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# Thermoelectricity: from the iron arc of Alessandro Volta to radioisotope thermoelectric generators

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## Abstract

We start with an overview of the fascinating history of thermoelectricity, which included such famous scientists as Luigi Galvani, Alessandro Volta, Thomas Johann Seebeck, Jean Charles Athanase Peltier, and even the philosopher Georg Wilhelm Friedrich Hegel. Then we move on to the basic concepts for describing thermoelectric phenomena and how, as our understanding of nature improves, thermoelectricity finds more and more applications. We formulate the requirements for the materials necessary for the wide practical use of thermoelectricity and will mention those that exist, and those that Nature has forgotten to create but will be discovered/invented by scientists. Finally, we enumerate several more significant applications of thermoelectricity.

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Supplementary material for this article is available [online](#)

Keywords: thermoelectricity, figure of merit, history of science, thermoelectric generator, materials for thermoelectricity

*‘Captain Nemo: Yes, professor, and there was no shortage of such sources. In fact, by establishing a circuit between two wires immersed to different depths, I’d be able to obtain electricity through the diverging temperatures they experience’*

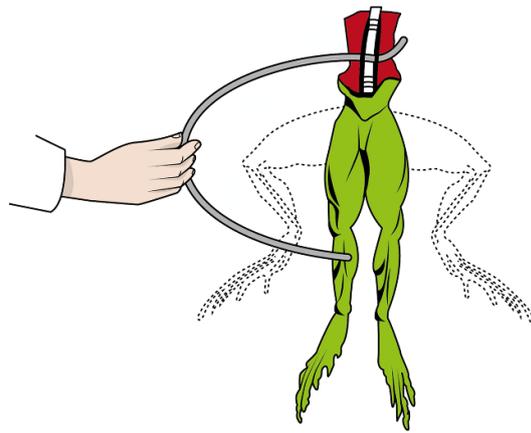
J. Verne, **Twenty Thousand Leagues Under the Sea**

It is difficult to surprise a modern person with questions about what electricity or heat transfer is—everyone has their own opinion on these matters. For some people this knowledge is purely theoretical, based on the study of physics, but for the majority this is learned from unpleasant sensation of the electrostatic discharge and shock which occurs when they touch the vehicle door, or from accidentally touching a hot iron. We are sure that a much smaller number of readers are familiar with the phenomenon of thermoelectricity, which is the subject of this article.

## 1. Dispute between Luigi Galvani and Alessandro Volta

In the middle of the 18th century, the study of electrical phenomena, including animal electricity, such as generated by an electric stingray, became a popular topic in science.

In view of this, physiologist Luigi Galvani, a professor at the University of Bologna, began to study what happens to a dissected frog when current is passed through it. As a result of numerous experiments, Galvani was convinced that every time he touched the nerves of a frog with a conductor attached to an electric machine, extracting a spark from it, the frog was seized by convulsive trembling. Further, Galvani continued his experiments and found the same contractions when connecting the muscles and nerves of

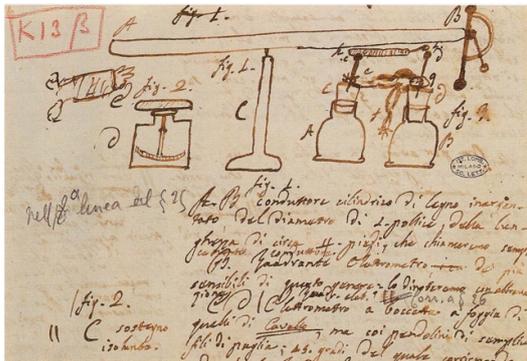


**Figure 1.** Galvani discovered that every time he touched the nerves of a frog with a bimetallic arc, the frog was seized by convulsive muscle contractions.

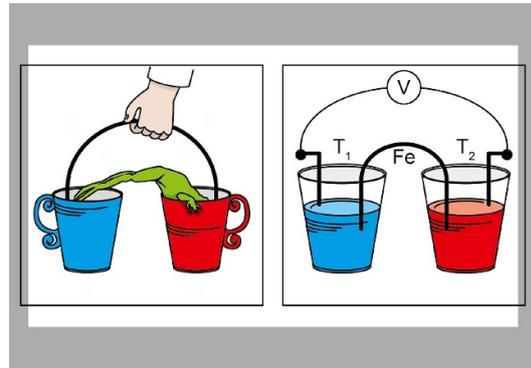
a freshly dissected frog with a bimetallic arc (figure 1).

At the same time, Galvani’s special attention was attracted by the fact that the contraction of the frog’s muscles turns out to be much stronger if the metal arc is composed in series of two different metals, for example, iron and copper (or, what is much better, of silver). These experiments led the famous Italian to the conclusion that electricity is inherent in the animal itself: a fluid, as it were, flows from the nerves to the muscles and a circuit is formed (like when the Leyden jar is discharged).

Alessandro Volta, a professor at the University of Pavia, was distrustful of the so-called animal electricity. Nevertheless, at the insistence of his colleagues, he repeated the experiments described in Galvani’s work (figure 2). As a result, his skepticism began to dissipate, and on 3 April, 1792, he writes to Galvani: ‘So, here I am at last converted. Since I myself became an eyewitness and observed these miracles, I have, perhaps, moved from distrust to fanaticism’ [1]. In a public lecture on 5 May, 1792, Volta talks about



**Figure 2.** Sketches of tools that used Alessandro Volta in experiments with frogs. ('Memoir about animal electricity, on 14 May, 1792'. Archive Volta, Sheet K13, Lombard Academy of Sciences and Letters).



**Figure 3.** Alessandro Volta used a conductor made of one metal as an arc, but he placed the ends of the frog muscle and the ends of the conductor in vessels with cold and hot water. One can easily see that this is the same scheme of the experiment with the frog which was originally drawn by Alessandro Volta in 1792 (see figure 2, upper right corner). In the right figure, instead of the frog muscle, a voltmeter is shown.

Galvani's experiments, extols them, but at the same time expresses the idea that the frog can only be a measuring device, an electrometer, ten times more sensitive than the already existing gold leaf electroscope. Volta persistently draws attention to one physical feature of Galvani's experiments: to cause muscle contraction, the metals forming the arc must be different. He asks: do metallic conductors really serve only to establish a connection by contacting each other, which provides the electric fluid with a path along which it naturally tends to go from one place to another? Is their role purely passive, or are they active agents that set the electric charge in motion [2]? In his further experiments, Volta shows that the muscle, in essence, does not participate in the generation of the phenomenon itself, its contraction is the effect of the flow of charge generated by the contact of two different metals. Thus, in fact, he discovers a phenomenon that is associated with a contact potential difference.

In his doubts, Volta goes further. As an arc, he tries to use a single metal conductor, but places the ends of the frog muscle and the ends of the arc in vessels of cold and hot water (figure 3). The muscle also contracts in this experiment, which allows the scientist to explain the flow of electrical fluid (charge) by uneven heating of the metal conductor. The connection between electric current and temperature difference had been discovered! He describes these experiments on 10 February, 1794 in his letter to Abbé Vassalli [3].

In the process of experiments with a metal arc, Volta realized that the passage of current through the muscles of a frog is nothing more than its flow in an acidic environment. As a result, he created his famous battery, the so-called voltaic column—a sequence of alternating plates of two metals (for example, lead and copper), separated by a cloth soaked in acid (vinegar) [4, 5]. Modern batteries work on the same principle today. The role of Alessandro Volta in thermoelectricity and a more complete list of the references are given in [6].

## 2. The Jena school and the discovery of Johann Seebeck

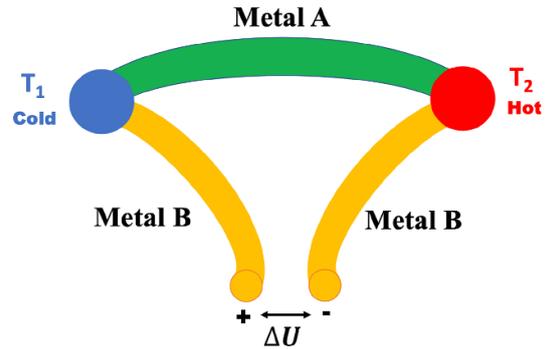
Thomas Johann Seebeck, German-Estonian physicist, chemist and physician was born in 1770 in the Hanseatic town of Revel (now Tallinn). At the age of 17 he moves to Germany to study medicine and in 1792 passes the final exams in medicine in Göttingen university with excellent marks. However, strongly influenced by the charismatic physics professor Georg Christoph Lichtenberg, Seebeck decides to devote himself to physics. In March 1802, Seebeck obtained his doctorate and moved to Jena. Here he finds himself in a seething intellectual environment whose central figure

is Johann Wolfgang Goethe, a great poet, passionate naturalist and explorer. As an influential Weimar court administrator and personal friend of the Duke of Saxe-Weimar-Eisenach, he helps young talents launch their academic careers.

Seebeck first met Goethe at a dinner on 3 December, 1803, where he also met his peer, the future famous philosopher Hegel, with whom they became friends. Goethe is looking for an assistant to help with his optical research, and Seebeck becomes an excellent choice for him. Their long collaboration led to the fact that the contribution made by Seebeck became an important part of the ‘Theory of Colors’—the main scientific work of Goethe [7]. However, the proximity to Goethe suppresses him, he leaves Jena. Finally, in 1818, after a series of wanderings around German university towns, Seebeck was elected a corresponding member of the Berlin Academy of Sciences for his work on optics. In December 1819, Seebeck writes his last letter to Goethe and finally becomes open to new challenges.

On 21 July, 1820, Oersted publishes his famous essay ‘Experiments on the effect of electric current on a magnetic needle’ [8], which opens the door to a new field of science—electromagnetism. Seebeck leaves aside his optical experiments and delves into Oersted’s ideas. Very soon, after several months of work, Seebeck comes to the main result of his scientific career—the discovery of a phenomenon that he called ‘thermomagnetism’, by analogy with Oersted’s ‘electromagnetism’. He reports this at a meeting of the Berlin Academy on 14 December, 1820 [9]. Two years later, Oersted visited Seebeck’s laboratory in Berlin in order to get acquainted with his experiments and, already in March 1823, reported Seebeck’s discovery at a meeting of the French Academy of Sciences. At the same time, he gives a physically correct interpretation of the new phenomenon and introduces the term ‘thermoelectricity’, which is accepted today, for its designation. Oersted praises Seebeck’s work, calling it ‘the most beautiful discovery that has grown out of his research.’

The quantitative characteristic of the thermoelectric effect is the Seebeck coefficient—the voltage between the ends of the conductor  $\Delta U$



**Figure 4.** The voltage generated by a thermocouple, created by two different metals A and B, having temperatures  $T_1$  and  $T_2$  at the ends respectively.

arising when applying the temperature difference between them  $\Delta T$  (measured in Kelvins):

$$S = -\frac{\Delta U}{\Delta T} = \frac{E}{\Delta T/\Delta x}, \quad (1)$$

where  $E = -\frac{\Delta U}{\Delta x}$  is the magnitude of the electric field arising in the conductor, and  $\nabla T = \frac{\Delta T}{\Delta x}$  is the temperature gradient.

Accordingly, the voltage generated by a thermocouple, created by two different metals A and B, having temperatures  $T_1$  and  $T_2$  at the ends, respectively (see figure 4), is:

$$\begin{aligned} \Delta U &= S_B(T_2 - T_1) - S_A(T_2 - T_1) \\ &= (S_B - S_A)(T_2 - T_1). \end{aligned} \quad (2)$$

Unfortunately, in ordinary metals it turns out to be very small (see table 1). Let us draw the reader’s attention to the fact that the Seebeck coefficients for different metals can have different signs. For example, when applying a reasonable temperature difference of 300 K to a thermocouple, one of the electrodes of which is bismuth ( $S_B = -72 \mu\text{V K}^{-1}$ ), and antimony ( $S_A = 47 \mu\text{V K}^{-1}$ ), the second, the generated voltage is only about 36 mV. Thus, in order to replace two conventional AA batteries used in computer mice, remote controls and many other gadgets, one would have to connect 100 such thermocouples and maintain a temperature difference of 300 K between their electrodes! Too much!

The generally accepted description of the properties of electrons in matter is based on the

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**Table 1.** Seebeck coefficient in normal metals [10].

Metal	Seebeck coefficient ( $\mu\text{V K}^{-1}$ ) (relative to platinum)
Bismuth	-72.0
Nickel	-16.4
Palladium	-5.6
Potassium	-9.0
Silver	+7.1
Copper	+7.4
Iron	+16.0
Antimony	+47.0

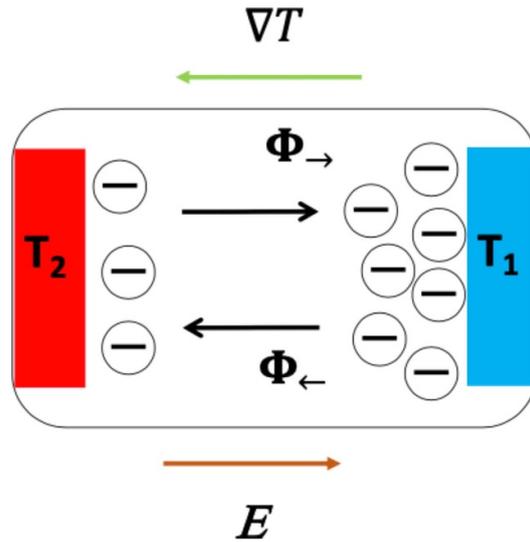
charged-particle gas model, so it is natural to consider a similar interpretation of the Seebeck effect's essence.

Consider a cylinder filled with a gas of charged particles. The left end of the cylinder is kept at a higher temperature  $T_2$ , while the right end is maintained at a colder temperature  $T_1$  (see figure 5). Clearly, the system is not in thermal equilibrium and therefore experiences uncompensated thermal energy flows  $\Phi_{\rightleftharpoons}$  due to the temperature difference. These flows are carried solely by particles and are determined by the product of their mean velocities  $v_{\rightleftharpoons}$  and mean concentrations  $n_{1,2}$ . Since matter is conserved, it follows that the two fluxes  $\Phi_{\rightarrow} = v_{\rightarrow}n_1$  and  $\Phi_{\leftarrow} = v_{\leftarrow}n_2$  must be equal. The thermal energies of particles at temperature  $T_2$  are higher than that ones at  $T_1$ , hence the average particle velocities, are such that  $v_{\rightarrow} > v_{\leftarrow}$ . It follows that the corresponding concentrations are not equal to each other either:  $n_1 < n_2$ .

Note that the concentration gradient turns out to be larger the smaller gas concentrations of charged particles. This allows one to qualitatively understand why good metals in general have very low values of the Seebeck coefficient, ( $S \approx 10 \mu\text{V K}^{-1}$ ), whereas for materials with low electron concentrations (doped semiconductors, semi-metals) the corresponding values turn out to be one or even two orders of magnitude higher: ( $S \approx 0.1 - 1 \text{ mV K}^{-1}$ ) (see below).

### 3. The further fate of the discovery of Seebeck

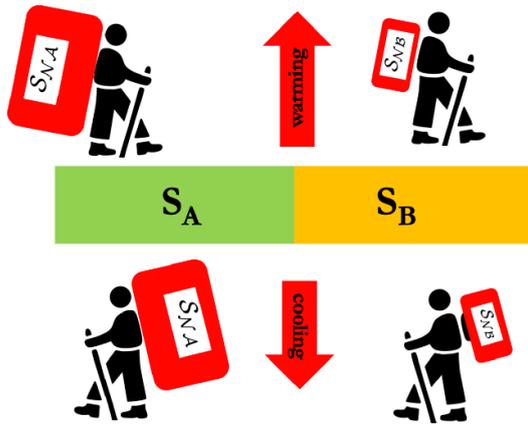
Thermoelectricity quickly found its application, at least in physical laboratories. So, the well-known



**Figure 5.** Applying a temperature gradient  $\nabla T$  to a gas of negatively charged particles results in the appearance of a concentration gradient, and consequently, an internal electric field  $E$  is generated.

Ohm's law was discovered and described by Ohm in two articles, published in 1826 and 1827. After the publication of the first article, Ohm was advised to abandon the galvanic battery as the source of current, since its electromotive force significantly changed during the measurement. More accurate results of the measurement for the second article were already obtained thanks to the use of a thermoelectric current source (copper-bismuth pair) capable of maintaining a constant voltage.

Further studies of the phenomenon discovered by Seebeck continued in the 1830s in the works of Jean Charles Athanase Peltier, where the reverse thermoelectric effect was discovered: it consists in heating or cooling of the junction of two conductors when an electric current flows through it. This phenomenon was studied several years later by a Russian physicist of German origin, one of the founders of electrical engineering, Heinrich Friedrich Emil Lenz. He placed a drop of water in a recess at the junction of two rods of bismuth and antimony (with resistance  $R$ ) and found that when an electric current ( $I$ ) flowed in one direction, the drop turned into ice, while when he changed the direction to the opposite, the ice melted. This simple and impressive experiment



**Figure 6.** A particle in a material carries a certain fraction of entropy, which is called entropy per carrier (also called molar entropy in thermochemistry). Because of the difference between the values of entropy per carrier in each given material  $S_{Ni}$ , the transport of particles across the boundary between two different materials is accompanied by absorption or release of heat. In the case in question  $S_{N_A} > S_{N_B}$ . This situation can be illustrated by the example of a traveller carrying a backpack and making a transfer at the airport from one company's plane to another. If the second company's hand luggage restrictions are stricter, the traveller is forced to reduce the weight of his bag by partially emptying it and leaving some items at the transfer point. Returning to our particles crossing the interface, this emptying of the bag corresponds to a release of entropy. On a return trip, by contrast, a passenger could buy something at Duty Free and fill the bag to the weight allowed by the first company's rules, which corresponds to a pumping out of entropy.

showed that when a current flows through the contact of two different metals, in addition to the known Joule heat ( $I^2R$ ), extra heat is released or absorbed, proportional to the first power of the current. The latter is called the *Peltier heat*.

One can easily understand the essence of the Peltier effect qualitatively by noticing that the entropy per particle  $S_{Ni}$  of a given material  $i$  and the Seebeck coefficient  $S_i$  are connected by the relation  $S_{Ni} = eS_i$  with  $i = A, B$ . The transport of particles is therefore associated with the transport of entropy.

Let us now consider a material  $A$  characterized by an entropy per particle  $S_{N_A}$  and a material  $B$  characterized by an entropy per particle  $S_{N_B}$  (see figure 6). Depending on the respective values

of  $S_{N_A}$  and  $S_{N_B}$  the particles crossing of the interface between the materials  $A$  and  $B$  results in the absorption or in the release of heat at the  $AB$  junction.

A few decades later, in the late 1880s, in the works of the German scientists Nernst and Ettingshausen, various thermomagnetic phenomena were discovered, where, besides the temperature difference, a magnetic field also came into play, but the microscopic nature of thermoelectricity remained incomprehensible.

Yes, but what about thermoelectricity?! As a matter of fact, until the 1930s, there was no understanding at the microscopic level of the structure of metals themselves. To create an appropriate theory, it was necessary at least to understand the structure of constituent atoms. Yet, the mathematical and conceptual apparatus necessary for this—quantum mechanics—was formulated only at the end of the 1920s. However, at the phenomenological level, the understanding of the phenomenon of thermoelectricity was moving forward. In the second half of the 19th century, in the works of Gibbs, Boltzmann, and other scientists, a new field of physics was developed—statistical mechanics, which studies systems of a large number of particles. The ability to describe their properties using classical mechanics is illusory: not only to solve, but even to write down the equations of classical mechanics for a large number of particles would be impossible. Instead, scientists discovered completely new, so-called statistical regularities, for a system of a large number of particles. They have understood that for the necessary description of properties here, excessive information (coordinates, velocities of all particles) is not required. It was necessary to learn to ask Nature new questions and understand how to get answers to them.

#### 4. Chemical and electrochemical potentials

Among new concepts of the statistical description, Gibbs in 1875 introduced the chemical potential  $\mu$ —the energy that should be expended to add one more particle to the system of many particles. Under equilibrium conditions, this value remains constant throughout the volume of the

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system—otherwise they would flow from one place to another. The concept of a chemical potential can be easily generalized to the case where the system is in an external field (by which, in what follows, we will mean an electric field with a potential  $\phi$ ). For this, to the chemical potential  $\mu$ , you just need to add the corresponding potential energy of a particle with a charge  $q$ , acquired by it when entering the system. Now the equilibrium condition is the constancy of the electrochemical potential  $\tilde{\mu} = \mu + q\phi$ .

Let us return to the experiment of Alessandro Volta in 1794. He placed the opposite ends of the iron conductor in boiling and icy water, thereby creating a temperature gradient in the system of free electrons in a metal. These electrons, together with the heater and cooler, do not present, strictly speaking, an equilibrium system: in order to maintain the temperature difference in it, heat must be continuously supplied and removed. However, if the ends are not connected with each other in an electrical circuit (say, by a frog's leg), the electrons displace at the first moment in such a way that their density would correspond to the local temperature (as for any gas at constant pressure: where it is colder, there density is higher). Yet, because they are charged particles, therefore, a non-zero electric field arises inside the metal, and a potential difference between the ends of the conductor. Here is the explanation of thermoelectricity, it was enough to know about the existence of free electrons in the metal (let us recall, the electron itself was discovered only in 1897).

How can the above words be turned into a useful formula for the Seebeck coefficient? It takes only a few lines. The electrochemical potential in the conductor remains constant:

$$\tilde{\mu} = \mu + q\phi = \text{const.} \quad (3)$$

It consists of two terms that compensate each other at equilibrium [11]. Therefore, its derivative with respect to the coordinate (we consider the conductor to be one-dimensional) must be equal to zero:

$$\frac{d\tilde{\mu}}{dx} = \frac{d\mu}{dx} + q\frac{d\phi}{dx} = 0. \quad (4)$$

The last derivative is simply the electric field strength taken with the opposite sign:  $E = -d\phi/dx$ . Thus, we arrive at the equation

$$\frac{d\mu}{dx} = qE. \quad (5)$$

The chemical potential now varies from point to point and depends on the local temperature value. Therefore, its derivative can be calculated first by differentiating with respect to temperature, and only then by differentiating the latter with respect to the coordinate:

$$\frac{d\mu}{dx} = \frac{d\mu}{dT} \frac{dT}{dx}. \quad (6)$$

In this way we arrive to the so-called Kelvin formula relating the Seebeck coefficient to the derivative of the chemical potential with respect to temperature:

$$S = \frac{E}{\Delta T/\Delta x} = \frac{1}{q} \left( \frac{d\mu}{dT} \right). \quad (7)$$

Let's say right away that this formula does not describe the thermoelectric effect in all cases of life, nevertheless it will be extremely useful for our further story.

### 5. How do electrons live in a metal?

A metal differs from insulator or semiconductor by the fact that that even at zero temperature each of its atoms donates at least one electron for common use. Hence, recalling that the Avogadro's number is equal to  $6.026 \times 10^{23} \text{ mol}^{-1}$  it is easy to see that one cubic centimetre of metal contains about  $10^{23}$  atoms. These electrons form some kind of gas filling the crystal lattice, whose nodes contain metal atom's ions. According to quantum mechanics, this gas, calling 'degenerate quantum ideal gas', possesses very unusual properties. The definition of 'quantum degeneracy' applied to this gas means that, unlike classical gas, its particles, the electrons, remain in a state of chaotic motion at enormous speeds, expressed as a percentage of the speed of light, even at a temperature equal to absolute zero. Surprisingly, being at zero temperature and moving chaotically, the electrons, due

to the whims of quantum mechanics, manage to avoid scattering from the ions in the lattice nodes.

So let us understand how electrons occupy a metal. To do this, we will start with two fundamental relations of quantum mechanics. First one is the uncertainty principle, formulated by German physicist Werner Heisenberg in 1927. The second important rule managing the coexistence of many electrons together is the so-called Pauli exclusion principle, according to which no two electrons can be in the same quantum state.

The state of a free electron is determined by its momentum ( $\mathbf{p} = \{p_x, p_y, p_z\}$ ) and the projection of its spin. According to uncertainty principle the accuracies in determination of the electron momentum projection ( $\Delta p_x$ ) and the corresponding coordinate ( $\Delta x$ ) are related by the inequality

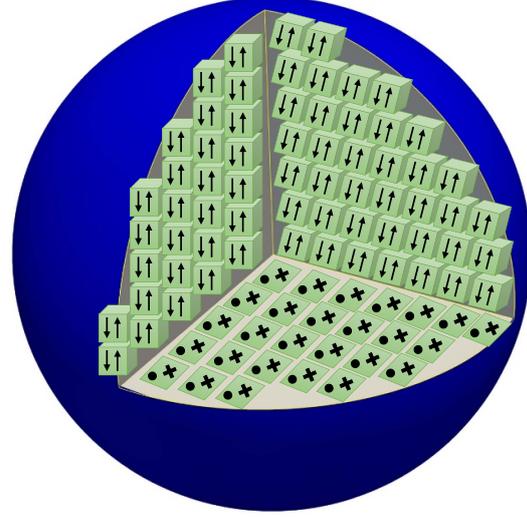
$$\Delta p_x \Delta x \geq 2\pi \hbar, \quad (8)$$

where  $\hbar = 1.054 \times 10^{-34}$  J×s. Thus, one state of an electron with a certain projection of the spin has in its disposition in six-dimensional space, that combines momenta and coordinates, a ‘cube’ of the volume

$$\Delta p_x \Delta p_y \Delta p_z \Delta x \Delta y \Delta z \geq (2\pi \hbar)^3. \quad (9)$$

A second electron can also be placed in it, with the opposite spin projection, but no more.

Let’s take a cube with sides  $\Delta x = \Delta y = \Delta z = 1$  cm. Then we will see that in the remaining three-dimensional momentum part of our, initially six-dimensional, space, the first two introduced electrons will occupy a cube of volume  $(2\pi \hbar)^3$  cm<sup>-3</sup>. The next electrons will already be forced to occupy the states with non-zero momenta. Gradually, with an increase in the number of electrons that we invite into the cube, the total volume of states they occupy will increase, taking the form of a solid sphere (the momentum of a particle determines its kinetic energy); the total kinetic energy of the system of particles placed in this way turns to remain minimal. The resulting volume is restricted by the so-called Fermi surface (in our simple case of free electron gas this is a sphere). The radius  $p_F$  of the Fermi sphere is determined by the maximum momentum we have reached in our construction (see figure 7). Let’s determine it.



**Figure 7.** Fermi surface is the surface in the momentum space which separates the occupied from unoccupied electron states at zero temperature (in the case under consideration of a free electron gas it is represented by the blue sphere). The up and down arrows represent electrons with the opposite spins filling the elementary cubes in 6-dimensional space; the dots and crosses represent the same objects but in the horizontal cutaway of the interior.

The volume of the sphere is  $4\pi p_F^3/3$ . There is volume  $(2\pi \hbar)^3$  per state. Thus, the number of such elementary cubes under the Fermi sphere is

$$\frac{4}{3} \frac{\pi p_F^3}{(2\pi \hbar)^3}. \quad (10)$$

Moreover, to determine how many electrons can fit within it, you need to multiply the obtained number by 2 (which corresponds to two different spin states). Thus, we see that the Fermi momentum is determined by the concentration of electrons in the box:

$$n = \frac{N}{\Delta x \Delta y \Delta z} = \frac{p_F^3}{3\pi^2 \hbar^3}, \quad (11)$$

which results in  $p_F^3 = 3\pi^2 \hbar^3 n$ . Accordingly, we also find the limiting energy of electrons whose momenta lie on the surface of the sphere:

$$\epsilon_F = \frac{p_F^2}{2m} = \frac{3^{2/3} \pi^{4/3} \hbar^2}{2m} n^{2/3}. \quad (12)$$

One cubic centimetre of metal contains about  $10^{23}$  atoms, and if each of them donates at least one electron for common use, then the Fermi energy will be about  $5 \times 10^{-19}$  J, i.e. about 3 eV = 34 800 K, which corresponds to a temperature 5 times higher than the temperature of the surface of the Sun! The velocities of electrons located in momentum space near the Fermi surface are enormous: they are a sizeable percentage of the speed of light.



**Figure 8.** Drawing a parallel, we can liken a skin of the melon with the Fermi surface, so at  $T = 0$  all electron states under the surface are occupied and cannot participate in the electron transport. For a finite temperature part of the electrons in the vicinity of the Fermi surface moves above the Fermi surface. Here the melon rind and encasing a melon in a protective wrapper symbolize sets of available states below and above the Fermi surface, respectively, which are participating in the transport.

## 6. Chemical potential and Seebeck coefficient of a metal

Let's return to thermoelectricity. As we have already seen above, knowing the chemical potential, more precisely, its temperature dependence, the Seebeck coefficient can be found using the Kelvin formula. The chemical potential of the degenerate electron gas at absolute zero temperatures simply coincides with the value of Fermi energy, i.e.  $\mu(T = 0)$  is determined by equation (12). Indeed, if we want to add one more electron to the electron gas of the fixed number of particles  $N$ , enclosed in a cube of the volume  $V$ , then this electron must be placed in momentum space close to the Fermi surface, all other positions inside the latter are already occupied.

However, this knowledge is not enough for our purpose: to find the Seebeck coefficient of the degenerated electron gas, its chemical potential should be differentiated by temperature, so we need to find out how it changes with increasing temperature. Let the absolute temperature of the electron gas be  $T$ , and the corresponding energy  $k_B T \ll \epsilon_F$ . The fact that the gas of electrons is now at a non-zero temperature means that the electrons previously occupying a state within a thin spherical layer  $\delta p$  in momentum space (melon rind in the figure 8 (left panel)) spread also into an outer layer of the same width, outside the Fermi surface (melon wrap in the figure 8 (right panel)). This fact allows us to relate  $\delta p$  with temperature:

$$\begin{aligned} \frac{p_F^2}{2m} - \frac{(p_F - \delta p)^2}{2m} &= \frac{(p_F + \delta p)^2}{2m} - \frac{p_F^2}{2m} \\ &\approx \frac{p_F \delta p}{m} \approx k_B T. \end{aligned} \quad (13)$$

It is easy to see that the volume of the first layer is  $4\pi p_F^2 \delta p - 4\pi p_F (\delta p)^2$  while the volume of the second layer is  $4\pi p_F^2 \delta p + 4\pi p_F (\delta p)^2$ . Their difference is  $\delta V = 8\pi p_F (\delta p)^2$ . The total number of particles  $N$  should not change in this case:  $\delta N = \delta(nV) = V\delta n + n\delta V = 0$  ( $n$  is the electrons concentration,  $\delta n$  is its variation in result of the increase of the volume occupied by electrons), whence

$$\begin{aligned} \frac{\delta n}{n} &= -\frac{\delta V}{V} = -\frac{8\pi p_F (\delta p)^2}{4\pi p_F^3/3} \\ &= -\frac{6m^2 (k_B T)^2}{p_F^4} = -\frac{3 (k_B T)^2}{2\epsilon_F^2}. \end{aligned} \quad (14)$$

Here we used equation (13).

Recall that the relationship between the Fermi energy and the electron density is determined by equation (12). Accordingly, a small decrease in density will lead to a small change in the chemical potential:

$$\mu(T) = \epsilon_F \left[ 1 - \frac{3 (k_B T)^2}{2\epsilon_F^2} \right]^{2/3} \approx \epsilon_F - (k_B T)^2 / \epsilon_F. \quad (15)$$

Our simplified calculation allowed us to find almost correct value of the coefficient in front of

the temperature dependent part of the chemical potential: in result of the accurate microscopic approach, it turns out to be  $\pi^2/12 \approx 0.82$  [12] instead of found above 1. Using equation (15) and the Kelvin formula (7), we find the correct statement that for a degenerate electron gas

$$S \sim -\frac{k_B^2 T}{e \epsilon_F}. \quad (16)$$

From this expression it immediately becomes clear why the Seebeck effect is so weak in good metals, where, as we have already seen, the value of the Fermi energy is very high ( $\epsilon_F \approx 3$  eV). Thus, for room temperatures, our estimate leads to a value for the Seebeck coefficient of the order of several micro volts per Kelvin, which coincides with the data from table 1 and makes them unsuitable for use as the elements of thermal voltage generators.

## 7. Seebeck effect in semiconductors

There are estimates showing that the cost of electricity generated at the beginning of the 20th century by direct combustion of fuel in a steam boiler and the conversion of steam pressure into mechanical work was almost 40 times lower than the cost of electricity generated by thermoelectric sources available at that time [13]. And only in 1929, based on the experimental discovery of high values (hundreds of micro volts per Kelvin) of the Seebeck coefficient in semiconductors, Soviet scientist Abram Ioffe put forward the idea that in order to increase the efficiency of thermoelements, metals should be replaced by semiconductors. To understand why exactly semiconductors are more promising materials for thermoelectric energy sources can be shown as follows.

When estimating the Seebeck coefficient in metals, we used the fact that the number of electrons does not change. In semiconductors, this is not the case, and the concentration of charge carriers depends very strongly (exponentially) on temperature, leading to a much stronger dependence of the chemical potential on it. This is what causes the large values of the Seebeck coefficient in semiconductors.

**Table 2.** Seebeck coefficient in semiconductors [10].

Semiconductor	Seebeck coefficient ( $\mu\text{V}/\text{K}$ )
Germanium	300
Silicium	440
Tellurium	500
Selenium	900

They are especially large in the so-called doped semiconductors, which are similar to the metals discussed above. To change their electrical properties, appropriate impurities are added which, by being incorporated into the crystal lattice, add or remove conducting electrons. As a result, in such a semiconductor, just as we have already seen with the example of a metal, a gas of free electrons is formed. Since the concentration of impurities is always small compared to the concentration of atoms of the semiconductor itself, the corresponding Fermi energy also turns out to be small. At sufficiently low temperatures (and they may well be room temperatures), this gas turns out to be degenerate and formula (16) can be used for the corresponding Seebeck coefficient of the semiconductor, only the Fermi energy in it will not be electronvolts, but only tens or hundreds of milli-electronvolts. Accordingly, the Seebeck coefficient will increase by tens or hundreds of times compared to its values in metals (see table 2).

## 8. The problem of the efficiency of a thermoelectric generator and methods for increasing it

The efficiency of a thermoelectric device is determined by the ratio of the Joule energy transferred to the load during the time  $\Delta t$  to the total thermal energy absorbed by the contact during the same time. For simplicity let us replace in our consideration the contact of two materials with different parameters by the homogeneous metallic wire. Moreover, let us assume that all resistance of the circuit is determined by the wire resistance itself. The Joule heat, obviously, is  $U^2 \Delta t / R$ , (where the thermoelectric voltage  $U$  is determined by equation (1), the resistance of the wire with resistivity  $\rho$ , length  $\Delta l$  and cross-sectional area  $A$  is

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$R = \rho \Delta l / A$ ). The total thermal energy absorbed is equal to the product of the heat flux  $q = \kappa \Delta T / \Delta l$  ( $\kappa$  is thermal conductivity), cross-sectional area  $A$  of the contact and time  $\Delta t$ :

$$\begin{aligned} \eta &= \frac{U^2 \Delta t / R}{q A \Delta t} = \frac{S^2 (\Delta T)^2 \Delta t}{\frac{\rho \Delta l}{A} \cdot \kappa \frac{\Delta T}{\Delta l} A \Delta t} \\ &= \frac{\sigma S^2}{\kappa} \Delta T = ZT \frac{\Delta T}{T}, \end{aligned} \quad (17)$$

where  $\sigma = 1/\rho$  is the electrical conductivity of the contact. The dimensionless quality index  $ZT = \sigma S^2 T / \kappa$  characterizes the efficiency of a thermoelectric device, and the number  $Z$  itself is called the thermoelectric figure of merit of the material, or the Ioffe number [14–16].

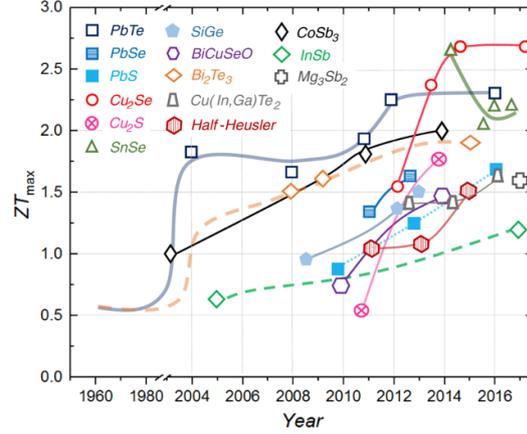
The value of quality index  $ZT$  reflects in what extend the thermoelectric process is reversible in the material. The process is completely reversible when the entropy production is zero; in this case the value  $ZT \rightarrow \infty$ , and the Carnot efficiency is reached.

Unfortunately, for metals, the quality index turns out to be very small: at characteristic operating temperatures of thermoelectric devices, its values are of the order of  $10^{-4}$  to  $10^{-3}$ .

It is clear that in order to increase the efficiency of a thermoelectric device, one should reduce the thermal conductivity of the material used while increasing its conductivity and the Seebeck coefficient. As we have seen above, the latter in metals is very small due to the huge concentration of electrons and, accordingly, large values of Fermi energy. On the other hand, high concentration of electrons in metal provides its high conductivity. Yet, as anyone knows who has ever stirred sugar in tea with a metal spoon and has burned their fingers, the metal also has a high thermal conductivity. Its conductivity is rigidly related to the electronic contribution to the thermal conductivity  $\kappa_e$ , by the so-called Wiedemann–Franz law [17, 18]

$$\frac{\sigma}{\kappa_e} = \frac{3e^2}{\pi^2 k_B T}. \quad (18)$$

However, in addition to electrons, heat in the metal is also transferred by the lattice vibrations. Their contribution  $\kappa_{ph}$  at room temperature can be quite



**Figure 9.** Timeline of the maximum figure of merit,  $ZT$ , values. Reproduced with permission from [19].

significant, so the efficiency should include the sum of both thermal conductivities:

$$ZT = \frac{3e^2}{\pi^2 k_B} S^2 \frac{\kappa_e}{\kappa_e + \kappa_{ph}}. \quad (19)$$

Thus, increasing the efficiency of a thermoelectric device in practice comes down to:

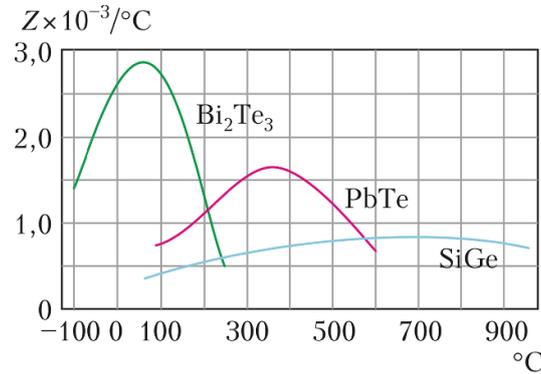
- Increase of the Seebeck coefficient of the material;
- Increase of its conductivity;
- Suppression of its lattice thermal conductivity.

The advancements in thermoelectric materials can be measured by the increasing value of  $ZT$  over time (see figure 9). In order for thermoelectric devices to become competitive with other renewable energy technologies (for example, solar and geothermal), it is necessary to achieve the values of their efficiency  $ZT \geq 4$  [20]. To reach this goal, a huge amount of research effort has been expended. Below we will introduce you to a few examples of such work.

## 9. New materials for thermoelectricity

### 9.1. Thermoelectric materials with 'panoscopic' defect structure

The decrease in thermal conductivity is possible largely due to the specially designed structure of the material. The lattice transfers heat



**Figure 10.** Figure of merit for three different thermoelectric materials versus temperature [21].

**Table 3.** Figure of merit of the most ‘promising’ thermoelectric materials [21].

Materials	$ZT$	Comments
Layered oxides ( $SrTiO_3$ ) <sub>n</sub> ( $SrO$ ) <sub>m</sub>	~ 0.34 at 1000 K	Very promising for high- $T$ applications
Bismuth chalcogenides ( $Bi_2Te_3, Bi_2Se_3$ )	~ 0.8 to 1.0 at room temperatures	$ZT$ temperature independent
Nanostructured bismuth chalcogenides (three-layer $Bi_2Te_3, Bi_2Se_3$ )	~ 2.4 at room temperatures	Have high electrical conductivity
Silicon-germanium alloys	~ 0.7 at room temperatures	The best thermoelectric materials at $T \sim 10^3 K$

by means of elastic waves propagating along it. These waves must be dispersed, just as breakwaters reflect storm waves off the coast of the seas and oceans. The problem of the effective suppression of the thermal conductivity is that it is necessary to dissipate lattice vibrations on all scales—from atomic to micron. This can be achieved by nanostructuring bulk thermoelectrics of a new generation by introducing into them different-scale scatterers of lattice vibrations. Such a ‘panoscopic’ use of microstructural defects enhances the scattering of elastic waves at their different wavelengths without suppressing electronic conductivity, which makes it possible to create thermoelectric materials with high performance. In nano-structured thermoelectric materials, transferring heat short waves can be dissipated by embedded in the lattice interstitial with characteristic sizes of nanometers, while long waves are scattered by micron-range defects with finely tuned architecture. Strategies for improving thermoelectric materials are directed towards

both modern bulk materials and the use of low-dimensional systems.

Nanostructuring of thermoelectric materials based on semiconductors, which reduces the thermal conductivity of the lattice with simultaneous increase in the Seebeck coefficient, has led to noticeable improvements in the conversion of thermal energy into electrical energy. However, even the most ‘promising’ materials cannot yet overcome the minimum requirement of  $ZT = 4$  (see figure 10 and table 3). In addition, the nanostructured materials created to date have a number of technological, environmental and economic disadvantages, such as their limited size, considerable production costs and the content of rare and toxic materials.

From a thermodynamic point of view the figure of merit and the ratio of the specific heats are linked by the relation  $\gamma = \frac{C_p}{C_v} \equiv 1 + ZT$ , where  $\gamma$  is the adiabatic constant,  $C_{p,v}$ , are specific heat capacities at constant pressure and volume respectively. This relationship highlights

the thermodynamic nature of the thermoelectric process, as stated in [6].

### 9.2. Thermoelectricity in electrolytes and ferromagnetic fluids

Scientists continue to search for environmentally friendly and economical new types of thermoelectric materials, such as polymers, ionic conductors, etc. Liquid electrolytes have recently become one of these objects. It turns out that the characteristic for them is Seebeck coefficient values that are usually an order of magnitude larger ( $S \approx 0.5 \text{ mV K}^{-1}$ ) than those of semiconductor materials, even nanostructured ones. In addition, they are made up of affordable and non-toxic elements. Unfortunately, the electrical conductivity of such liquids is several orders of magnitude lower than that of doped semiconductors, so liquid electrolytes were considered inefficient for utilizing the dissipated heat.

More recently, a new impetus to the search for thermoelectric materials suitable for practical applications has been given by studies of ionic liquids [22]. The latter are molten salts, liquid both at room temperature and at temperatures well above  $100^\circ\text{C}$  (some may exceed  $300^\circ\text{C}$ ). Unlike liquid electrolytes, along with large Seebeck coefficients, ionic liquids have high electrical conductivity, which ensures their high efficiency ( $ZT \approx 2$ ). To date, the highest value of the Seebeck coefficient obtained over a wide temperature range in an ionic liquid system exceeds  $2 \text{ mV K}^{-1}$ . Thus, ionic liquids are promising candidates for utilizing heat losses, for example, converting heat from a car muffler into electricity, which will be enough to operate an air conditioner that cools its interior.

The Seebeck coefficient of liquid electrolytes can also be increased by introducing magnetic nanoparticles (ferrofluid) into their volume. Their slow drift under the influence of temperature difference and interaction with electrodes improves the thermoelectric properties of the liquid. The existing understanding of the thermoelectrochemical nature of complex liquids is still far from complete, however, active experimental and theoretical research is being carried out in this exciting area, promising



Figure 11. The Mars Rover 'Perseverance'.

long-awaited applications in the utilization of heat losses that harm not only the economic, but also the ecology of our environment. The ferrofluids mentioned above are the working fluid for new generation thermogenerators, which are currently being developed by scientists in collaboration with industry engineers.

## 10. A few words about applications

Currently, thermoelectric devices have the widest range of applications ranging from power generation to radiation receivers. The reliability and simplicity of thermoelectric devices allows them to be used even when traditional energy sources are more efficient.

*Powering of the remote vehicles.* Jules Verne, in his novel 'Twenty Thousand Leagues Under the Sea', published in 1870, discussed the possibility that Nautilus could be powered by a thermoelectric battery fed by the difference in water temperatures at different depths. Modern nuclear submarines, as we know, use more traditional steam turbines. But on spacecraft that are sent to the depths of space, there really are thermoelectric energy sources. The fact is that outside the planet Mars, sunlight is too weak to power a spacecraft with solar panels. Therefore, the electricity necessary for the operation of on-board systems is provided by converting the heat into electricity using thermoelectric couples. The Mars Rover 'Perseverance' (see figure 11) carries a radioisotope power system which is called a 'Multi-Mission Radioisotope Thermoelectric



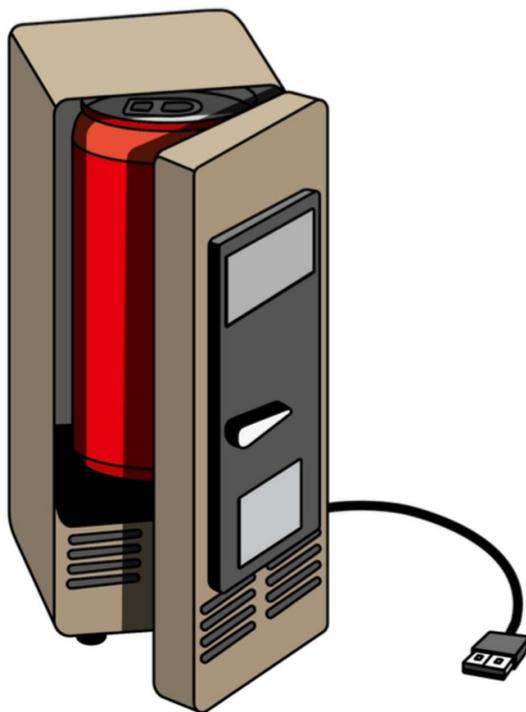


Figure 13. Thermoelectric Coke cooler.

sources with no moving parts are still in operation, allowing the spacecraft to make scientific discoveries after more than 35 years of operation.

*Cooling.* In addition to thermocouples, devices operating on the Peltier effect principle are widely used. These are coolers for various products: seat cooling/heating systems in cars, small refrigerators (see figure 13). The semiconductor pair  $Bi_2Te_3 - Sb_2Te_3$  is usually used as a working material in such devices.

A convenient feature of the Peltier effect is that it can be tuned from cooling to heating by a mere reversing of the current direction. This property is used in a machine called a thermocycler, which is programmed to rapidly alter the temperature of the reaction every 30–60 s to allow DNA denaturing and synthesis. The polymerase chain reaction gained widespread recognition due to its prominent use in COVID-19 testing.

Special value the coolers based on the Peltier effect acquire in miniaturization of electronic devices. Indeed, the temperature of a laptop processor determines its performance. Its overheating

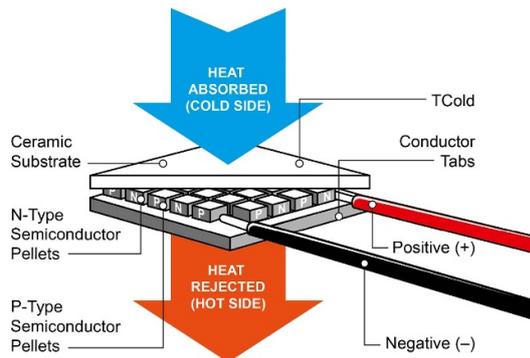


Figure 14. Peltier module is a thermal control device that has both ‘warming’ and ‘cooling’ effects. By passing an electric current through the module, it is possible to keep the surface at the target temperature.

can cause instability of the system, slower charging and shorter battery life. The thermoelectric cooler directly contacts the overheated surface, cooling it and making computer to run smooth and stable. A thermoelectric cooler plays the role of a heat pump which transfers heat from one side of the device to the other (see figure 14).

*Charging Mobile Phones?* Due to Russian missile strikes causing electricity blackouts in Ukraine, one of the authors of this article (S.G.Sh.) had to learn how to charge a cell phone, notebook, or LED light in the absence of regular power supply. This led him to discover a wide range of large power banks known as charging stations. However, the ultimate question was how to charge these power banks (see figure 15). While using roaring generators on the streets may not be a viable solution for apartment dwellers, commercial solar panels could be a good option when outdoors during the summer. However, during the winter months in Kyiv, they may not be particularly helpful.

Professional interests led to think about thermoelectricity. If it is possible to warm up a cup of tea using a food warmer with a tea light, why do not use it to heat a thermocouple? However, it seems that corresponding devices are just not available. The illustration involving powering up a computer mouse, as discussed in section 2, implies that approximately 150 bismuth-antimony thermocouples would be required to replace three



**Figure 15.** In order to charge various gadgets in absence of a regular power supply one has to rely on charging stations. However, the problem arises how to charge them if the power supply is not restored. Since the candles and even more powerful food warmers are in use in the emergency situations, it would be useful to have a possibility to charge the stations using thermoelectricity.

conventional AA batteries, which generate 4.5 V, necessary to charge a cell phone battery. The energy balance estimate seems to be even less favourable. Indeed, indeed, to raise the temperature of a 250 ml cup of black tea from 10°C to 90°C, approximately  $8.4 \times 10^4$  J of energy are required. Noting that to charge a 5000 mA × h cell phone battery of 4 V voltage, one needs the energy  $20 \text{ W} \times \text{h}$  or  $7.2 \times 10^4$  J, which is quite comparable with the energy needed to heat a cup of black tea. Obviously, this is too optimistic estimate, because we completely ignored rather low efficiency of thermoelectric devices. Nevertheless, this suggests that there is ample opportunity to bring thermoelectricity from space to everyday life in poorly electrified areas.

#### Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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#### Conflicts of interest

The authors declare no conflict of interest.

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