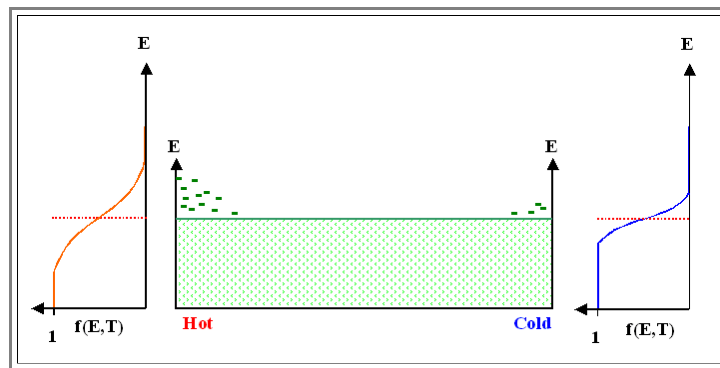


# Thermoelectric effects

## Seebeck Effect

### Advanced

- First of all, in considering thermoelectric effects, we have to realize that we are dealing with a *non*-equilibrium situation.
  - A general theory of non-equilibrium is beyond our means, suffice it to say that Lars **Onsager**, with a paper entitled "*Reciprocal relations in irreversible processes*" induced some fundamental insights as late as **1930**; he received the Nobel price for his contribution to non-equilibrium thermodynamics in **1968** - for chemistry, of all things.
- However, what we should be aware of, is the essential statement of non-equilibrium theory:
  - As long as there is no equilibrium, we always have *currents* of something trying to establish equilibrium by reducing a gradient in something else that is the actual cause of the non-equilibrium. A gradient in the electrical potential, e.g., causes our well-known electrical currents, and a gradient in a concentration causes diffusion currents.
  - But we must abstract even more, and consider things like entropy currents as well as all kinds of combinations of gradients and currents.
- While Onsager discovered some quite general relations between gradients and currents, we will not delve into details here, but only look a bit more closely at what causes the Seebeck effect.
- For that, we still treat the thermoelectric effect with equilibrium thermodynamics, simply assuming that *locally* we are not very far from equilibrium and thus can still use band structure models with a Fermi energy (which is only a well defined quantity for equilibrium) and resulting carrier distributions.
  - In the simplest possible case, what we will get for a long bar of metal, hot at one end and cold at the other, is something like this:



- At the hot end, the Fermi distribution is "soft", and we have a noticeable concentration of electrons well above the Fermi energy. At the cold end, the Fermi distribution is sharp, and we have fewer electrons above the Fermi energy.
  - The drawing, of course, grossly exaggerates the real situation. Note also that the total concentration of electrons at both ends is the same - even so the drawing does not show this because the holes below the Fermi energy are not included.
  - Note too, that the Fermi energy is constant throughout the material (we neglect any possible effects of the temperature on the Fermi energy, as we have it, for example, in [doped semiconductors](#)).
  - As always, electrons go to where the energy is lower; the electrons would tend to move from the hot end to the cold end, thereby transporting energy and thus equilibrating the temperature eventually. Equilibrium, with a constant temperature everywhere will be achieved.
  - An equally valid alternative interpretation just looks at the concentration gradient of the electrons in energy space, which would automatically drive a kind diffusion current until the concentration (and thus the temperature) is equalized.
  - Yet another way of looking at it is to consider that the average momentum of the electrons at the hot end is larger than that of the electrons at the cold end. They would therefore "run away" faster (taking energy with them) than the electrons from the other end would "run in".
- However, since we keep the *temperature difference* constant, all this *cannot happen*. We will have to maintain constant but different temperatures and therefore different energy distributions at both ends of the metal bar.
  - If nothing happens, we will lose the electrons with large momentum faster than we gain electrons with smaller momentum; and a temperature gradient cannot be maintained. The only way to change that, is to lower the potential at the hot end somewhat, i.e. make the ends positively charged, and to raise it at the cold end.
  - The potential difference must build up until it is large enough to exactly counteract the net loss of "hot" electrons due to momentum imbalance.

This is essentially the reason why we find a **thermovoltage**.

- Note that the junction is not directly essential. However, if you just plug a wire from one material into your Voltmeter and heat up the middle part, leaving the two ends cold (and at the same temperature), your potential along the wire may change, but at the two ends you have the same potential, and it is the potential difference between the two ends you measure
- Plucking the hot end into your Voltmeter is a bit unpractical, so you necessarily end up with a junction to some other material. The other material now will also have a hot end and a cold end, and thus develop a potential difference.
- Since the potential at the other end can only have *one* value, you will now get a potential difference between the *two* cold ends which depends, of course, somehow on the choice of materials.

Still, there is a potential difference between the hot and cold end of one piece of material, and even so it cannot be measured directly, we can measure it indirectly somehow and tabulate the values.

- We can do this, with somewhat more involved but similar reasoning not only for metals, but also for semiconductors. The table below gives some absolute values and shows that semiconductors are good candidates for actual thermocouples, because their **Seebeck voltage** is fairly large. The values are for about room temperature, or about **700 °C** for the last three materials

Material	Al	Cu	Ag	W	(Bi,Sb) <sub>2</sub> Te <sub>3</sub>	Bi <sub>2</sub> (Te,Se) <sub>3</sub>	ZnSb	InSb	Ge	TiO <sub>2</sub>
<b>Seebeck voltage [μV/K]</b> (V <sub>hot</sub> - V <sub>cold</sub> )	-0,20	+3,98	+3,68	+5,0	+195	-210	+220	-130	-210	-200

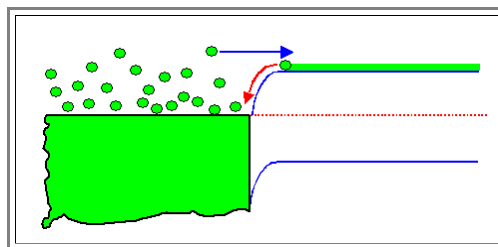
**Surprise!** There are positive (as expected) *and* negative valued of the voltage. What does it mean?

- Simply that you are looking at *positively charged* carriers being responsible for the Seebeck effect - **holes**, in other words.
- Not so surprising for semiconductors, perhaps, but somewhat unexpected for **Al**. But, as we should know, conduction in **Al** relies heavily on holes, as evidenced, e.g., in its [positive Hall coefficient](#) while most other metals have a negative one

### Peltier Effect

Understanding qualitatively the Seebeck effect does not help much to understand the Peltier effect.

- Again, lets look at some simple junction, this time an ohmic conduct of a metal to a semiconductor.



- Shown is an equilibrium situation, where the Fermi energy is constant throughout, and the flow of electrons across the junction must be equal in both directions. Note that only the high-energy end electrons of the Fermi distribution in the metal makes it across the junction, whereas all electrons of the semiconductor can flow into the metal.
- The electrons of the metal thus also transport some thermal energy out of the metal, but in equilibrium exactly the same amount is gained by the semiconductor electrons, which are high-energy electrons in the metal.

Now consider some external voltage driving some net current through the junction in either direction.

- If this current is an electron current flowing from the metal into the semiconductor, it *still* transports some thermal energy out of the metal, but since it is now much larger than the electron current flowing back, we have a *net transport of thermal energy* out of the metal, which therefore *must cool down* – and that's it; nothing happens to the semiconductor part due to these.
- If the current is reversed, the flow of thermal energy reverses, too, and now the metal at the contact gets up.
- It is conceivable then (also far from clear) that the total effect in terms of temperature change in the metal is proportional to the current *I* flowing.

Note, however, that as a completely independent process, you always have ohmic heating (or Joule heating) which is simply given by the total power **P** dumped into the system via

$$P = U \cdot I = R \cdot I^2$$

- with  $U$  = voltage applied,  $R$  = total series resistance of the system.
- Since this general heating of the whole device is proportional to  $I^2$ , it can easily overwhelm any cooling effect that might be there.
- If you want to use the Peltier effect as an elegant way of cooling something, you must not only choose your materials very carefully, but also optimize your system design and working points.
- That this is possible is evidenced by the successful marketing of **Peltier cooling elements**, mostly for scientific applications. Here is a table with technical data from a major supplier (EURECA Messtechnik GmbH, Am Feldgarten 3 D-50769 Köln, GERMANY):

### Micro Peltier Elements

Module	$I_{\max}$ [A]	$Q_{\max}$ [W]	$U_{\max}$ [V]	$dT_{\max}$ [K]	Dimensions					Unit Price [Euro]
					A [mm]	B [mm]	C [mm]	D [mm]	H [mm]	
TECM-4-4-1b/69	1,4	0,7	0,9	69	4,3	4,3	4,3	4,3	2,95	28,75
TECM-4-5-1/67	0,7	0,4	1,0	67	3,4	3,4	3,4	5,0	2,30	29,50
TECM-5-7-1/67	0,7	0,9	2,2	67	5,0	5,0	5,0	6,6	2,30	38,50
TECM-7-8-2/67	0,7	1,7	3,9	67	6,6	6,6	6,6	8,3	2,30	52,50
TECM-9-12-4/67	0,7	3,5	8,0	67	9,1	9,9	9,1	11,5	2,30	66,25
TECM-12-6-4/69	1,7	4,4	4,3	69	6,0	12,0	6,0	12,0	2,75	57,50

In this class you will find elements with various geometries and electrical parameters. For this reason, these elements are suited for very different and partly exotic requests as you have in the research. Our support will help you with the selection and the startup of the elements in consideration of your particular requests.

Generally you will receive these elements in small quantities from stock.