed at the junctions of two dissimilar conductors if a current is flowing in the circuit is known as Peltier effect.
- Peltier effect and Seebeck effect are linked by Thomson effect according to which when a current is passed through a single wire in which temperature gradient exists, heat exchange with the surround must take place if the temperature gradient is to be maintained.