Thermoelectricity

Thermal electromotive forces, Seebeck and Peltier effect:

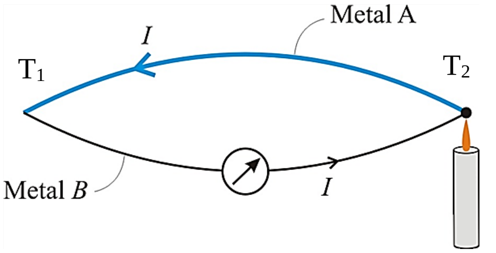


Fig. 1: Thermocouple

In 1826, Thomas Johann Seebeck discovered an effect, known as ***Seebeck effect*** that ***a current flows in a circuit consisting of two different metals A and B when a difference of temperature is maintained between the two junctions, as shown schematically in Fig.1.*** There is, therefore, an e.m.f. in such a circuit depends on thermal conditions, called ***thermal electromotive force*** or ***Seebeck e.mf.*** The combination of two different metals in which thermal e.m.f. is produced is called a ***thermocouple***, Seebeck arranged 35 metals in a series in such a way that, when any two comprise a circuit, the current flows across the hot junction from the metal occurring earlier to that occurring later in series. Seebeck's list comprises:

Bi—Ni—Co—Pd—Pt —U —Cu—Mn —Ti—Hg—Pb—Sn—Cr—Mo—Rh—Ir —Au—Ag Zn— W— Cd—Fe—As— Sb—Te.

The Seebeck e.m.f. arises from the fact that the density of free electrons in a metal differs from one metal to another and, in the same metal, depends on temperature. When two different metals are joined and two junctions are kept at different temperatures, electron diffusions at the junctions take place at different rates. There is a net motion of the electrons, as though the electrons were driven by non-electrostatic field. Energy expended in the current flow is supplied by the absorption of heat from the external source.

A complementary phenomenon to Seebeck effect was discovered by Jean C.A. Peltier in 1834 which is known as ***Peltier effect***. He observed that at constant temperature when current is passed across a junction of two different metals heating or cooling of the junction takes place depending on the direction of the flow of the current and the quantity of Peltier heat is proportional to the charge which crosses the junction, In Fig. 2 when-Current flows in junction from bismuth (Bi) to antimony (Sb), heat is absorbed in the junction which is, therefore, cooled, but on reversing the direction of the current heat is evolved, and the junction is heated. The Peltier e.m.f. of a junction of metals A and B, π_{AB} is defined as the heat absorbed or liberated per unit of electricity crossing the junction. Thus

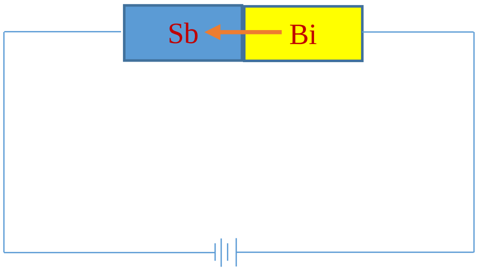


Fig. 2

$$\pi_{AB} = \frac{\text{Peltier heat}}{\text{Charge transferred}} \tag{1}$$

π_{AB} depends on the nature of the two metals and also on the temperature of the junction, but is independent of any other junction that may be present.

Thomson effect:

The evolution or absorption of heat when electric current passes through a circuit composed of a single material that has a temperature difference along its length. This transfer of heat is superimposed on the common production of heat associated with the electrical resistance to currents in conductors. If a copper wire carrying a steady electric current is subjected to external heating at a short section while the rest remains cooler, heat is absorbed from the copper as the conventional current approaches the hot point, and heat is transferred to the copper just beyond the hot point. This effect was discovered (1854) by the British physicist William Thomson (Lord Kelvin).

Positive Thomson effect

In positive Thomson effect, it is found that hot end is at high potential and the cold end is at a low potential. Heat is evolved when current is passed from hotter end to the colder end and heat is absorbed when current is passed from colder end to hotter end. The metals which show positive Thomson's effect are Cu, Sn, Ag, Cd, Zn, etc.

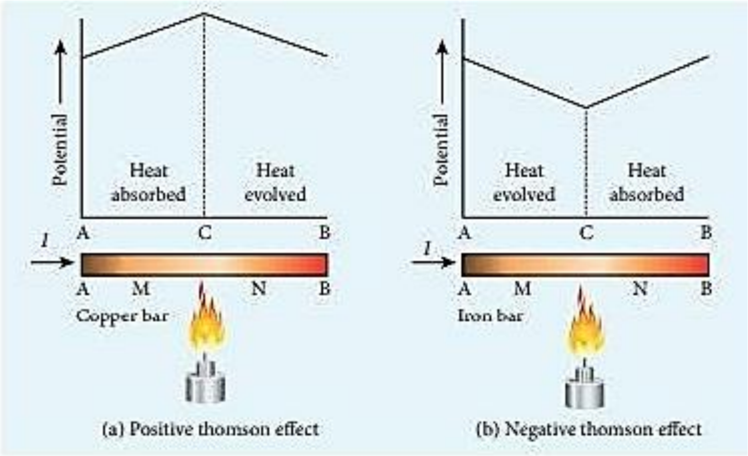


Fig. 1 Positive and negative Thomson effect

Consider a copper bar AB heated in the middle at the point C and current flowing in the direction from point A to the point B in figure 1. When no current is flowing, the point M and N are equidistant from point C and hence at the same temperature. When a current is passed from A to B, point N shows higher temperature compared to M. Similarly, point B will show higher temperature as compared to point A. It means from point A to point C, heat is absorbed and from point C to point B heat is evolved. This is known as positive Thomson effect.

Negative Thomson effect

In negative Thomson effect it is found that the hot end is at a low potential and the cold end is at a higher potential. Heat is evolved when current is passed from colder end to the hotter end and heat is absorbed when current flows from hotter end to colder end. The metals which show negative Thomson's effect are Fe, Co, Bi, Pt, Hg, etc.

Consider an Iron bar AB heated in the middle at the point C and current flowing in the direction from point A to the point B in figure 2. When no current is flowing, the point M and N are equidistant from point C and hence at the same temperature. When a current is passed from A to B, point N shows lower temperature compared to M. Similarly, point B will show lower temperature as compared to point A. It means from point A to point C, heat is evolved and from point C to point B heat is absorbed. This is known as negative Thomson effect.

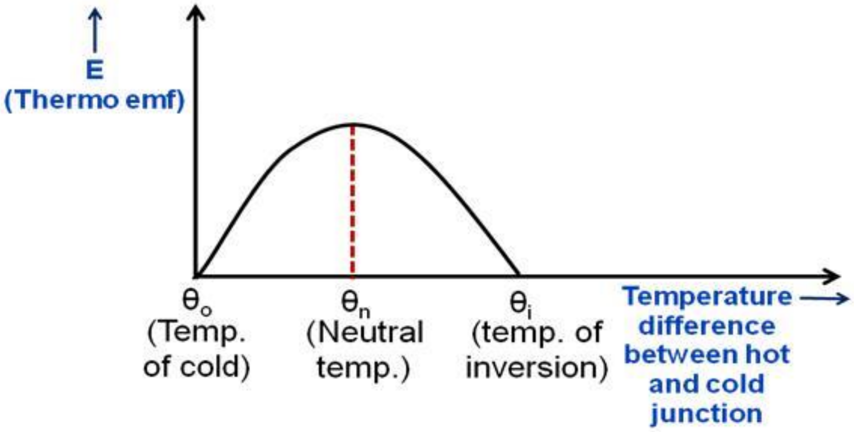
Thomson coefficient (σ)

The amount of heat energy absorbed or evolved when one-ampere current flows for one second (one coulomb) in a metal between two points which differ in temperature by 1°C is called Thomson coefficient. It is denoted by σ. Its unit is volt per °C.

Neutral Temperature and Temperature of Inversion

If we increase the temperature of the hot junction of a thermocouple keeping the temperature of the cold junction constant, the thermo e.m.f. will increase with the temperature. The thermo e.m.f. rises to a maximum at a temperature (θn) called **neutral temperature**.

Again if we further increase the temperature then the e.m.f. gradually decreases and eventually becomes zero at a particular temperature (θi) called **temperature of inversion**.



<u>Home work:</u> The e.m.f. of a thermocouple, one junction of which is kept at 0 ℃ is given by $\boldsymbol{E = 1784\,t - 2.4\,t^2}$. Find the neutral temperature.
Hints: at neutral temperature, the slope (dE/dt) is zero.

Laws of addition of thermal electromotive forces:

In measuring thermo e.m.f., it is always necessary to insert some apparatus in the circuit. This introduces some addition of junctions of different metals in the circuit and it is, therefore, important to define the laws of addition of this extra junctions in the same circuit. There are two such laws:

<u>(1) Law of Intermediate Metals:</u> The presence of an additional metal into any Circuit does not alter the whole e.m.f. in the circuit, provided the additional metal is at the same temperature of the point at which it is inserted.

<u>(2) Law of Intermediate Temperatures</u>: The e.m.f. of a couple with junctions at T_1 and T3 is the sum of the e.m.f. of two couples of the same metals, one with junctions at T_1 and T_2 and other at T_2 and T_3 as shown in Fig. 3. In other words, e.m.f.

$$[e]_1^3 = [e]_1^2 + [e]_2^3 \qquad (2)$$

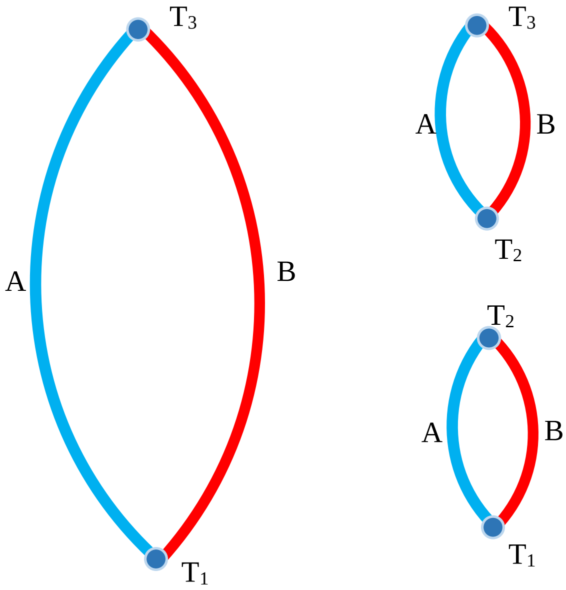


Fig. 3

Thomson coefficient

We know that on carrying a charge q round the circuit the heat absorbed at hot junction at T_2 is π_2q, measured in absolute units, and that given up at T_1 is π_1q. Now the heat absorbed or given up is proportional to the temperature of the junction. Hence

$$\frac{\pi_2 \mathrm{q}}{\pi_1 \mathrm{q}} = \frac{T_2}{T_1}$$

$$\frac{\pi_2}{\pi_1} = \frac{T_2}{T_1}$$

and, therefor

$$\frac{\pi_2 - \pi_1}{\pi_1} = \frac{T_2 - T_1}{T_1}$$

Putting $\pi_2 - \pi_1 = e$ (total e.m.f. in the circuit)

$$e = \pi_1 \left(\frac{T_2 - T_1}{T_1} \right) \tag{3}$$

If one junction is kept at constant temperature T_1, then π_1 is constant and, therefore, $e \propto (T_2 - T_1)$. But in actual practice it was found that, as a result of heating a junction of two different metals the e.m.f. increased at first, then diminished, and, passing through zero, actually became reversed. Obviously, it indicates that e is not proportional to T_2 - T_1, This led Lord Kelvin (Prof. Wm. Thomson) to the conclusion that along with Peltier effect there is another source of e.m.f. - existing between the different parts of a metal at different temperatures. Thus if σ be the e.m.f.

due to unit difference of temperature between two points of it, then $\int_{T_1}^{T_2}\sigma dT$ is the total e.m.f. between points at temperatures T_1 and T_2. Taking σ_A and σ_B as the values of a for metal A and B respectively then, our equation of e.m.f. for the whole circuit becomes

$$e=\pi_2-\pi_1+\int_{T_1}^{T_2}(\sigma_B-\sigma_A)dT \tag{4}$$

$$e=\pi_1\left(\frac{T_2-T_1}{T_1}\right)+\int_{T_1}^{T_2}(\sigma_B-\sigma_A)dT$$

The quantity σ is called the Thomson co-efficient. If the current flows in the direction of e.m.f. heat is absorbed to maintain the current in the circuit. But if the direction of current is reversed, heat is liberated for a corresponding reason. The sign of σ can, be positive or negative, σ is positive for the metals Cd, Zn, Age. Cu and negative for Fe, Pt and Pd.

Thermo-electric power:

Eq. (4) can be written in the following form

$$e=\pi_2-\pi_1+\int_{T_1}^{T_2}(\sigma_B-\sigma_A)dT \tag{5}$$

$\frac{d\pi}{dT}$ is the rate of change of Peltier co-efficient (or Peltier e.m.f.) with temperature for two metals π_2 and π_1 are the upper and lower limits of integral $\int\frac{d\pi}{dT}dT$. Again, Eq. (5) can be written as

$$e=\int_1^2\left\{\frac{d\pi}{dT}-(\sigma_A-\sigma_B)\right\}dT \tag{6}$$

Differentiating with respect to T, we get

$$\frac{de}{dT}=\frac{d\pi}{dT}-(\sigma_A-\sigma_B)$$

$\frac{de}{dT}$ is called thermo-electric power for two metals. This is the rate of change of e.m.f. in the couple with the change of temperature in one junction. The thermo-electric power $\frac{de}{dT}$ has plotted against temperature T as shown in Fig. 4. In this diagram the elementary area PQ gives the e.m.f. acting round the couple, temperature difference being dT. Total electro-motive force in the couple is the sum of the elementary areas such as PQ and this is the area of the whole figure ABCD for temperature difference T_2 - T_1.

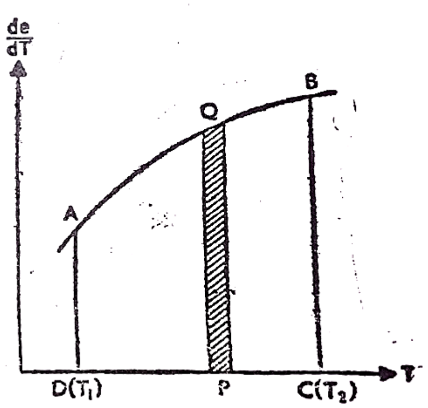
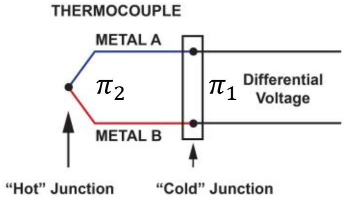


Fig. 4

Thermodynamics in Thermoelectricity



It can be seen that, Peltier and Thomson effects are reversible process. If the joule heating is neglected then thermocouples can be compared with a heat engine. So we can apply second law of thermodynamics in a ideal thermocouple. Let a thermocouple of A and B metals having junction temperatures T_1 and T_2. If $\pi_2 \; and \; \pi_1$ is the Peltier e.m.f. and σ_B, σ_A is their Thomson coefficient then total e.m.f. is

$$e = \pi_2 - \pi_1 + \int_{T_1}^{T_2} (\sigma_B - \sigma_A) dT$$

From which we can write,

$$\frac{de}{dT} = \frac{d\pi}{dT} - (\sigma_A - \sigma_B) \tag{1}$$

For the flow of q amount of charge, the amount of heat absorbed at the hot junction is $\frac{\pi_1 q}{J}$

And the amount of heat evolved at cold junction is $\frac{\pi_2 q}{J}$ $[As \; W = JH]$

the amount of heat absorbed and evolved due to Thomson effect are $\frac{q}{J}\sigma_A dT$ and $\frac{q}{J}\sigma_B dT$ respectively. Where J is the mechanical equivalent of heat. Now according to second law of thermodynamics, we can write for a reversible process,

$$\frac{dQ}{T} = 0$$

So

$$\frac{q}{J}\left[\frac{\pi_2}{T_2} - \frac{\pi_1}{T_1} + \int_{T_1}^{T_2} \frac{\sigma_B}{T} dT - \int_{T_1}^{T_2} \frac{\sigma_A}{T} dT\right] = 0$$

$$\int_{T_1}^{T_2} \frac{d}{dT}\left(\frac{\pi}{T}\right) dT - \int_{T_1}^{T_2} \frac{(\sigma_A - \sigma_B)}{T} dT = 0$$

$$\int_{T_1}^{T_2} \left[\frac{d}{dT}\left(\frac{\pi}{T}\right) - \frac{(\sigma_A - \sigma_B)}{T}\right] dT = 0$$

$$\frac{d}{dT}\left(\frac{\pi}{T}\right) - \frac{(\sigma_A - \sigma_B)}{T} = 0$$

$$\sigma_A - \sigma_B = T \frac{d}{dT}\left(\frac{\pi}{T}\right) \tag{2}$$

$$\sigma_A - \sigma_B = T\left(\frac{1}{T}\frac{d\pi}{dT} - \pi \frac{1}{T^2}\right)$$

$$\sigma_A - \sigma_B = \frac{d\pi}{dT} - \frac{\pi}{T} \tag{3}$$

Substituting the value of $(\sigma_A - \sigma_B)$ from eqn. 1, we get,

$$\frac{d\pi}{dT} - \frac{de}{dT} = \frac{d\pi}{dT} - \frac{\pi}{T}$$

$$\frac{de}{dT} = \frac{\pi}{T}$$

$$\pi = T\frac{de}{dT} \tag{4}$$

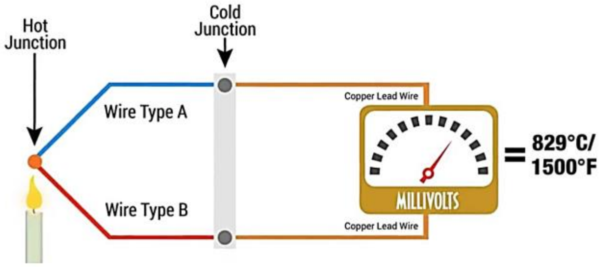
Putting this value of π in equation 2 we get,

$$\sigma_A - \sigma_B = T\frac{d}{dT}\left(\frac{de}{dT}\right)$$

$$\sigma_A - \sigma_B = T\frac{d^2e}{dT^2} \tag{5}$$

Application of Thermal Electromotive Force:

(1) Thermocouple:



Thermo e.m.f. produced in a thermocouple can be used for measuring the amount of radiant heat. One of these measuring devices is a thermocouple. As the effect produced in one couple is very low, a number of them is arranged in series to multiply the effect. A more sensitive device is Boy's radio-micrometer. The galvanometer and the couple are combined in one instrument. The loop connected to an antimony-bismuth couple hangs in between the poles of a horse-shoe magnet. When current flows in the loop due to heating of the thermocouple junction there will be deflection of the loop. The magnitude of the deflection gives indication about the amount of heat.

(2) Pyro-electricity:

Certain crystals, especially tourmaline, if heated at one end becomes positively charged and the other negatively charged but on being cooled the polarity changes. Heating or cooling can be done with reference to atmospheric or any other temperature. This phenomenon is known as Pyro-electricity. If the crystals are broken up, each part exhibits pyro-electricity. If heating or cooling is done to tourmaline powder, the particles arrange themselves in chains, owing to the polar charges, just as iron filings do when magnetized. Boracite, quartz and fluor are among the pyro-electric materials.

(3) Piezo-electricity

It is discovered by J. Curie and P. Curie that if the crystals which exhibit pyro-electricity are t3ubj-2cted to compression or tension, opposite charges of electricity appear at ends of the crystals. This phenomenon is known as Piezo-electricity. The sign of the charges produced at the end of the crystal under compression is similar to those produced by cooling the crystal, while tension produces the charges with -similar sign as those produced by heating the crystal.

Practical Thermocouple

1. Type K Thermocouple (Nickel-Chromium / Nickel-Alumel): The type K is the most common type of thermocouple. It's inexpensive, accurate, reliable, and has a wide temperature range.

   Temperature Range:
   Thermocouple grade wire, –454 to 2,300F (–270 to 1260C)
   Extension wire, 32 to 392F (0 to 200C)

Accuracy (whichever is greater):

- Standard: +/- 2.2C or +/- .75%
- Special Limits of Error: +/- 1.1C or 0.4%

2. Type J Thermocouple (Iron/Constantan): The type J is also very common. It has a smaller temperature range and a shorter lifespan at higher temperatures than the Type K. It is equivalent to the Type K in terms of expense and reliability.

   Temperature Range:

- Thermocouple grade wire, -346 to 1,400F (-210 to 760C)
- Extension wire, 32 to 392F (0 to 200C)

Accuracy (whichever is greater):

- Standard: +/- 2.2C or +/- .75%
- Special Limits of Error: +/- 1.1C or 0.4%

3. Type T Thermocouple (Copper/Constantan): The Type T is a very stable thermocouple and is often used in extremely low temperature applications such as cryogenics or ultra-low freezers.

   Temperature Range:

- Thermocouple grade wire, -454 to 700F (-270 to 370C)
- Extension wire, 32 to 392F (0 to 200C)

Accuracy (whichever is greater):

- Standard: +/- 1.0C or +/- .75%
- Special Limits of Error: +/- 0.5C or 0.4%

4. Type E Thermocouple (Nickel-Chromium/Constantan): The Type E has a stronger signal & higher accuracy than the Type K or Type J at moderate temperature ranges of 1,000F and lower. See temperature chart (linked) for details.

   Temperature Range:

- Thermocouple grade wire, -454 to 1600F (-270 to 870C)
- Extension wire, 32 to 392F (0 to 200C)

Accuracy (whichever is greater):

- Standard: +/- 1.7C or +/- 0.5%
- Special Limits of Error: +/- 1.0C or 0.4%

5. Type N Thermocouple (Nicrosil / Nisil): The Type N shares the same accuracy and temperature limits as the Type K. The type N is slightly more expensive.

   Temperature Range:

- Thermocouple grade wire, -454 to 2300F (-270 to 392C)

- Extension wire, 32 to 392F (0 to 200C)

Accuracy (whichever is greater):

- Standard: +/- 2.2C or +/- .75%
- Special Limits of Error: +/- 1.1C or 0.4%

NOBLE METAL THERMOCOUPLES (Type S,R, & B):

Noble Metal Thermocouples are selected for their ability to withstand extremely high temperatures while maintaining their accuracy and lifespan. They are considerably more expensive than Base Metal Thermocouples.

6. Type S Thermocouple (Platinum Rhodium - 10% / Platinum): The Type S is used in very high temperature applications. It is commonly found in the BioTech and Pharmaceutical industries. It is sometimes used in lower temperature applications because of its high accuracy and stability.

   Temperature Range:

- Thermocouple grade wire, -58 to 2700F (-50 to 1480C)
- Extension wire, 32 to 392F (0 to 200C)

Accuracy (whichever is greater):

- Standard: +/- 1.5C or +/- .25%
- Special Limits of Error: +/- 0.6C or 0.1%

7. Type R Thermocouple (Platinum Rhodium -13% / Platinum): The Type R is used in very high temperature applications. It has a higher percentage of Rhodium than the Type S, which makes it more expensive. The Type R is very similar to the Type S in terms of performance. It is sometimes used in lower temperature applications because of its high accuracy and stability.

   Temperature Range:

- Thermocouple grade wire, -58 to 2700F (-50 to 1480C)
- Extension wire, 32 to 392F (0 to 200C)

Accuracy (whichever is greater):

- Standard: +/- 1.5C or +/- .25%
- Special Limits of Error: +/- 0.6C or 0.1%

8. Type B Thermocouple (Platinum Rhodium – 30% / Platinum Rhodium – 6%): The Type B thermocouple is used in extremely high temperature applications. It has the highest temperature limit of all of the thermocouples listed above. It maintains a high level of accuracy and stability at very high temperatures.

   Temperature Range:

- Thermocouple grade wire, 32 to 3100F (0 to 1700C)
- Extension wire, 32 to 212F (0 to 100C)

Accuracy (whichever is greater):

- Standard: +/- 0.5%
- Special Limits of Error: +/- 0.25%

References:

1. Concepts of Electricity and Magnetism – M.S. Huq, A.K. Rafiqullah, A.K. Roy
2. Physics – Halliday, Resnick, Krane -5th edition
3. https://www.wikipedia.org