1
Thermodynamics and Thermoelectricity

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1.1
Milestones of Thermoelectricity

Thermoelectric effects result from the interference of electrical current and heat flow in various materials. This interaction, characterized by a coupling parameter called *thermopower*, allows the *direct* conversion of heat to electricity [1–4]; conversely, cooling may be achieved by the application of a voltage across a thermoelectric material.

Almost 200 years after the first discoveries in thermoelectrics by Seebeck in 1823 [5–7], it is now again a very active period of observing thermoelectric (TE) phenomena, materials, and their application in devices. The search for green technologies, for example, converting waste heat generated by industrial facilities and car engines into usable power, pushes scientists to pick up "old" effects with new classes of materials with higher TE efficiency to develop practical applications using the advantages of TE power generation. For an overview of a variety of applications, see, for example, the following books and review articles [8–33].

A similar situation was encountered in the late 1950s when the usage of semiconductors as TE materials was the origin for a revival of thermoelectrics [34]. This is directly connected with the investigations by Goldsmid and Douglas [35] and the Ioffe group [36], who considered both thermodynamics and solid-state approaches. They extended the previous developments to the microscopic area, opening the door for material engineering and practical applications [1, 2, 37–55].

A recommendable overview on the early years of TE research had been given by Finn [52, 56, 57]. Historical facts can be found in several textbooks on thermoelectricity, see, for example, [8, 13, 15, 36, 42, 58]. Clearly, thermoelectricity is influencing and has influenced two branches of physics decisively, see Figure 1.1. On the one hand, it all began with investigations of electromagnetism, but the interest started in thermodynamics as well. Here, we would like to give a retrospective view on some of the milestones in the development of thermoelectricity.

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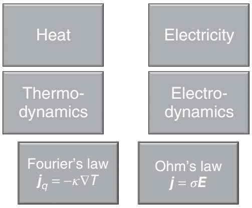

Figure 1.1 Two branches of physics combined.

At the same time, we would like to acknowledge some of those scientists who made an especially valuable contribution to its development in the early years.

1.1.1
Discovery of the Seebeck Effect

Today, the phenomenon in which a temperature gradient in a currentless circuit consisting of different materials produces a primary voltage is known as the Seebeck effect, named after the German-Baltic physicist Thomas Johann Seebeck. However, some hints on TE effects are known from times before Seebeck. Lidorenko and Terekov [59] mentions the studies by the Petersburg academician Aepinus, carried out in 1762 and reviewed in Ref. [60], see also [61]. Sometimes, Volta is also considered as the first person to discover the TE effects. With regard to this point, we refer to several articles by Anatychuk and other authors [62–66]. His bibliographical research indicates that the first experiment on the TE phenomenon had been reported by A. Volta in a letter to A.M. Vassalli written on February 10, 1794:

> *"... I immersed for a mere 30 seconds the end of such arc into boiling water, removed it and allowing no time for it to cool down, resumed the experiment with two glasses of cold water. It was then that the frog in the water started contracting, and it happened even two, three, four times on repeating the experiment till one end of the iron previously immersed into hot water did not cool down."*[1] More details of the experiments can be found in Refs [67, 68] and references therein.

The role of Alessandro Volta in thermoelectricity is particularly addressed in an article by Pastorino [69]. Volta's observations are based on Galvani's experiments [66, p. 28]: "*The novel discovery that eventually led to the recognition of thermoelectricity was first disclosed in 1786 and published in book form in 1791. Luigi Galvani noticed the nerve and muscle of a dissected frog contracted abruptly when placed between dissimilar metal probes. Alessandro Volta, in 1793, concluded that the electricity which caused Galvani's*

Alessandro Giuseppe Antonio Anastasio Volta (1745–1827)

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[1] Translation of a letter to professor Antonio Maria Vassalli (accademia delle scienze di torino).

frog to twitch was due to the interaction of the tissue with metals that were dissimilar. This observation, though not of the Seebeck effect eventually did lead indirectly to the principle of the thermocouple that also uses dissimilar conductors (but in a quite different way) to create an emf[2] *as a measure of temperature. Pioneers of thermoelectricity built on Volta's observation."* Volta's contributions are highlighted and concluded in Ref. [64] as follows:

1) *"A. Volta organized these experiments deliberately, bearing in mind the discovery of thermoelectromotive forces arising due to temperature difference. This distinguished A. Volta's experiments from those of Seebeck who rejected the electrical nature of thermomagnetism effect that he had discovered."*
2) *"A. Volta discovered immediately and directly the origination of thermoelectromotive forces, unlike Seebeck, who observed the magnetic effect of TE current excited by thermoelectromotive forces in a closed circuit."*
3) *"A. Volta as talented and experienced experimenter first excluded the distortions that might take place in his experiments due to galvanic EMF caused by inhomogeneity of metal wires. For this purpose he first selected inhomogeneous arcs which in the absence of temperature difference in the wire did not result in the origination of electromotive forces even on such primitive EMF indicator as prepared frog."*
4) *"Direct observation of thermoEMF by A. Volta took place 27 years earlier than Seebeck observed the thermomagnetism effect."*

Korzhuyev and Katin have a different opinion on the contribution of Galvani and Volta to thermoelectricity, see [65, p. 16]:

> *Due to the above ambiguity of terms, present-day specialists in history of physics in their attempts to determine the researcher pioneer of thermoelectricity encounter difficulties. As the trailblazers of thermoelectricity "prior to T. Seebeck," apart from the above-mentioned Volta, Ritter, Shweiger, Aepinus, the names of Ch. Oersted (1822), J. Fourier (1822) et al.* [8][3] *are referred to. Having analyzed the effects observed by the above authors, we have concluded that the process of discovery of thermoelectricity as phenomenon in its modern "physical" understanding can be represented by the schematic*
>
> **Aepinus, G&V ⇒ Seebeck ⇒ Peltier, Thomson,**
>
> *where Aepinus, Galvani and Volta are the "forerunners" of discovery, and Peltier and Thomson – scientific "successors" of Seebeck who obtained decisive results for the formation of the respective division of physical science.*

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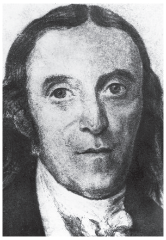
[2] "Electromotive force."
[3] Citation of [70].

They conclude with two points:

1) *"Thermoelectric effect observed by Volta in his experiments with the iron wire is of a complicated nature and is classified in the paper as predominantly* galvanothermal effect (GTE) *related to temperature dependence of electrode potentials of the cell Fe/H_2O/Fe."*
2) *"Heuristic analysis of formulae of G&V effects that included substitution of media and actions, as well as compiling of effects combinations according to procedure* [2],[4] *indicates the possibility of existence of new phenomena related to G&V effects that are partially represented in this paper."*

Johann Wilhelm Ritter (1776–1810)

The German Scientist Franz Peters stated in his review book [58] that Ritter and Schweigger observed electrical currents created by temperature gradients before Seebeck. Johann Wilhelm Ritter (1776–1810), a German physicist, is nowadays known for the discovery of the ultraviolet light (by chemical means) and the invention of the first dry battery. From his discoveries, it can be seen that his primary interest had focused on electricity, in particular on electrochemistry and electrophysiology. In 1799, he investigated and carried out the electrolysis of water. One year later, he did experiments on electroplating. In 1801, he observed TE currents and investigated artificial electrical excitation of muscles. With the first observation, he paved way for the scientific foundation of thermoelectricity by Seebeck.



Johann Salomo Christoph Schweigger (1779–1857)

Another scientist who observed TE currents before Seebeck is supposed by Peters to be Johann Salomo Christoph Schweigger (1779–1857), who was a professor of chemistry at the university of Halle[5] and editor of the "Journal für Chemie und Physik." Schweigger's physical work was also concentrated on the investigation of electricity. In 1808, he developed and constructed an electrometer to measure the electrical force by the magnetic one. He is famous for having developed the electromagnetic multiplicator named after him. Peters dated his observation of TE currents to the year 1810 [58].

Despite all these facts, Thomas Johann Seebeck is regarded today as the discoverer or scientific founder of thermoelectricity. He called the phenomena he investigated "thermomagnetism" as he reported for the first time on August 16, 1821, at a session at the Berlin Academy of Sciences. The following facts are collected

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[4] Author's note: Citation of [71].

[5] Author's note: Today: Martin-Luther-University Halle-Wittenberg, Saxony-Anhalt, Germany.

mainly from the two publications of Velmre [6, 7] containing more detailed biographical information about Seebeck.

Thomas Johann Seebeck (1770–1831)

Thomas Johann Seebeck was born on April 9, 1770, in Tallinn[6], the capital and largest city of Estonia. His father, Johann Christoph, was a wealthy merchant. His father's wealth gave him a kind of independence in his later studies. As discoverer of the Seebeck effect, he is a key person in the development of thermoelectricity as a scientific branch, but there are other things he is less known for, such as the discovery of the piezooptic effect and photoelasticity in 1813. By investigating tempered glass blocks/plates, he described how mechanical stress in an amorphous transparent material (plastics/glass) can cause the material to be birefringent. Photoelasticity, which had been later rediscovered by the English physicist David Brewster, is concerned with the determination of residual stress in glasses. Seebeck summarized all of his early research on optics in a contribution to Goethe's work in natural sciences "Zur Farbenlehre." Seebeck also contributed to the development of photography, as he described the solar spectrum in the natural colors of silver chloride in 1810. With that, he is a forerunner of interference color photography, which led to the invention of holography. But his now most famous impact in science is the widespread investigation of TE materials although he misinterpreted the results of his experiments as "thermomagnetism." He investigated materials we call today semiconductors and stated that the following materials, such as *Bleiglanz* (Galena, PbS), *Schwefelkies* (pyrite, FeS_2), *Kupferkies* (chalcopyrite, $CuFeS_2$), *Arsenikkies* (arsenopyrite, AsFeS), *Kupfernickel* (nickeline NiAs), *weisser Speiskobalt* (white skutterudite, $(Co,Ni)As_{3-x}$), all of which display Bismuth-like behavior, and *Kupferglas* (chalcocite, Cu_2S), *Buntkupfererz* (bornite, Cu_5FeS_4), *blättriger Magnetkies* (pyrrhotite, $Fe_{1-x}S$), which display an Antimony-like behavior, exhibit a stronger "thermomagnetism" when they are in contact with copper than other materials he had investigated.

After his graduation in 1788 at Reval Imperial Grammar School, Seebeck went to Berlin and later on to Göttingen to begin studies in medicine, which he finished in 1792 with excellent marks. Later, he shifted to Bayreuth to study physics. This was possible because of his father's inheritance, which allowed him independent studies without practicing medicine. In March 1802, Seebeck received the doctor of medicine degree in Göttingen. Afterward, he shifted to Jena, which had a great influence on him, because he found a very stimulating intellectual atmosphere with the famous "Jenaer Romatikerkreis" in which natural philosophers were active, like Oken, Schelling, the Schlegel brothers, and Ritter, the "romantic physicist" who founded the discipline of electrochemistry. This was also the time when the long-lasting friendship with Goethe and the philosopher Hegel began.

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6) Author's note: Formerly known as Reval.

In 1818, Seebeck went to Berlin and became a member of the Prussian Academy of Sciences. On August 16, 1821, he gave a first report on "thermomagnetism" of a galvanic circuit in a session at the Berlin academy. Three further talks on this topic followed on October 18 and 25, 1821, as well as on February 22, 1822, the results of which were published in Refs [5, 72]. One key topic in physics of the nineteenth century was the discovery of electromagnetism by Oersted in 1820 and further investigation of the phenomenon afterward. Oersted sent out a circular letter written in Latin to his colleagues and institutes "*Experimenta circa effectum confliktus electrici in acum magneticam*" [73]. Seebeck, recognizing this, gave up his studies in optics to go over to investigate electricity and magnetism and re-examined the Volta theory [74].

Even though Alessandro Volta may have been the discoverer of the TE effect, Seebeck was the first to carry out a series of detailed investigations on TE materials, see Table 1.1 taken from Ioffe's textbook [36, 42]. On December 10, 1831, Seebeck died in Berlin.

Parallel to Seebeck, there were several scientists doing similar experiments. Independently of Seebeck, Julius Conrad von Yelin discovered on March 1, 1823, thermomagnetic currents in metals [77, 78]. He was very confident about his results, as he expressed in his letter [79]:7)

> *From a letter of Yelin's (Munich May, 6th 1823)*
> *You will receive in a few days an essay in which I explain the whole thermo-magnetism from the known laws of electro-magnetism in a very simple way. I am curious how I come along with these statements with Mr. Dr. Seebeck, who as Mr. Prof. Oersted informed in the recent February issue of the "Annalen der Chemie" that he also and indeed as is evident earlier than me found that an unequal heating makes all metals to electro-magnets (I observed these phenomena first at a simple copper arc on March, 14th). Since Mr. Seebeck had concealed his discovery, then this is not depriving my discovery's merit, and as Galilei with Jupiter's moons, Kleist with the gain-bottle [Leyden bottle] and Kunkel the phosphorus have been discovered for the second time, I will give myself credit as the discoverer of the new, very important phenomena of the thermo-magnetism and their effects on the geogeny and crystal formation.*

In Figure 1.2, Seebeck's classical experiment is sketched. In a closed circuit of two dissimilar metallic conductors, one of the soldered junctions between the conductors is heated. A magnetic needle is positioned near this arrangement and then deviated. The declination angle is proportional to the temperature difference between the two (hot and cold) junctions. As a result of his experiments, Seebeck proposed his "thermomagnetische Reihe"8), which is actually a TE series, see [36, 42] and Table 1.1. Finally, it was Oersted who provided a physically correct explanation of the phenomenon that the *electric current* in the circuit is due to the

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7) Translation from the German original.
8) *engl.* Thermomagnetic series.

Table 1.1 Seebeck series, Justi's, and Meissner's thermoelectric series taken from Refs [36, 42, 75, 76]

Seebeck 1822	**Justi 1948**		**Meißner 1955**			
			Metals		**Semiconductors**	
PbS	Bi	−80	Bi	−70	MoS	−770
Bi	Co	−21	Co	−17.5	ZnO	−714
Bi-amalgam	Ni	−20	Ni	−18	CuO	−696
Ni	K	−14	K	−12	Fe_2O_3 (400 °C)	−613
Co	Pd	−8	Pd	−6	FeO	−500
Pd	Na	−7	Na	−4.4	Fe_3O_4	−430
Pt Nr 1	Pt	−5	Pt	−3.3	FeS_2	−200
U	Hg	−5	Hg	−3.4	MgO_3H_2	−200
Au Nr 1	C	−3.5			SnO	−139
Cu Nr 1	Al	−1.5	Al	−0.6	Fe_2O_3 (50 °C)	−60
Rh	Mg	−1.5	Mg	−0.4	CdO	−41
Au Nr 2	Pb	−1.0	Pb	−0.1	CuS	−7
Ag	Sn	−1.0	Sn	+0.1	FeS	+26
Zn	Cs	−0.5	Cs	+0.2	CdO	+30
C	Y	−1.0	Y	+2.2	$GeTiO_3$	+140
Cu Nr 3	Rh	+1.0	Rh	+2.5	NiO	+240
Pt Nr 4	Zn	+1.5	Zn	+2.9	Mn_2O_3	+385
Cd	Ag	+1.5	Ag	+2.4	Cu_2O	+474
Steel	Au	+1.5	Au	+2.7	Cu_2O	+1000
Fe	Cu	+2.0	Cu	+2.6	Cu_2O	+1120
As	W	+2.5	W	+1.5	Cu_2O	+1150
Sb	Cd	+3.5	Cd	+2.8		
SbZn	Mo	+6.5	Mo	+5.9		
Fe	Fe	+12.5	Fe	+16		
	Sb	+42	Sb	+35		
	Si	+44				
	Fe	+49	Fe	+400		
	Se		Se	+1000		

heat and coined the term "thermo-électricité"[9] instead of Seebeck's chosen term [80, 81]. Oersted was the one [80] who brought thermoelectricity to the attention of several French scientists, such as father and son Becquerel, Fourier, Melloni, Pouillet, and Nobili.

Fourier and Oersted made the first thermopile for TE power generation in collaboration, see [82].

From a mathematical point of view, a voltage, the Seebeck voltage, can be measured due to a temperature difference

$$V_\alpha = -\int_{T_\mathrm{c}}^{T_\mathrm{h}} \alpha(T)\,\mathrm{d}T, \tag{1.1}$$

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[9] *engl.* Thermoelectricity.

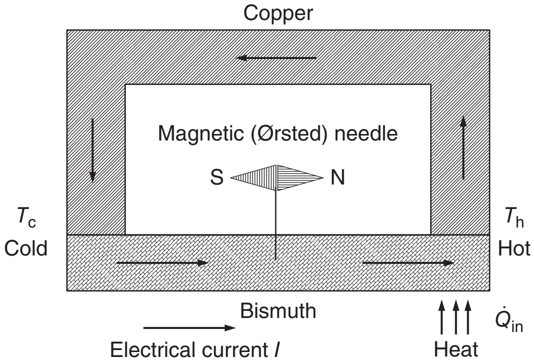
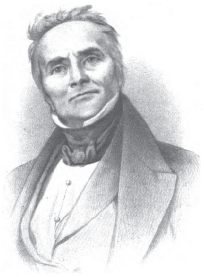


Figure 1.2 Schematics of Seebeck's classical experiment.

where $\alpha(T)$ is the Seebeck coefficient of a material. If this coefficient is supposed to be independent of temperature or if small temperature differences are assumed, the relation (1.1) simplifies to

$$V_\alpha = -\alpha\,(T_\mathrm{h} - T_\mathrm{c}). \tag{1.2}$$

1.1.2
Discovery of the Peltier Effect



Jean C. A. Peltier
(1785–1845)

Jean Charles Athanase Peltier was born in 1785 in a modest family in northern France. As apprentice watchmaker from an early age, he showed great technical skills. He then developed his self-taught scientific knowledge in the fields of human physiology, electrical phenomena, and later meteorology, of which he is now considered a precursor. More about his life and his scientific work can be found in a book written by his son Ferdinand Athanase Peltier [83].

His great experimental skills allowed him to develop galvanometers and electrometers of very high precision, which were essential to the discovery of heat absorption measurement by circulating electric current. This effect, thoroughly studied by Peltier, soon became a subject of communication to the French Academy of Sciences (April 21, 1834).

Additional experimental proof of the effect had been given by Emil Lenz in 1838, as he observed that water could be frozen at an electrical junction by passage of an electric current. Lenz also found that if the electric current is reversed, the ice can be melted again [84].

A schematic of the Peltier effect is shown in Figure 1.3, where two different materials (different electronic heat capacities) are in contact. After this, Peltier continued his work on thermoelectricity and coupled it with his other works in

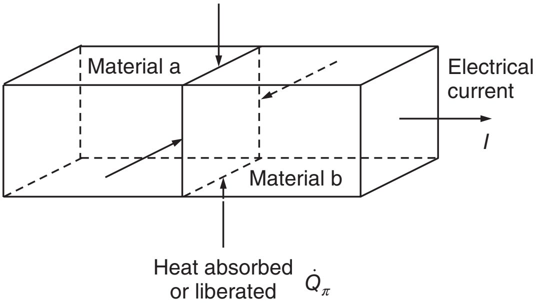


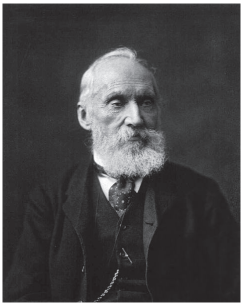
Figure 1.3 Schematics for the Peltier effect.

electromyology and meteorology. As an ending of his large contribution to science, his latest work on “electrical meteorology” was published in 1844, see [85].

Besides the irreversible Joule heat, which is found in all conductors, the Peltier heat flow $\dot{Q}_\pi \propto I$ occurs if a current passes through the material, which is reversed if the orientation of the current is reversed. The proportionality factor between the current and the absorbed heat released is the Peltier coefficient, which is in relation to the Seebeck coefficient α given by the first Thomson (Kelvin) relation $\Pi = \alpha T$, where T denotes the absolute temperature. So, the Peltier heat power is found as

$$\dot{Q}_\pi = \alpha T I. \tag{1.3}$$

1.1.3
Discovery of the Thomson Effect



Lord Kelvin (1824–1907)

A first theoretical description of TE effects had been given by William Thomson (later known as Lord Kelvin) in 1851, as he brought the observed effects in harmony with the two laws of thermodynamics [86]. He combined the descriptions of the Seebeck and Peltier effects into a single expression by using thermodynamic arguments and providing decisive arguments in favor of a compact and complete description of all phenomena [86–90]. Furthermore, he found in this theoretical analysis of the relationship between both effects that an additional effect has to occur, which is named after him. The Thomson effect describes the generation or absorption of heat along a homogeneous conductor that is under a thermal gradient **and** carries an electric current. It is a distributed Peltier effect due to the temperature dependence of the Seebeck coefficient, leading to the Thomson coefficient, that is, $\tau = T\, {}^{d\alpha}/_{dT}$, which manifests the second Thomson (Kelvin) relation. If $\alpha(T)$ =const., then $\tau = 0$.

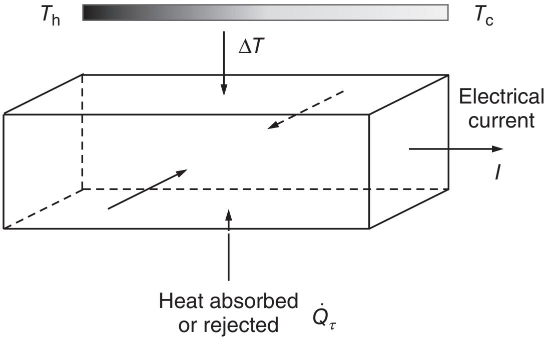


Figure 1.4 Schematics of the Thomson effect.

In Figure 1.4, a schematic of the Thomson effect is shown. It is found that

$$d\dot{Q}_\tau = I \cdot \tau \cdot \frac{\partial T}{\partial x} \cdot dx.$$

Thomson spoke of convection of heat in the nominal direction of the current in a conductor and introduced the term "specific heat of electricity" [89]. His theory of thermoelectricity can be considered as the first reasonable theory in nonequilibrium thermodynamics [90, 91]. A comprehensive overview of Thomson's work in his historical background is given by Finn [52, 56, 57].

1.1.4
Magnus' Law

Heinrich Gustav Magnus (1802–1870)

In 1851, the German chemist and physicist (Heinrich) Gustav Magnus discovered that the Seebeck voltage does not depend on the distribution of the temperature along the metals between the junctions, see, for example, [92]. There he wrote: "*There is no way that in a homogeneous conductor a power-supplying potential difference is caused by a temperature difference alone.*"[10] This is an indication of the fact that thermopower is a thermodynamic state function. Obviously, the direct correlation is the physical basis for a thermocouple, which is often used for temperature measurements, see [93].

Magnus was born on May 2, 1802, in Berlin, and he died there on April 4, 1870. Magnus also made his contributions to the field of chemistry, but today he is better known for his contributions to physics and technology [94]. He became especially famous for his physical explanation of a phenomenon in the field of

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[10] Translation from German: "Im homogenen Leiter können auf keine Weise allein durch Temperaturdifferenzen stromliefernde Potentialdifferenzen hervorgerufen werden," see [75, pp. 74–75].

fluid mechanics. This effect, the Magnus effect, named after him, describes the occurrence of a shear force effect (force) of a rotating body (cylinder or sphere) in a fluid flow.

In 1822, Magnus studied chemistry, physics, and technology at the "Berliner Universität" (today Humboldt University). In 1827, he received his PhD on a topic on the chemical element tellurium. Afterward, he visited Berzelius' laboratory at the Stockholm Academy of Sciences and then the "Sorbonne" in Paris, where he stayed with Gay-Lussac and Thénard. He returned to Berlin, and after completing his "Habilitationsschrift" on mineral analysis in 1831, he started lecturing physics and technology at the university.

In Kant's article [95], Magnus' work is acknowledged as follows[11]: *"Particularly Magnus worked in the physical area on some questions of the expansion of the gases caused by heat and fluid mechanics (Magnus effect). His works were often inspired by practical problems: for example, he designed a special mercury thermometer – the geothermometer – to investigate the change in temperature with depth of mine shafts. He was above all a brilliant experimentalist and in the end he was not satisfied until all feasible attempts have been 'tried out' to get a result."*

1.1.5
Early Performance Calculation of Thermoelectric Devices

In 1885, it was Lord John William Rayleigh (fka J.W. Strutt) who suggested power generation using the Seebeck effect [96]. Although there are erroneous results in this work, it can be considered as an origin of the concept of direct energy conversion. Thermoelectricity is just a principle of direct energy conversion [1–4, 36, 45, 47, 97], and the application of this principle to build solid-state devices recently regained new interest among scientists and technologists. Currently, the focus is the development of novel and advanced materials reaching higher performance in devices. Until now, the lack of sufficiently high performance is one of the main reasons why there is no broad commercial application of TE devices yet [10–12]. There was a long time period following the exploration of the TE effects in which there was a great interaction of experiment and theory in the field.

1.1.6
First Evaluation of the Performance of a Thermoelectric Device by E. Altenkirch

The German scientist Edmund Altenkirch (1880–1953), one of the pioneers of technological thermoelectricity, studied mathematics and physics in Berlin and was interested in theoretical investigations at an early stage. He was stimulated by the lectures of Max Planck. Later, he turned his focus to problems in technical physics.[12]

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[11] As a translation from German.

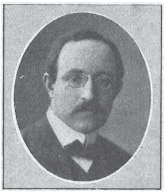
[12] An overview is given in the German book by Unger/Schwarz "Edmund Altenkirch-Pionier der Kältetechnik" [98].

Two theoretical papers by E. Altenkirch, who was certainly inspired by former investigations, especially those by Lord Rayleigh [96], are particularly worth mentioning. In Reference [99], he formulated the efficiency of a thermopile from the material properties that are relevant for practical devices [98, 100].

By comparing his results with the efficiency of the Carnot cycle, Altenkirch called the thermopile[13] in his article a "rather imperfect thermodynamic engine." In a subsequent paper, he described the effectiveness of TE cooling [100]. Altenkirch gave the first evidence that a good TE material should have a large Seebeck coefficient α, a high electrical conductivity σ (low electrical resistivity ϱ) to minimize the Joule heat, and a low thermal conductivity κ to retain the heat at the junctions and maintain a large temperature gradient. A patent in collaboration with Gehlhoff demonstrates that Altenkirch not only conducted theoretical investigations but was also interested in practical applications [102].

Early thermal conductivity measurements by Eucken [103–106] on solids quickly revealed that point defects found in alloys significantly reduce lattice thermal conduction – a fact that became important for the improvement of TE materials.

1.1.7
Benedicks' Effect



Carl Axel Fredrik Benedicks (1875–1958)

The TE effects described by Carl Benedicks directly contradict the law of Magnus, which is valid for chemically and physically homogeneous thermoelements or thermocouples. A discussion about this can be found in Section I of [107]. His contributions to the field of thermoelectricity have been valued in Ref. [108] as follows: *"In the light of modern physics, some of Benedicks theories and interpretations of TE phenomena and some of his solutions to problems concerning physical properties of steel seem to be outdated and are subject to criticism. Nevertheless, during his lifetime they arouse great interest in international circles."*

The Swedish physicist Carl Axel Fredrik Benedicks was born on May 27, 1875 in Stockholm and died there on July 16, 1958. Already in his early years, his thoughts turned to the theoretical studies of minerals and metals. He studied natural sciences at the University of Uppsala, where he received his PhD in 1904 on the work *"Recherches physiques et physiochimiques sur l'acier au carbone,"* see [109].[14] In 1910, he became a professor of physics at the University of Stockholm. He is known as the father of Swedish metallography, as he established a special research laboratory. He pioneered in the field of metal microscopy.

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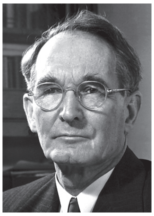
[13] Thermopiles have been used since their invention by Oersted and Fourier around 1823 to generate electrical energy for various purposes. A great deal of historical information about thermopiles can be found in Refs [58, 101].

[14] *engl.* Physical and physicochemical research on carbon steel.

Benedicks and his coworkers claimed [110–114] that Magnus' law was not valid even if the element was perfectly homogeneous physically as well as chemically. Fuschillo opposed to Benedicks' conclusions and findings [115]. Domenicali [107] also mentioned that, in order to explain Benedicks' effect, one has to go beyond Onsager theory. The transport entropy per particle/carrier should then depend not only on the temperature gradient but also on the temperature itself, and a higher order approximation has to be taken into account. In summary, it is stated in Ref. [107]: *"In any case the effects reported by Benedicks and his co-workers seem to be very small and not particular reproducible, so that until affirmative evidence is produced we shall not deal with these reported effects any further."*

There is a variety of works dedicated to the topic as follows. In a review on Benedicks' book [113] in Nature [116], the Benedicks effect is explained as *"the homogeneous electrothermic effect."* The Czech scientist Jan Tauc reported on this in several publications, see, for example, [51, p. 147] and [38] as well as references therein. A theoretical description of the Benedicks effect based on a nonlocal theory was given by Mahan [117]. Mahan points in his work to Tauc [38, 118–120] and Grigorenko *et al.* [121]. Piotrowski and coworkers revisited the problem by the application of a nonlinear theory [122]. In a recent review article by Martin *et al.* [26] it was stated that *"the Magnus law has been verified for extremely homogeneous metals."*[15] On the other hand, it was pointed out that an effect can be observed in case of steep thermal gradients in nondegenerate semiconductors.

1.1.8
The Bridgman Effect


Percy Williams Bridgman
(1882–1961)

The U.S. physicist Percy Williams Bridgman, who was born on April 21, 1882, in Cambridge, Massachusetts, and died on August 21, 1961, in Randolph, New Hampshire, is famous for his work on properties of matter under high pressure: 'The Nobel Prize in Physics 1946 was awarded to Percy W. Bridgman *"for the invention of an apparatus to produce extremely high pressures, and for the discoveries he made therewith in the field of high pressure physics".*', see [123].

He is further known for his studies on the electrical conductivity of metals and crystal properties. Two methods for single crystal growth, named after him, are the *horizontal* and *vertical* Bridgman methods. More about his life and a list of publications can be found in Refs [124, 125]. He contributed numerous works on thermoelectricity and its connection to thermodynamic concepts, see, for example, [126–136]. The effect that he proposed in Ref. [127] is defined:

> *'The Bridgman effect (named after P. W. Bridgman), also called the internal Peltier effect, is a phenomenon that occurs when an electric current passes*

---

[15] Citation of [115].

> *through an anisotropic crystal - there is an absorption or liberation of heat because of the nonuniformity in current distribution.'*

Two good reviews and calculations of TE effects in anisotropic materials and systems can be found in Refs [107, 137]. In Reference [137], it is stated that *"the thermoelectric anisotropy has important consequences in the form of thermoelectric eddy currents and the Bridgman effect"*.

1.1.9
Semiconductors as Thermoelectric Materials

The contribution of Russian scientists to the advancement of thermoelectricity is unmitigated. One of the most widely known names is Abram Fedorovich Ioffe.

After graduating from Saint Petersburg State Institute of Technology in 1902, A.F. Ioffe spent 2 years as Wilhelm Conrad Roentgen's assistant in his Munich laboratory. Ioffe completed his PhD at Munich University in 1905. From 1906, Ioffe worked in the Saint Petersburg (from 1924 Leningrad) Polytechnical Institute. In 1952–1954 A.F. Ioffe headed the Laboratory of Semiconductors of the Academy of Sciences of the USSR, which in 1954 was reorganized into the Institute of Semiconductors.

In the late 1950s and in the 1960s, Ioffe made extensive investigations on semiconductors as TE materials and initiated with that a revival of thermoelectrics [34, 36, 39, 138–144]. His achievements can be summarized as follows:

1) Altenkirch already showed in his works [99, 100] what Ioffe denoted as the material's or intrinsic figure of merit [36], which is defined as

   $$z = \frac{\alpha^2 \, \sigma}{\kappa}. \tag{1.4}$$

   Ioffe was the first to use z extensively for characterizing the quality/efficiency of thermoelectrics.
2) The concentration of charge carriers in a TE material, which is optimal for large z, was determined. It turned out to be rather high: $\approx 10^{19}\,\mathrm{cm}^{-3}$ at room temperature. This means that the best thermoelectrics should be degenerated semiconductors or semimetals.
3) The first estimation of the efficiency of semiconductors for TE refrigeration and heating was made. The efficiency appeared to be of interest for practical applications.
4) Ioffe and his coworkers built thermogenerators based on PbS in 1942–1945 [139].16)

The "conventional" figure of merit as defined by Ioffe is exactly valid merely for Seebeck and Peltier devices made of materials with constant parameters depending neither on temperature nor on position [146]. It explicitly appears in formulae

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16) A historical overview was given by Glen Slack at ICT 2011 in Traverse City, Michigan, USA [145].

for the efficiency η, which contain only the material properties but no geometrical parameters of the device, see Section 2.3. However, if the material properties are no longer constant (temperature/position dependence), other factors will appear, such as the working conditions, which can be taken into account in "effective" performance parameters as the effective power factor and effective TE figure of merit of a device [147]. As a scientific leader, Ioffe directed a whole group including Stil'bans and further coworkers dealing with problems of TE energy conversion [138, 139].

1.1.10
Thermoelectric Applications – Excitement and Disappointment 1920–1970

It is a known fact that during and after the world wars, thermoelectricity was actively studied for use in valuable technologies, primarily for cooling and power generation for military as well as for civilian uses. The political and economic importance of such devices made advances more difficult and slow to publicize particularly between the Eastern European and Western countries.

1.1.10.1 Construction of the First Thermoelectric Generator

One of the early pioneers of thermoelectricity in the United States was Maria Theresa Telkes (later nicknamed the "Sun Queen"). She was born in Budapest, Hungary, on December 12, 1900. She worked as a biophysicist in the United States, after completing her PhD in physical chemistry in Hungary.

Maria Theresa Telkes
(1900–1995)

From 1939 to 1953, she was engaged in solar energy research at Massachusetts Institute of Technology. In the 1930s, Maria Telkes made a thorough study on the materials Pb S and Zn Sb, which had already been observed by Seebeck more than a century ago, and in her report [148], these materials *"were stated to produce the best couple for thermoelectric energy conversion"* [149]. Telkes is known for creating the first (solar) TE power generator in 1947 [41, 150, 151] and the first TE refrigerator in 1953 using the principles of semiconductor thermoelectricity.[17]

Telkes's generator efficiencies had reached about 5%, and by the 1950s, cooling from ambient below 0 °C was demonstrated, which has ultimately led to some viable industries. Many thought thermoelectrics would soon replace conventional heat engines and refrigeration, and interest and research in thermoelectricity grew rapidly at major appliance corporations such as Westinghouse, universities, and national research laboratories [36, 37, 44, 45, 47, 49, 54, 152]. However, by the end

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[17] A "Preliminary Inventory of the Maria Telkes Papers" can be found at the library of the Arizona State University. A list of the contents is provided in the "Arizona Archives Online" under *http://www.azarchivesonline.org/xtf/view?docId=ead/asu/telkes_acc.xml*.

of the 1960s, the pace of progress had slowed with some discussion that the upper limit of zT might be near 1 and many research programs were dismantled (despite several reports of $zT > 1$).

Ioffe's contributions were already mentioned as he promoted the use of semiconductors in thermoelectrics and semiconductor physics to analyze the results and optimize the performance. Materials with high TE figures of merit are typically heavily doped semiconductors, the best known are the tellurides of antimony, bismuth, and lead. Ioffe and his institute in Saint Petersburg actively pursued TE research and development in the USSR, leading to some of the first commercial TE power generation and cooling devices. Ioffe was one of the first to promote the use of alloying to reduce the lattice thermal conductivity by point defects.

Without doubt, H. Julian Goldsmid is an outstanding personality in thermoelectricity in the twentieth century. One of the first verifications of 0 °C TE cooling was demonstrated by Goldsmid in 1954 using thermoelements based on Bi_2Te_3 [35]. Furthermore, he was one of the first to utilize the TE quality factor, identifying the importance of high mobility and effective mass combination and low lattice thermal conductivity in semiconductors that when properly doped produce good TE materials. Now Goldsmid is active a lifespan since more than 60 years in the field and authored many introductory books [33, 37, 152].

In the search for high zT materials, a general strategy guided by the quality factor has been to look for small band-gap semiconductors made of heavy elements. Slack summarized the material requirements succinctly in the "phonon-glass electron-crystal" (PGEC) concept that the phonons should be disrupted as in a glass, but electrons should have high mobility as they do in crystalline semiconductors [153].

1.1.11
Thermoelectric Industry –Niche Applications 1970–2000

The reliability and simplicity of thermoelectricity enable niche applications for this solid-state technology even while conventional processes are more efficient. Besides thermocouples, a small but stable industry to produce Peltier coolers based on $Bi_2Te_3-Sb_2Te_3$ was formed, which now produces coolers for a variety of products ranging from optoelectronics, small refrigerators, and seat/cooling systems. The need for reliable, remote sources provides some niche applications for TE power generation. The advancement in the science, technology, and commercial use of thermoelectricity has led to a number of focused scientific meetings and organizations, the largest of which is the "International Thermoelectric Society" with meetings since 1970 [154].

1.1.11.1 Thermoelectric Generators for Space

For space exploration missions, particularly beyond the planet Mars, the light from the sun is too weak to power a spacecraft with solar panels. Instead, the electrical power is provided by converting the heat from a ^{238}Pu heat source into electricity using TE couples. Such radioisotope thermoelectric generators (RTG) have been used by NASA in a variety of missions such as Apollo, Pioneer, Viking, Voyager, Galileo, and Cassini. With no moving parts, the power sources for Voyager are still operating, allowing the spacecraft to continue to make scientific discoveries after over 35 years of operation. The Curiosity rover on Mars is the first rover powered by thermoelectrics using a multi-mission RTG (MMRTG).

1.1.12

New Concepts in Thermoelectricity 2000-Present

Interest in thermoelectricity was renewed in the 1990s with the influx of new ideas. The hope that engineered structures will improve zT, particularly at the nanometer scale, has reinvigorated research in TE materials [31, 155, 156]. While some of these ideas have shown to be ineffective, others have led to entirely new classes of complex TE materials [11].

The global need for alternative sources of energy has revived interest in commercial applications [157] and stimulated interest in developing inexpensive and environmentally friendly TE materials.

For spreading thermoelectrics throughout Europe, another outstanding researcher and communicator of thermoelectricity, David Michael Rowe, OBE (1939–2012), has to be mentioned. Rowe greatly contributed to the dissemination of thermoelectricity, particularly by editing the "*CRC Handbooks of Thermoelectrics*" 1995, 2006, and 2012 [15–18].

This section concludes with a timeline of TE and related research (see Table 1.2).

1.2

Galvanomagnetic and Thermomagnetic Effects

If the material is anisotropic or an additional magnetic field is applied, the theoretical description of the additionally appearing phenomena becomes more complicated in comparison to the pure "thermoelectric" case in an isotropic medium. By taking into account both electric fields $\mathbf{E}$ and magnetic fields $\mathbf{B}$, a generalization of Maxwell's equations of electromagnetic fields under the influence of temperature gradients is obvious, see, for example, [20, 196–203]. Sometimes, the phenomenon described in these works is called "*thermoelectric induction.*" Here we will not go into detail of these phenomena because it is beyond the scope of this book, but at least we want to provide some references where such details can be found. The thermodynamic theory of galvano- and thermomagnetic effects was reviewed in great detail by Fieschi in several articles [204–207]. A bunch of textbooks, chapters, and review articles are also dedicated to the topic [54, 75, 76, 208–217].

The most influential scientists who investigated the effects in the late nineteenth century are shown in Figure 1.5. The works they did have been focused on metals as in thermoelectricity as well. The classical works [218–228] are discussed and reviewed in Ref. [208].

Table 1.2 Milestones in thermoelectricity

Date	Event	Source(s)
1762	*"Memoirs comprising precise description of tests with tourmaline"* by Aepinus, first observations in the field of thermoelectricity	[59, 60, 158]
1800	Voltaic pile	[159]
1801	Observation of TE currents by J. W. Ritter	[58]
1810	Observation of TE currents by J. S. C. Schweigger	[58]
1820	Oersted's letter *"Experimenta circa effectum confliktus electrici in acum magneticam"* – Discovery of electromagnetism	[73]
1821	Seebeck's first talk and report on the phenomenon *"thermomagnetism"*	[6, 7, 58]
1822	Heat conduction theory by J. B. J. Fourier	[160–162]
1823	First correct explanation of the phenomenon by Oersted coining the term *"thermo-électricité"*	[80, 81]
1824	Carnot cycle – heat engine efficiency	[163, 164]
1827	Ohm's law investigated with help of a thermopile	[165, 166]
1834	Discovery of the Peltier effect by J. C. A. Peltier – DC current through a Bi–Sb junction	[167]
1838	Experiment – freezing a water droplet via the Peltier effect by E. Lenz	[84]
1843	Studies on DC current producing heat investigated by J. P. Joule	[168]
1851	Discovery of the Thomson effect, derived by W. Thomson (Lord Kelvin)	[86]
1851	Magnus' law	[92]
1866	E. Becquerel studied Zn–Sb and Cd–Sb thermoelectrics	[169]
1885	First proposal of a TE generator by Lord Rayleigh	[96]
1909	Comprehensive theory of TE generation by E. Altenkirch	[99]
1910	PbTe, Bi_2Te_3, and Te as thermoelectrics by W. Haken	[170]
1911	Theory of TE refrigeration by E. Altenkirch	[100]
1911	Crystal thermal conductivity measured by A. Eucken	[103–105]
1914	Discovery of the relation of lattice thermal conductivity to heat capacity by P. Debye	[171]
1918	Reports on the Benedicks effect	[110–114]
1926	Discovery of the Bridgman effect	[127]
1928	Electron band theory of crystals by M. J. O. Strutt	[172]
1928	Mass fluctuation decreases lattice thermal conductivity	[106]
1945	Phonon drag effect by Gurevich	[173–175]
1947	Construction of a TE generator by M. Telkes	[150]
1949	Theory of semiconductor thermoelements (published) by A. F. Ioffe	[138–140]
1954	Cooling from ambient temperature down below 0°C with thermoelectricity by Goldsmid and Douglas	[35]

Table 1.2 (*Continued*)

Date	Event	Source(s)
1956	Solid solutions, Si–Ge alloys by Ioffe	[36]
1957	Thermoelectric book by Ioffe and coworkers	[36]
1957	Discovery of $CoSb_3$ as thermoelectrics by Dudkin and Abrikosov	[176, 177]
1972	TAGS by Skrabek/Trimmer	[178, 179]
1979	Concept of minimal lattice thermal conductivity by G. A. Slack	[180]
1982	Observation of the decrease of lattice thermal conductivity in ice by Ross and Anderson	[181]
1993	Application of nanotechnology leading to advances in the efficiency of TE materials	[182, 183]
1995	Phonon glass/electron crystal (PGEC) concept by G. A. Slack	[153]
1995	Filled skutterudites by JPL, GM, UM, ORNL	[184–186]
1997	Oxide thermoelectrics by Teresaki	[187–189]
2001	Bi_2Te_3/Sb_2Te_3 superlattice by Venkatasubramanian	[190]
2002	Pb Te–Pb Se quantum dots by Harman	[191]
2004	LAST material by Kanatzidis	[192]
2007	Bulk nanocomposites by Tang	[193]
2008	Nanocomposites $(Bi_xSb_{1-x})_2Te_3$ by Poudel	[194]
2008	Tuning resonances in Pb Te by Heremans	[195]

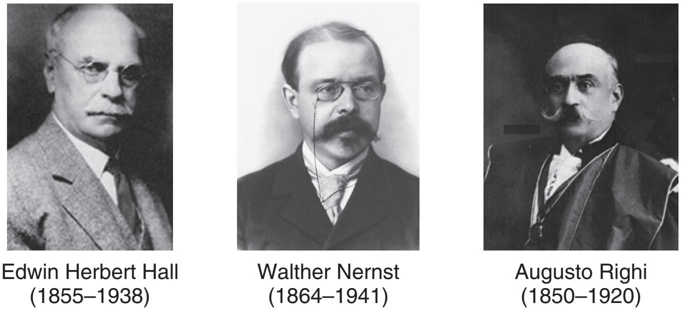

Edwin Herbert Hall (1855–1938)
Walther Nernst (1864–1941)
Augusto Righi (1850–1920)

Figure 1.5 The name givers of galvanomagnetic and thermomagnetic effects. In addition, Albert Freiherr von Ettingshausen (1850–1932) and Sylvestre Anatole Leduc (1856–1937) have to be mentioned.

As for TE materials, the galvano- and thermomagnetic effects can be found to be more pronounced in semiconductor materials. In the two articles [229, 230], the effects found in semiconductor materials are illustratively described in comparison to TE effects. For a more scientific way of description of these effects in semiconductor materials, the reviews [212, 231] are recommended for study.

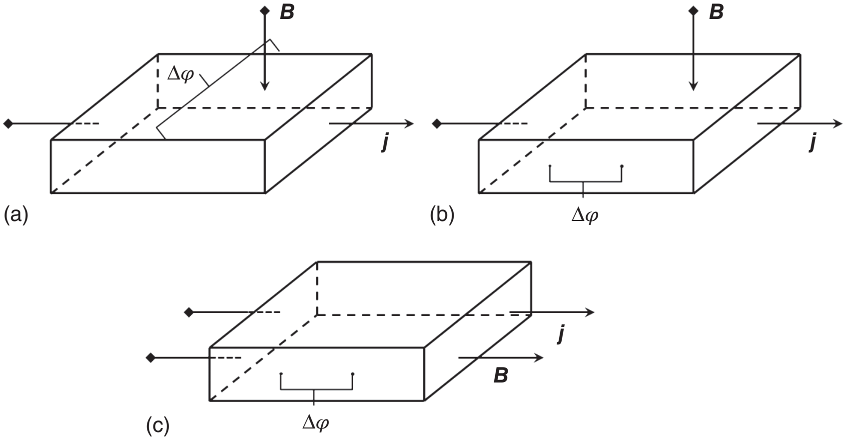


Figure 1.6 Schematics of the different effects: (a) transversal effects, (b) longitudinal effects in a transverse field, and (c) longitudinal effects in a longitudinal field (adapted from Figures 154–156 in Ref. [76, pp. 311–312]).

There is a clear definition of the effects to be studied given by Meissner, as *galvanomagnetic effects* are caused by an electric current on the one hand, and *thermomagnetic effects* are caused by a heat flow on the other hand, see [76]. A distinction is made between *transversal* and *longitudinal* effects. In the first case, the primary current (either heat or electric current) is perpendicular to the produced effect, whereas in the longitudinal case, both variables are supposed to have the same direction.

A more detailed distinction is made between *“transversal,” “longitudinal effects in the transverse field”* and *“longitudinal effects in the longitudinal field.”* In the transversal effect, see Figure 1.6(a), the magnetic field is perpendicular to the original electric current (density) or heat flux. This effect is found to be perpendicular to both the current/flux and the magnetic field. For the longitudinal effects in the transverse field, see Figure 1.6(b), the magnetic field is perpendicular to the original electric current (density) or heat flux, but the effect is parallel to the current/flux. For longitudinal effects in the longitudinal field, the magnetic field and the effect are parallel to the original electrical current (density) or heat flux, see Figure 1.6(c).

Another possibility to distinguish between different processes is led the thermal condition. The effect is called *isothermal* if there is no temperature gradient present in the direction perpendicular to the primary current. An *adiabatic* effect is characterized by the fact that there is no heat flow in the direction perpendicular to the primary current. Various local effects are theoretically possible. In Reference [206], a number of 560 is proposed. This is found in a situation where the transport coefficients are tensors, that is, they are anisotropic, see Section 21.7 in Ref. [215, p. 240ff] as well as Table 21.5 on [215, p. 242]. Fourteen effects with a transverse magnetic field and four with a longitudinal magnetic field out of these 560 theoretically possible effects and their corresponding phenomenological coefficients between these coefficients are discussed in detail in Ref. [207] (summarized in Table 1 of this reference).

Here, we want to discuss some of them to give a brief overview. First, we assume that the material is isotropic. The primary flow or gradient is applied in x-direction and the magnetic field is directed in the transverse z-direction. The already discussed “thermoelectric” coefficients show in general a dependence on the magnetic field. They can be seen as longitudinal thermogalvanomagnetic coefficients [213]. Now, definition of a number of transversal thermogalvanomagnetic coefficients shall be given without any claim to completeness.

1.2.1
The Hall Coefficient

If there is no temperature gradient in any direction, then a transverse electric field E_y can be observed if an electrical current density j_x is applied while a magnetic field B_z is present. The corresponding coefficient is the so-called Hall coefficient R_H, which is defined as follows:

$$|R_\mathrm{H}| = \frac{E_y}{j_x\, B_z}. \tag{1.5}$$

The signs of the Hall coefficient and the other transverse coefficients can be determined from Figure 1.7.

1.2.2
The Nernst Coefficient

The Nernst effect can be seen as transversal equivalent of the Seebeck effect. If a longitudinal temperature gradient $\frac{\mathrm{d}T}{\mathrm{d}x}$ is present with a magnetic field B_z, a transverse electric field E_y results. The corresponding coefficient, the Nernst coefficient $\mathcal{N}$, is defined as

$$|\mathcal{N}| = \tfrac{E_y}{B_z} / \tfrac{\mathrm{d}T}{\mathrm{d}x}. \tag{1.6}$$

Note that there is no electrical current present in any direction.

1.2.3
The Ettingshausen Coefficient

The Ettingshausen effect is identified to be equivalent to the Peltier effect. Although this is the case, the Ettingshausen coefficient P_E is defined in terms of the transversal temperature gradient and not the heat flow, that is,

$$|P_\mathrm{E}| = \frac{1}{j_x\, B_z}\, \frac{\mathrm{d}T}{\mathrm{d}y}. \tag{1.7}$$

1.2.4
The Righi–Leduc Coefficient

If a longitudinal temperature gradient, ${}^{\mathrm{d}T}/_{\mathrm{d}x}$, and a transverse magnetic field B_z are present, not only a transverse electric field E_y but also a transversal temperature gradient ${}^{\mathrm{d}T}/_{\mathrm{d}y}$ result. This observed effect is called Righi–Leduc effect, and the corresponding coefficient S_{RL} is defined as

$$S_{\mathrm{RL}} = \frac{1}{B_z}\ \frac{\mathrm{d}T}{\mathrm{d}y}\Big/\frac{\mathrm{d}T}{\mathrm{d}x}. \tag{1.8}$$

The introduced effects and coefficients are highlighted and illustrated in the following Table 1.3 and Figure 1.9.

The correlation between the introduced effects can be seen in Figure 1.8

1.2.5
Devices Using Galvano- and Thermomagnetic Effects and the Corresponding Figure of Merit

The galvano- and thermomagnetic effects can be used in solid-state devices as in TE elements for either cooling [230] or power generation [232] (Figure 1.9).

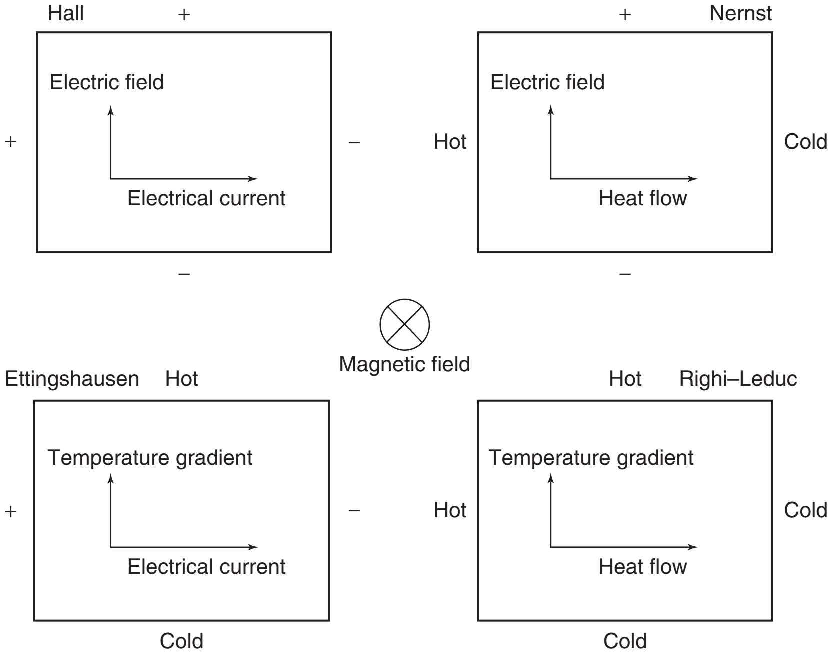


Figure 1.7 Transversal thermogalvanomagnetic effects. The coefficients are positive if the effects have the same directions as shown in the schematics (adapted from Ref. [152, Figure 4-1, p. 83]).

Table 1.3 Transport coefficients in isotropic conductors.

Name of the coefficient	Symbol	Definition	Conditions
Electrical conductivity	ϱ	$\frac{E_x}{j_x}$	$j_y = j_z = 0, \nabla T = 0$
Thermal conductivity	κ	$-\dot{q}_x / \frac{\mathrm{d}T}{\mathrm{d}x}$	$\mathbf{j} = 0, \frac{\mathrm{d}T}{\mathrm{d}y} = \frac{\mathrm{d}T}{\mathrm{d}z} = 0$
Seebeck coefficient	α	$E_x / \frac{\mathrm{d}T}{\mathrm{d}x}$	$\mathbf{j} = 0, \frac{\mathrm{d}T}{\mathrm{d}y} = \frac{\mathrm{d}T}{\mathrm{d}z} = 0$
Peltier coefficient	Π	$\frac{\dot{q}_x}{j_x}$	$j_y = j_z = 0, \nabla T = 0$
Hall coefficient	R_H	$\frac{E_y}{j_x\ B_z}$	$j_y = j_z = 0, \nabla T = 0$
Nernst coefficient	$\mathcal{N}$	$\frac{E_y}{B_z} / \frac{\mathrm{d}T}{\mathrm{d}x}$	$\mathbf{j} = 0, \frac{\mathrm{d}T}{\mathrm{d}y} = \frac{\mathrm{d}T}{\mathrm{d}z} = 0$
Ettingshausen coefficient	P_E	$\frac{1}{j_x\ B_z} \frac{\mathrm{d}T}{\mathrm{d}y}$	$j_y = j_z = 0, \nabla T = 0$
Righi–Leduc coefficient	S_RL	$\frac{1}{B_z} \frac{\mathrm{d}T}{\mathrm{d}y} / \frac{\mathrm{d}T}{\mathrm{d}x}$	$\mathbf{j} = 0, \frac{\mathrm{d}T}{\mathrm{d}z} = 0$

$\mathbf{j}$ is the electrical current density; $\dot{\mathbf{q}}$ is the heat flux; T is the (absolute) temperature; $\mathbf{E}$ is the electric field; $\mathbf{B}$ is the magnetic field (if $\mathbf{B}$ is nonzero, then it is supposed to lie in the z-direction).

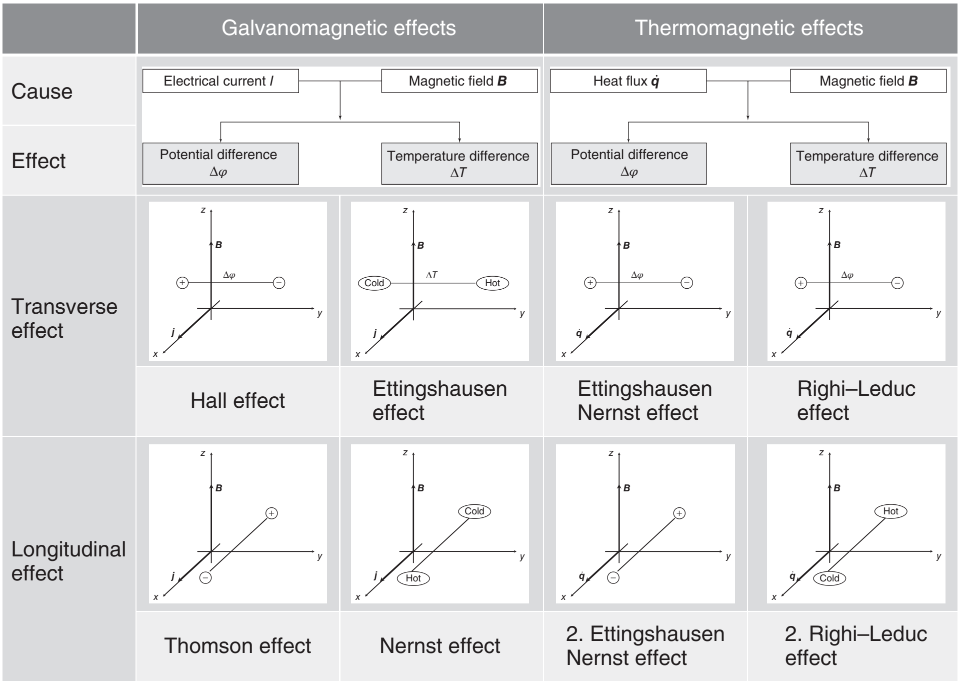


Figure 1.8 Effects and their causes: Four galvanomagnetic and thermomagnetic effects (require a magnetic field) and two TE effects and their correlations (adapted from Ref. [229, p. 126]).

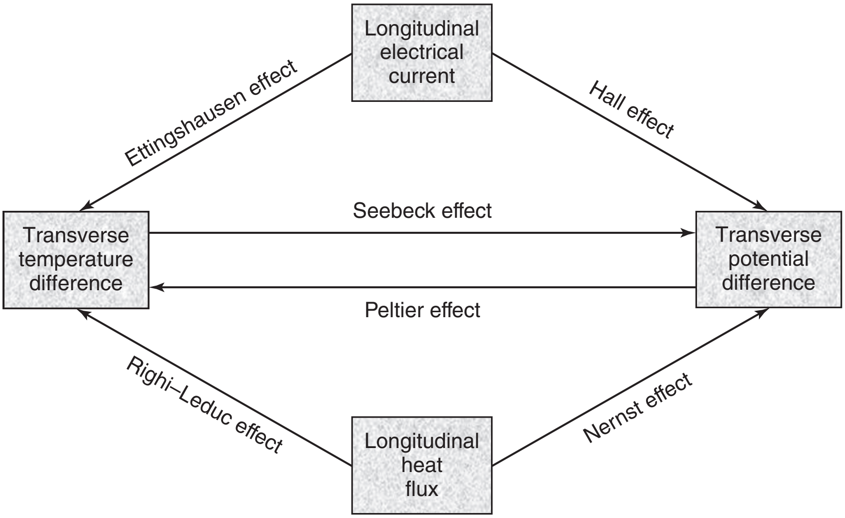


Figure 1.9 Galvanomagnetic and thermomagnetic effects (adapted from Ref. [217, Figure 9.66, p. 846]).

Several works are dedicated to investigate such devices and their performance [232–254]. Analogous to the TE case, the so-called "*thermomagnetic figure of merit*" can be defined (Table 1.4). In general, the calculations for thermomagnetic devices have to be performed in 3D as in an anisotropic crystal, the orientation of the fields and the current densities have to be specified. In Cartesian coordinates, that is, $(x, y, z) \equiv (x_1, x_2, x_3)$, the *isothermal thermomagnetic figure of merit* is given by

$$Z_{ji}^{\text{iso}} = \frac{(\mathcal{N}_{ji}^{\text{iso}}\ B_k)^2}{\kappa_{ii}^{\text{iso}}\ \varrho_{jj}^{\text{iso}}}, \tag{1.9}$$

see [247]. Note that there are different definitions of the thermomagnetic figure of merit in the literature [253], for example, taking the adiabatic resistivity

$$\varrho_{jj}^{\text{ad}} = \varrho_{jj}^{\text{iso}} + (E_{ij}^{\text{iso}}\ B_k)\ (\mathcal{N}_{ji}^{\text{iso}}\ B_k), \tag{1.10}$$

where

$$\varrho_{jj}^{\text{ad}} = {}^{E_j}\!/_{j_j}; \quad j_i = j_k = {}^{\partial T}\!/_{\partial x_j} = {}^{\partial T}\!/_{\partial x_j} = \dot{q}_i = 0 \tag{1.11}$$

and

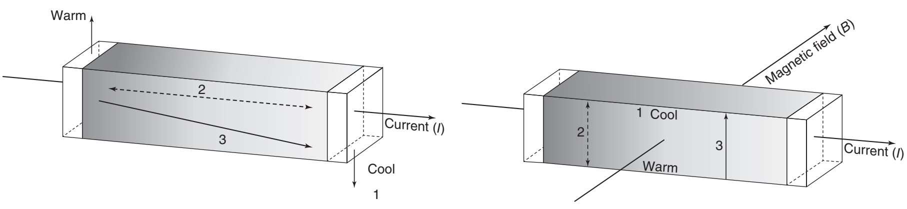
$$E_{ij}^{\text{iso}}\ B_k = {}^{({}^{\partial T}\!/_{\partial x_i})}\!/_{j_j}; \quad j_i = j_k = {}^{\partial T}\!/_{\partial x_j} = {}^{\partial T}\!/_{\partial x_j} = \dot{q}_i = 0 \tag{1.12}$$

a relation between isothermal and adiabatic thermomagnetic figure of merit can be found

$$Z_{ji}^{\text{ad}} = \frac{Z_{ji}^{\text{iso}}\, T}{1 - Z_{ji}^{\text{iso}}\, T} \quad \text{or} \quad Z_{ji}^{\text{iso}} = \frac{Z_{ji}^{\text{ad}}\, T}{1 + Z_{ji}^{\text{ad}}\, T}, \tag{1.13}$$

see [247, 253].

Table 1.4 Comparison between thermoelectric and thermomagnetic figure of merit.



Thermoelectric figure of merit $Z_{TE} = \frac{\alpha^2}{\varrho\ \kappa}$		**Thermomagnetic figure of merit** $Z_{TM} = \frac{\mathcal{N}^2\ B^2}{\varrho_L\ \kappa_T}$	
Effect	**Requirements**	**# Effect**	**Requirements**
Thermoelectric cooling (Peltier effect)	Large Seebeck coefficient (α)	1 Thermomagnetic cooling (Ettingshausen effect)	Large thermomagnetic coefficients ($\mathcal{N}$) Large magnetic field (B)
Joule heating	Low resistivity (ϱ)	2 Joule heating	Low longitudinal resistivity (ϱ_L)
Heat conduction	Low thermal conductivity (κ)	3 Heat conduction	Low transverse thermal conductivity (κ_T)

Both of which contain three effects: (1) Peltier (TE) or Ettingshausen (TM) cooling, (2) Joule heating, and (3) Fourier heat conduction. The electrical resistivity of the material produces heat (Joule heating). It is observed that half of this Joule heat flows to the cold end. Heat transported via conduction flows from the warm to the cold end of the material. In a cooling device, both effects, that is, Joule heating and Fourier heat conduction, reduce the cooling effectiveness. (Table and Figures adapted from Ref. [230, p. 76])

1.3
Historical Notes on Thermodynamic Aspects

Although Max Planck was never directly involved in the history of thermoelectricity, his contribution to the development of thermodynamic concepts and, especially, the second principle of thermodynamics is notable. Strongly influenced by the work of Rudolf Clausius, he studied in detail the concept of entropy in his doctoral thesis defended in 1879 [255]. His thesis, similarly to his later works, remained unknown for a long time while his contemporaries, Gibbs and Boltzmann, found more echo. By his large and fierce correspondence with Wilhelm Ostwald, “Energétiste convaincu,” Max Planck also contributed to the end of the violent conflict that Boltzmann had with the positivists, headed by Ernst Mach.

In the 1930s, Lars Onsager proposed a theoretical description of linear nonequilibrium thermodynamic processes where the coupled thermodynamic forces and fluxes are described in a very general form. In two major articles, the fundamentals of thermodynamics of dissipative transport were developed in a consistent manner [256, 257]. A summary can be found in a later work of Onsager [258]. Onsager expressed his initial thoughts on the dissipation function and the principle of least dissipation of energy, see [256, S 5, p. 420] and also [257, S 5, p. 2276].

The thermodynamic theory of TE phenomena in isotropic media was first worked out by Callen [210, 259] and is presented in more detail in de Groot's monograph [260]. Usually denoted as Onsager–de Groot–Callen theory, it might be called a "first approximation" theory of TE transport, giving a coherent thermodynamic description of TE processes on a phenomenological level. Domenicali's fundamental article [107] summarizes the principles of steady-state thermodynamics applied to a TE system out of thermostatic equilibrium. He pointed out that a complete description of the state includes the determination of the "electrochemical potential" from the overall electronic and crystalline structure of all phases constituting the TE system (see Table 1.4).

The introduction of the irreversible entropy production in the form of an equality is a very old problem mentioned by Lord Kelvin himself. Tolman and Fine [261] were probably the first to point out that the entropy production of a TE process can be considered as a measure of the total irreversibilities. Before this, Bridgman discussed the relation between thermodynamics and thermoelectrics in several articles [126, 129, 131, 133]. At the beginning of the 1930s, Sommerfeld and Frank provided a review about the statistical theory of TE phenomena in metals, but without considering entropy production [262]. Their calculation was based on Darrow's report [263]. In 1952, Haase [264] presented a review about the thermodynamic phenomenological theory of irreversible processes containing considerations about thermoelectrics as well. During the 1950s and 1960s, a very active period of thermoelectrics, there were many works dedicated to the topic of this review. For a small selection, we draw the reader's attention to [107, 204–206, 265–279]. Another work should be particularly emphasized: Sherman *et al.* stated in Ref. [271] that the conditions that maximize the efficiency of a TE generator are precisely the conditions that minimize the irreversibility process, allowing a closer approach to the Carnot cycle where entropy production is zero. This concept has been extended by Clingman [273, 274] for TE generator and TE cooler.

After a very active period, the interest in thermoelectricity collapsed under the weight of inflated hopes, because there had been no significant advances in practically achieved material efficiency after the mid-1960s. As basic research in thermoelectrics lay stagnant for 30 years after that, meanwhile some materials and commercial applications, in particular of customized Peltier coolers, were still developed. In this period, there were a few works produced on this topic [280–288].

New ideas and materials in the mid-1990s brought thermoelectrics back into the scope of research. The search for green technologies, for example, for converting

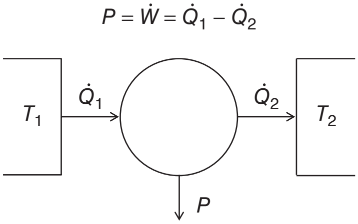


Figure 1.10 Carnot engine.

waste heat generated by car engines into usable power, pushes scientists to pick up "old" effects with new classes of materials with higher TE efficiency to enable practical applications using the advantages of TE power generation [15, 16, 289]. An overview of different applications is given by Riffat and Ma [9]. The reader will find the thermodynamic theory of TE materials and devices in the period from the 1990s to the present day in, for example, [290–315] and references therein. In the next sections, we provide a summary from our point of view.

1.4
Basic Thermodynamic Engine

Let us consider a basic thermodynamic system composed of two thermostats at temperatures T_1 and T_2, respectively (see Figure 1.10). The engine located in between these thermostats receives the entering heat flow $\dot{Q}_1$ from the source (at temperature T_1), and the sink absorbs the rejected heat flow $\dot{Q}_2$. Since the power produced, or received, by the engine is P, then the energy budget of the complete system is given by:

$$P = \dot{W} = \dot{Q}_1 - \dot{Q}_2.$$

The efficiency goal for any thermodynamic engine is the reduction of the entropy production. Then, for a perfect engine called endoreversible engine, the entering entropy flow, $\dot{Q}_1/T_1$, and outgoing entropy flow, $\dot{Q}_2/T_2$, should be equal, so,

$$\frac{\dot{Q}_1}{T_1} = \frac{\dot{Q}_2}{T_2}.$$

By combining these two expressions, we get the relation between the power and the entering heat flow,

$$\dot{W} = \dot{Q}_1 \left(1 - \frac{T_2}{T_1}\right).$$

For an endoreversible engine, *the Carnot expression of the efficiency* is then

$$\eta_C = \frac{\dot{W}}{\dot{Q}_1} = \left(1 - \frac{T_2}{T_1}\right).$$

In order to achieve an efficient system, we need to reach these two goals:

1) Find a good working fluid that produces as little dissipation as possible under standard working conditions.
2) Find a good system that permits quasi-perfect transport of the entropy between both thermostats.

1.5
Thermodynamics of the Ideal Fermi Gas

1.5.1
The Ideal Fermi Gas

The ideal Fermi gas, which shall be considered here, is a physical model assuming a vast number of noninteracting *identical* particles with half-integer spin, in equilibrium at temperature T. The essential difference between the ideal Fermi gas and its classical counterpart is rooted in the half-integer electron spin angular momentum, which governs the statistical distribution of the single-particle energies of the many-body system. The relationship between fermion spin and statistics derives from the canonical anticommutation rules for the second-quantized creation and destruction operators that act in the occupation-number space. Satisfying these anticommutation rules amounts to satisfying the Pauli exclusion principle.

The ideal Fermi gas can be characterized by intensive parameters such as pressure, temperature, and chemical potential. The zero temperature condition is interesting since it puts forth the consequence of the quantum nature of the constituents of the Fermi gas. At zero temperature, the single-particle energies are distributed up to a maximum called the Fermi level, which is the value then taken by the chemical potential (zeroth-order term of the Sommerfeld expansion). The Fermi level also defines a temperature below which the system is considered as degenerate, that is, when quantum effects become dominant. A consequence of the quantum nature of the Fermi particles is that even at zero temperature, there is a nonzero pressure whose origin is defined by the Pauli exclusion principle: the fermions cannot condense neither in momentum space nor in configuration space, which implies that maintaining a spatial separation between the fermions involves the necessary existence of a pressure.

Now let us briefly comment on the interacting Fermi system. An *adiabatic* switching on of the interparticle pair interaction that conserves spin, particle number, and momentum yields some changes to the ideal Fermi system. With the assumption that one particle with well-defined spin and momentum is added to the system, which just before the interaction is switched on is in its ground state, the particle becomes dressed[18] by the interaction with the other particles. The new state is that of an excited particle with the *same* spin and momentum, but characteristic of a different Hamiltonian since inclusion of a new particle modified

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[18] One of the most important changes in the particle properties is mass renormalization.

the particle number and energy. The elementary excitations of the interacting Fermi system are the so-called quasiparticles, which are characterized by their spin, effective mass, momentum, and magnetic moment. The new state induced by switching on the interaction may decay into other states; in other words, the quasiparticles have a finite lifetime. Because of the presence of a nonzero interaction between its constituents, the interacting Fermi system is often called a Fermi liquid in analogy with an ordinary classical liquid characterized by finite interactions and nonnegligible correlations between its constituents. Therefore, there cannot be a phase transition between a Fermi gas and a Fermi liquid since the words "gas" and "liquid" are not related here to actual phases of the Fermi system, but rather to the absence or presence of an interaction; in other words, there is no change in any intensive parameter of a Fermi system, which may switch on or switch off an interparticle interaction. Considering the free electron gas as a working fluid does not imply that operation of the heat engine constituted by a TE cell could be based on a liquid–gas phase transition.

1.5.2
Electron Gas in a Thermoelectric Cell

It is possible to obtain a schematic but useful description of how a TE cell operates by using an analogy with a closed volume that contains a working fluid, which here is an electron gas assumed to be ideal. The electron gas thus considered is a noninteracting system albeit elastic collisions ensure that the microscopic velocity distribution allows the definition of a temperature. The electrochemical potential of the electron system is the analogue of the partial pressure, p_{part}, and reads:

$$\mu_{\mathrm{e}} = \mu_{\mathrm{c}} + e\,\mathcal{V}, \tag{1.14}$$

where μ_{c} is the chemical potential, e is the electric charge, and $\mathcal{V}$ the electric potential. In the classical description, the gas is suitably characterized by a Maxwell–Boltzmann distribution, but this is not possible for the electron gas: electrons satisfy the Pauli exclusion principle, and hence, as an assembly of indistinguishable particles, they obey the Fermi–Dirac quantum statistics at equilibrium. In terms of intensive variables, the correspondence between the classical gas and the Fermi gas is:

$$\text{Classical gas: } p_{\mathrm{part}}, T \longleftrightarrow \text{Fermi gas: } \mu(r, T), T,$$

where r is the local position. Thanks to the aforementioned correspondence, one may define schematically a TE cell by considering a charged gas enclosed in a volume, see Figure 1.11. Each end of the volume is maintained at another temperature: T_{h} on the hot side and T_{c} on the cold side.

From the kinetic theory of gases, we infer that on the hot side, the system is characterized by a large average particle velocity and a low gas density; conversely, on the cold side, the density is high and the average velocity is low. There is a clear dissymmetry between the carrier populations at both ends of the cell; this dissymmetry is maintained owing to the presence of diffusion currents. As a result,

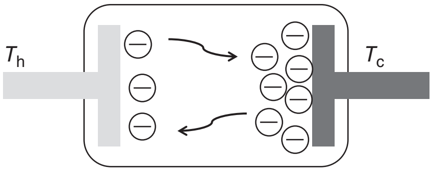

Figure 1.11 Schematic of a thermoelectric cell with a charged gas.

a difference in the electrochemical potentials $\Delta\mu_e$ is *directly* triggered by the temperature difference ΔT. One may then define the thermopower or Seebeck coefficient as the ratio $\alpha = -\frac{1}{e}\,{}^{\Delta\mu_e}/_{\Delta T}$, and it appears that the two intensive variables, temperature and electrochemical potential, are coupled.

The system thus described is not in thermodynamic equilibrium since a heat current goes through the gas; however, with the system being closed, the average matter current is zero on average, which means that the two convection currents, cold-to-hot side and hot-to-cold side, compensate each other. Note that heat transport is performed by conduction in the absence of an average particle transport, but also by convection. To simplify the present analysis, we neglect conduction through the walls of the volume. This approximation, rather common in the description of thermodynamic engines, neglects heat leaks through the walls. In TE systems, this leakage exists since the crystal lattice acts as a finite thermal resistance in parallel to the Fermi gas and, hence, deteriorates rather drastically the device ability to convert heat into work. This degradation is due to the phonons, which act as damped oscillators. However, note that there is a phonon-driven mechanism called phonon drag that contributes, though modestly, to the dissymmetry between the hot and cold populations, thus increasing the thermopower.

Here, we focus on the properties of the working fluid. From a thermodynamic point of view, the process includes two isothermal steps and two adiabatic steps. This idealized description puts forth the fact that the performance of the working fluid will be optimized if the particles interact neither with each other nor with the crystal lattice in order to ensure adiabaticity of two of the steps. Kinetic equations should not be introduced here. This would go beyond of the scope of this book.

1.5.3
Entropy Per Carrier

To characterize the behavior of the working fluid, we consider the entropy transported between the two ends of the cell. We consider that the closed volume behaves as two connected compartments with volumes V_1 and V_2, which, respectively, contain N_1 and N_2 particles. The total particle number is fixed: $N = N_1 + N_2$.

Now we assume that p number of particles (with $p \ll N$) move from one compartment to the other.

The total volume remains unchanged. The statistical entropy of the system is given by the accessible configurations defined as follows:

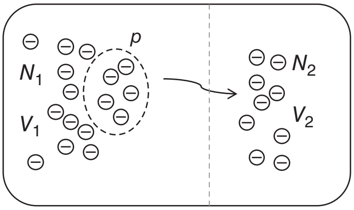

Figure 1.12 Schematic view of the basic entropy per carrier calculation.

- Ω denotes the number of configurations with N_1 particles in compartment 1 and N_2 particles in compartment 2, with probability $P(N_1) \propto \Omega$. Ω' denotes the configurations with $N_1' = N_1 - p$ particles in compartment 1 and $N_2' = N_2 + p$ particles in compartment 2, with probability $P(N_1') \propto \Omega'$.

The resulting variation of entropy reads:

$$dS = k_B \ln \frac{\Omega'}{\Omega} = k_B \ln \frac{P(N_1')}{P(N_1)}, \tag{1.15}$$

where k_B is the Boltzmann constant. The binomial law gives:

$$P(N_1) = \frac{N!}{N_1!N_2!} \left(\frac{V_1}{V}\right)^{N_1} \left(\frac{V_2}{V}\right)^{N_2} \tag{1.16}$$

so

$$dS = -k_B \ln \frac{N_1'!}{N_1!} + k_B \ln \frac{N_2'!}{N_2!} + k_B \ln \left(\frac{V_2}{V_1}\right)^p, \tag{1.17}$$

which, after using Stirling's approximation,[19] becomes

$$dS = -p\, k_B \ln \frac{n_2}{n_1}, \tag{1.18}$$

where n_1 and n_2 are the carrier densities in the respective volumes, that is, $n_1 = {}^{N_1}/_{V_1}$ and $n_2 = {}^{N_2}/_{V_2}$. Within the framework of statistical mechanics, the entropy per carrier, S_N, is defined by dividing the given expression by p:

$$S_N = -k_B \ln \frac{n_1}{n_2} \tag{1.19}$$

and, as a result, the free enthalpy becomes:

$$dG = -T\,dS = pk_B T[\ln(n_2) - \ln(n_1)] = p(\mu_2 - \mu_1), \tag{1.20}$$

an expression from which we obtain the chemical potential:

$$\mu_c(T) = k_B T \ln \frac{n(T)}{n_0}, \tag{1.21}$$

where n_0 is a constant that depends on the choice of the zero on the energy scale.

Several conclusions from the elementary model, see also Figure 1.12, may be drawn at this stage:

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[19] An approximation for factorials: $\ln(n!) \approx n \ln n - n + \mathcal{O}(n)$. It's named after James Stirling though it was first stated by Abraham de Moivre [316–318].

- The population dissymmetry becomes larger as the gas density decreases. As a consequence, an insulating material, which has very few free carriers, boasts a thermopower much higher than that of a metal, host of a dense gas.
- The adiabatic behavior corresponds to the free, that is, ballistic, transport of the carriers.
- The thermal conductivity of the gas has two contributions: one is the conduction that results from the microscopic energy transfer as particles collide in the gas; the other is the convection.
- The conduction does not contribute to the entropy transport and thus only acts as a thermal leak process, because it does not contribute to any motion of the carriers, in contrast with the convective contribution.
- The convection contributes to the transport of entropy, which must be maximal.
- The carrier mobility thus must be maximal.
- As a consequence, the electrical conductivity is optimal if the carrier mobility is maximal.
- The electrical conductivity may become maximal as the electron gas density increases, but in this case, the ability to transport entropy falls drastically.

1.5.4
Equation of State of the Ideal Electron Gas

Though they are similar at a first glance, the Fermi gas is different from the classical ideal gas because of the quantization of the energy levels that are accessible to the carriers: the electrons are distributed on the energy levels with the additional constraint that they have to fulfill the Pauli exclusion principle. The energy distribution at equilibrium is that of Fermi–Dirac, which ensures the allocation of electrons in the accessible energy states.

Let W_i be the number of ways to distribute N_i indistinguishable particles over S_i states of energy E_i. This number defined at equilibrium is constrained by the laws of conservation of energy and matter:

$$\sum_i N_i = N, \tag{1.22}$$

$$\sum_i E_i N_i = E_{\text{total}}. \tag{1.23}$$

As for all isolated systems in thermodynamic equilibrium, the carriers' distribution is that which yields a maximal entropy:

$$\mathrm{d}S = 0 = k_{\mathrm{B}}\,\mathrm{d}\ln W = k_{\mathrm{B}}\,\mathrm{d}\left(\sum_i \ln \frac{S_i!}{(S_i - N_i)!N_i!}\right) \tag{1.24}$$

with the constraints of conservation of matter and energy that read:

$$\sum_i \mathrm{d}N_i = 0, \tag{1.25}$$

$$\sum_i E_i\,\mathrm{d}N_i = 0. \tag{1.26}$$

The problem is then defined by the three equations (1.24)–(1.26). An elegant way to solve it is to build a unique expression from these. This can be done by the introduction of Lagrange multipliers. Then, both constraints are introduced in the expression of the entropy using the two multipliers β_1 and β_2:

$$\sum_i \left[\ln\left(\frac{S_i}{N_i} - 1\right) - \beta_1 - \beta_2 E_i \right] \mathrm{d}N_i = 0. \tag{1.27}$$

Note that dS is not modified since $\beta_1 \sum_i \mathrm{d}N_i = 0$ and $\beta_2 \sum_i E_i \mathrm{d}N_i = 0$. As a result, the following equality

$$\ln\left(\frac{S_i}{N_i} - 1\right) - \beta_1 - \beta_2 E_i = 0 \tag{1.28}$$

must be satisfied for all i.

From a thermodynamic point of view, the Lagrange multipliers act as two thermodynamic potentials of the system under consideration. As for all potentials, their equilibrium values are reached when entropy is maximal. In the present case, one of these multipliers is associated to the particle number, and the other to the energy:

$$\beta_1 = -\frac{\mu_\mathrm{c}}{k_\mathrm{B} T} \quad \text{and} \quad \beta_2 = \frac{1}{k_\mathrm{B} T}.$$

Specifically, this means that β_2 is linked to the temperature and $\beta_1 = -\mu_\mathrm{c}\beta_2$ is linked to the chemical potential. With these multipliers, the energy distribution function takes the following form:

$$f(E) = \left.\frac{N_i}{S_i}\right|_{E=E_i} = \frac{1}{1 + \exp\left[{}^{(E-\mu_\mathrm{c})}/_{(k_\mathrm{B}T)}\right]}, \tag{1.29}$$

which is naturally the Fermi–Dirac distribution applicable for fermions (electrons or holes). At low temperatures, the function $f(E)$ takes values close to 1 if $E < \mu_\mathrm{c}$ and close to 0 if $E > \mu_\mathrm{c}$. At zero temperature, the chemical potential is identically equal to the Fermi energy ϵ_F. At equilibrium, the chemical potential μ_c and the temperature T are constant, as the pressure and temperature are in a classical fluid.

If one deals with a two-component Fermi gas, the electrochemical potentials have to be distinguished as one would do for the partial pressures of a multicomponent classical fluid.[20] The number of free carriers is obtained by the integral of the product of the occupation probability $f(E)$ and the density of states $g(E)$. By choosing the bottom of the conduction band as the reference for the energy, it is found that for a nondegenerate gas,

$$n(T) = n_0 \exp\left[{}^{\mu_\mathrm{c}}/_{(k_\mathrm{B}T)}\right] \tag{1.30}$$

for the electrons, where $n_0 = 2(2\pi m_\mathrm{c}^\star k_\mathrm{B} T/h^2)^{3/2}$, with $m_\mathrm{c}^\star$ being the effective mass of the electrons in the material. In accordance with Gibbs' formula, the chemical potential of the free electron gas reads as defined in Eq. (1.21).

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[20] In the case of an electron/hole system, two chemical potentials, $\mu_{\mathrm{c,n}}$ and $\mu_{\mathrm{c,p}}$, may be defined.

In the case of silicon, the equation of state for the free electron gas can be written as

$$N = AT^{3/2} \exp\left[{}^{\mu_c}\!/\!_{(k_B T)}\right] \tag{1.31}$$

with

$$A = \frac{2.5 \times 10^{19}}{300^{3/2}} \left(\frac{m_c^\star}{m} \right)^{3/2} V, \tag{1.32}$$

where V is the volume of the gas.

1.5.5
Temperature Dependence of the Chemical Potential $\mu_c(T)$

As already implied within Eq. (1.21), the chemical potential is a function of the temperature. This dependence can already be rather complex in basic model systems. In an ideal Fermi gas, with Fermi energy defined as $\epsilon_F = \mu_c(T = 0)$, the temperature dependence of the chemical potential is approximately given by a Sommerfeld expansion of the energy to

$$\mu_c(T) = \epsilon_F \left[1 - \frac{\pi^2}{12} \left(\frac{k_B T}{\epsilon_F} \right)^2 - \mathcal{O}(T^4) \right]. \tag{1.33}$$

However, as shown in Figure 1.13, this approximation is already not valid for degenerate semiconductors at elevated temperatures and its failure is even more pronounced in the nondegenerate limit of charge carrier concentration. As a solution, the temperature-dependent chemical potential has to be obtained by an iterative solution of $n[\mu_c(T)]$ under the constraint of conserved number of additional carriers N [319, 320]. Precisely, it is

$$n = \frac{N}{\Omega} = \frac{1}{\Omega} \int_{\mu_c - \Delta E}^{\mathrm{VB}^{\max}} \mathrm{d}E\, g(E)[f(\mu_c, T) - 1] + \int_{\mathrm{CB}^{\min}}^{\mu_c + \Delta E} \mathrm{d}E\, g(E)\, f(\mu_c, T), \tag{1.34}$$

where n is the extrinsic or inherent charge carrier concentration and Ω is the unit cell volume. The density of states is given by $g(E)$. The Fermi–Dirac function $f(\mu_c, T)$ is defined as $f(\mu_c, T) = [\exp\left({}^{(\epsilon - \mu_c)}\!/\!_{(k_B T)} + 1\right)]^{-1}$. The limits of integration are given by valence and conduction band edge energies ($\mathrm{VB}^{\max}$ and $\mathrm{CB}^{\min}$, respectively) and the chemical potential μ_c itself. The parameter $\Delta E \geq 10\ k_B T$ has to be set sufficiently accurate to ensure convergence of the integrals even in the limit of low carrier concentrations. By changing the temperature T, the chemical potential $\mu_c(T)$ has to be adapted to fulfill the constraint $N(T) = N(T = 0\ \mathrm{K})$, that is, the total charge has to be conserved. By iterative solution, the exact temperature dependence of the chemical potential $\mu_c(T)$ is introduced, as depicted in Figure 1.13.

For cooler applications feasible, at low temperatures ($T \leq 100$ K) and low temperature differences ($\Delta T \leq 30$ K), the Sommerfeld approximation gives an accurate description of the temperature-dependent chemical potential and $\Delta\mu_c(\Delta T) \leq 5$ meV. However, this crude approximations fails for the TE generator

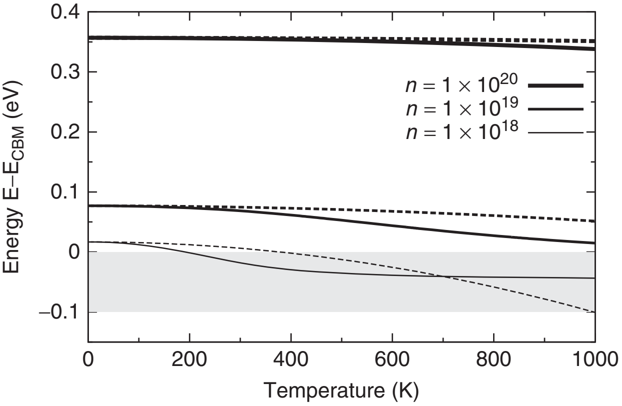

Figure 1.13 Dependence of the chemical potential on the applied temperature as calculated within a parabolic two-band semiconductor model without approximation [solid lines, using Eq. (1.34) and within the Sommerfeld approximation [dotted lines, using Eq. (1.33). The temperature-dependent chemical potential is calculated for three different charge carrier concentrations. An incomplete description within the Sommerfeld approximation can be clearly seen for charge carrier concentrations below 1×10^{20} cm^{-3}. For the sake of clarity, the effective masses of the conduction band edge and valence band edge are assumed to be identical ($m_{\mathrm{VB}}^{\max} = m_{\mathrm{CB}}^{\min} = m_{\mathrm{el}}$). The band gap (light gray shaded area) is chosen to be 100 meV.

case at higher temperatures ($T \geq 300$ K) and large temperature differences ($\Delta T \geq 100$ K). Here, the chemical potential varies in the order of 50 meV with a monotonic dependence on the temperature. Especially, the saturation of $\Delta\mu_{\mathrm{c}}(\Delta T)$ at higher temperatures due to bipolar carrier conduction cannot be described within a Sommerfeld approximation and demands for full analysis by using Eq. (1.34).

1.6
Linear Nonequilibrium Thermodynamics

Classical thermodynamics, which is useful for describing equilibrium states, provides very incomplete information on the actual physical phenomena, which are characterized by irreversibility and nonequilibrium states. Accounting for the rates of the physical processes, irreversible thermodynamics thus extends the equilibrium analyses and establishes links between the measurable quantities, while nonequilibrium statistical physics provides the tools to compute these.

1.6.1
Forces and Fluxes

Let us assume that at the macroscopic scale, the states of a thermodynamic system may be characterized by a set of extensive variables X_i. At equilibrium, these variables assume values that yield the maximum of the entropy $S \equiv S(\{X_i\})$. Now, we are interested in situations where the system has been put under nonequilibrium conditions and is allowed to relax. The response of a system upon which constraints are applied is the generation of fluxes, which correspond to transport phenomena. When the constraints are lifted, relaxation processes drive the system to an equilibrium state. Energy dissipation and entropy production are associated to transport and relaxation processes, which have characteristic times. As the dynamics of the variables X_i is typically much slower than that of the microscopic variables, one may define an *instantaneous entropy*, $S(\{X_i\})$, at each step of their slow relaxation. The differential of the function S is:

$$\mathrm{d}S = \sum_i \frac{\partial S}{\partial X_i} \mathrm{d}X_i = \sum_i F_i \mathrm{d}X_i, \tag{1.35}$$

where each quantity F_i is the intensive variable conjugate of the extensive variable X_i.

The notions of forces and fluxes are best introduced in the case of a discrete system: one may imagine, for instance, two separate homogeneous systems prepared at two different temperatures and placed in thermal contact through a thin diathermal wall, which implies that they are weakly coupled. The thermalization process triggers a flow of energy from one subsystem to the other, to which an extensive variable taking the values X_i and X_i' is associated, so that $X_i + X_i' = X_i^{(0)}$ = constant and $S(X_i) + S(X_i') = S(X_i^{(0)})$. The equilibrium condition maximizing the total entropy is given by:

$$\left.\frac{\partial S^{(0)}}{\partial X_i}\right|_{X_i^{(0)}} = \left.\frac{\partial (S + S')}{\partial X_i} \mathrm{d}X_i\right|_{X_i^{(0)}} = \frac{\partial S}{\partial X_i} - \frac{\partial S'}{\partial X_i'} = F_i - F_i' = 0, \tag{1.36}$$

which implies that if the difference $\mathcal{F}_i = F_i - F_i'$ is zero, the system is in equilibrium; otherwise, an irreversible process takes place and drives the system to equilibrium. The quantity $\mathcal{F}_i$ thus acts as a *generalized force* (or affinity) permitting the evolution of the system toward equilibrium.

The rate of variation of the extensive variable X_i characterizes the response of the system to the applied force:

$$J_i = \frac{\mathrm{d}X_i}{\mathrm{d}t} \tag{1.37}$$

so that a given flux cancels if its conjugate affinity cancels and, conversely, a finite affinity yields a finite conjugated flux. It thus appears that the relationship between affinities and fluxes characterizes the changes due to irreversible processes.

1.6.2
Linear Response and Reciprocal Relations

Consider a continuous medium in local equilibrium, where at a given point in space and time $(\boldsymbol{r}, t)$, the flux J_i is mathematically defined as dependent on the force $\mathcal{F}_i$, but also on the other forces $\mathcal{F}_{j\neq i}$:

$$J_i(\boldsymbol{r}, t) \equiv J_i(\mathcal{F}_1, \mathcal{F}_2, \cdots). \tag{1.38}$$

The given definition implies that the nonequilibrium dynamics is governed by direct effects: each flux depends on its conjugate affinity, but *also* by indirect effects: each flux depends on the other affinities as well. Not far from equilibrium, $J_i(\boldsymbol{r}, t)$ can be obtained by a Taylor expansion:

$$\begin{aligned} J_k(\boldsymbol{r}, t) &= \sum_j \frac{\partial J_k}{\partial \mathcal{F}_j} \mathcal{F}_j + \frac{1}{2!} \sum_{i,j} \frac{\partial^2 J_k}{\partial \mathcal{F}_i \mathcal{F}_j} \mathcal{F}_i \mathcal{F}_j + \cdots \\ &= \sum_j L_{jk} \mathcal{F}_+ \frac{1}{2} \sum_{i,j} L_{ijk} \mathcal{F}_i \mathcal{F}_j + \cdots, \end{aligned} \tag{1.39}$$

where the quantities $L_{jk} \equiv \partial J_k / \partial \mathcal{F}_j$ are the elements of the matrix $[\mathcal{L}]$ of the *first-order* kinetic coefficients; they are obtained by the equilibrium values of the intensive variables F_i. The matrix $[\mathcal{L}]$ thus characterizes the *linear response* of the system.

In the linear regime, the source of entropy reads:

$$\sigma_S = \sum_{i,k} L_{ik} \mathcal{F}_i \mathcal{F}_k. \tag{1.40}$$

Since $\sigma_S \geq 0$, the kinetic coefficients satisfy

$$L_{ii} \geq 0 \quad \text{and} \quad L_{ii} L_{kk} \geq \frac{1}{4}(L_{ik} + L_{ki}). \tag{1.41}$$

In 1931, Onsager put forward the idea that there exist symmetry and antisymmetry relations between kinetic coefficients [256, 257]: the so-called *reciprocal relations*, $L_{ik} = L_{ki}$, must exist in all thermodynamic systems for which transport and relaxation phenomena are well described by linear laws. Note that Onsager's results have been generalized to account for situations where a magnetic field and/or a Coriolis field may play a rôle; in this case, one must check whether the studied quantity is invariant under time reversal transformation or not [321].

1.7
Forces and Fluxes in Thermoelectric Systems

1.7.1
Thermoelectric Effects

A naive definition would state that thermoelectricity results from the coupling of Ohm's law and Fourier's law. The TE effect in a system may rather be viewed as the result of the mutual interference of two irreversible processes occurring simultaneously in this system, namely heat transport and charge carrier transport. In thermoelectricity, three effects are usually described:

1) The Seebeck effect, which is the rise of an electromotive force in a thermocouple, that is, across a dipole composed of two conductors forming two junctions maintained at different temperatures, under zero electric current.

2) The Peltier effect, which is a thermal effect (absorption or production of heat) at the junction of two conductors maintained at the same temperature with a current flowing.
3) The Thomson effect, which is a thermal effect due to the existence of a temperature gradient along the material. The effect only exists if the Seebeck coefficient is a function of the temperature.

It is important to realize here that these three “effects” all boil down to the same process: At the microscopic level, an applied temperature gradient causes the charges to diffuse,[21] so the Seebeck, Peltier, and Thomson effects are essentially the same phenomenon, that is, thermoelectricity, which manifests itself differently as the conditions for its observation vary. Broadly speaking, when a temperature difference is imposed across a TE device, it generates a voltage, and when a voltage is imposed across a TE device, it generates a temperature difference. The TE devices can be used to generate electricity, measure temperature, cool or heat objects. For a thermocouple composed of two different materials A and B, the voltage is given by:

$$\mathcal{V}_{\mathrm{AB}} = \int_{T_{\mathrm{c}}}^{T_{\mathrm{h}}} (\alpha_{\mathrm{B}} - \alpha_{\mathrm{A}})\,\mathrm{d}T, \tag{1.42}$$

where the parameters $\alpha_{\mathrm{A/B}}$ are the Seebeck coefficients or thermopowers.

1.7.2
Forces, Fluxes, and Kinetic Coefficients

The main assumption of Onsager's work is based on the hypothesis that the system evolution is driven by a minimal production of entropy where each fluctuation of any intensive variable undergoes a restoring force to equilibrium [322]. Though the system itself produces dissipation, one may use well-defined thermodynamic potentials at each time step for the analysis of the quasistatic processes, bringing the system back to equilibrium, so that the classical quasistatic relation between heat and entropy variation $\mathrm{d}S = \delta Q_{\mathrm{qs}}/T$ may be extended to finite time response thermodynamics in the following flux form:

$$\mathbf{j}_S = \frac{\mathbf{j}_Q}{T}. \tag{1.43}$$

The Onsager force–flux derivation is obtained from the laws of conservation of energy and matter. If we consider the complete energy flux, then the first principle of thermodynamics gives the expression of the total energy flux $\mathbf{j}_E$, heat flux $\mathbf{j}_Q$, and particles flux $\mathbf{j}_N$,

$$\mathbf{j}_E = \mathbf{j}_Q + \mu_{\mathrm{e}}\mathbf{j}_N. \tag{1.44}$$

These fluxes are conjugated to their thermodynamic potential gradients, which, as general forces, derive from the thermodynamic potentials. The question of

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[21] One may see an analogy with a classical gas expansion.

the correct expression of these potentials is out of the scope of this chapter, but it can be shown that the correct potentials for energy and particles are $^1/_T$ and $^{\mu_e}/_T$, respectively, see [321]. The corresponding forces can be expressed as their gradients

$$\mathbf{F}_N = \nabla\left(-\frac{\mu_e}{T}\right), \quad \mathbf{F}_E = \nabla\left(\frac{1}{T}\right), \tag{1.45}$$

and the linear coupling between forces and fluxes can simply be derived by a linear set of coupled equations with kinetic coefficient matrix $[L]$,

$$\begin{bmatrix}\mathbf{j}_N \\ \mathbf{j}_E\end{bmatrix} = \begin{bmatrix}L_{NN} & L_{NE} \\ L_{EN} & L_{EE}\end{bmatrix}\begin{bmatrix}\nabla\left(-\frac{\mu_e}{T}\right) \\ \nabla\left(\frac{1}{T}\right)\end{bmatrix},$$

where $L_{NE} = L_{EN}$. The symmetry of the off-diagonal term is fundamental in the Onsager description since it is equivalent to a minimal entropy production of the system under nonequilibrium conditions [322]. A first experimental verification of the Onsager reciprocal relations had been given by Miller for different materials [270]. As we already pointed out, the minimal entropy production is not a general property of nonequilibrium processes. However, under steady-state conditions, a fluctuating thermodynamic potential will undergo a restoring force due to the presence of another potential. This mechanism has to be symmetric, and so do the off-diagonal terms of the kinetic matrix.[22] From a microscopic point of view, this equality also implies the time reversal symmetry of the processes.[23] By extension, processes at microscopic scale should be "microreversible." Since the irreversibility is a statistical consequence of the number of particles inside the considered system, then, at a microscopic scale, "irreversible thermodynamics" simply becomes a "reversible dynamics."

1.7.3
Energy Flux and Heat Flux

In order to treat properly heat and carrier fluxes, it is more convenient to rewrite the second equation of the given matrix formulation for $\mathbf{j}_Q = \mathbf{j}_E - \mu_e \mathbf{j}_N$. By doing this, it is advantageous to change slightly the first force in order to let μ_e appear explicitly and not only $\nabla(-^{\mu_e}/_T)$. By using the development

$$\nabla\left(-\frac{\mu_e}{T}\right) = -\frac{1}{T} \quad \nabla\mu_e - \mu_e\nabla\left(\frac{1}{T}\right),$$

a straightforward calculation gives

$$\begin{bmatrix}\mathbf{j}_N \\ \mathbf{j}_Q\end{bmatrix} = \begin{bmatrix}L_{11} & L_{12} \\ L_{21} & L_{22}\end{bmatrix}\begin{bmatrix}-\frac{1}{T}\nabla\mu_e \\ \nabla\left(\frac{1}{T}\right)\end{bmatrix} \tag{1.46}$$

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[22] The off-diagonal terms of the kinetic matrix are symmetric, only if the correct thermodynamic potentials of the system have been chosen. In the case of a Fermi gas, the correct potentials are $^{\mu_e}/_T$ and $^1/_T$.

[23] This time reversal symmetry is broken under the application of Coriolis or magnetic force.

with $L_{12} = L_{21}$ and the kinetic coefficients become

$$L_{11} = L_{NN}, \ \ L_{12} = L_{NE} - \mu_{\mathrm{e}} L_{NN}, \ \ L_{22} = L_{EE} - \mu_{\mathrm{ee}}(L_{EN} + L_{NE}) + {\mu_{\mathrm{e}}}^2 L_{NN}.$$

By derogation from electronic systems, which are described based on a charge density distribution, the electric field derives from the electrochemical potential μ_{e}

$$\mathbf{E} = -\frac{\nabla \mu_{\mathrm{e}}}{e} = -\frac{\nabla \mu_{\mathrm{c}}}{e} - \nabla \mathcal{V}, \tag{1.47}$$

where $\mathcal{V}$ is the electrical potential.

1.7.4
Thermoelectric Coefficients

Depending on the thermodynamic working conditions, the TE coefficients can be derived from the two expressions of particle and heat flux density.

1.7.4.1 Decoupled Processes

By using expression (1.46) under isothermal conditions, we get the electrical current density in the form

$$\mathbf{j} = \frac{-eL_{11}}{T} \nabla \mu_{\mathrm{e}}, \tag{1.48}$$

where $\mathbf{j} = e\mathbf{j}_N$. This is an expression of Ohm's law, then the isothermal electrical conductivity is

$$\sigma_T = \frac{e^2}{T} L_{11}. \tag{1.49}$$

Alternatively, if we consider the heat flux density in the absence of any particle transport, or under zero electric current, then we now get

$$\mathbf{j} = \mathbf{0} = -L_{11}\left(\frac{\nabla \mu_{\mathrm{e}}}{T}\right) + L_{12} \nabla \left(\frac{1}{T}\right), \tag{1.50}$$

and the heat flux density becomes

$$\mathbf{j}_{Q_J} = \frac{1}{T^2}\left(\frac{L_{21}L_{12} - L_{11}L_{22}}{L_{11}}\right) \nabla T, \tag{1.51}$$

which is the Fourier law, where the thermal conductivity under zero electric current (open circuit) is

$$\kappa_J = \frac{1}{T^2}\left(\frac{L_{11}L_{22} - L_{21}L_{12}}{L_{11}}\right). \tag{1.52}$$

Finally, we can also consider the thermal conductivity under zero electrochemical gradient (closed circuit), then we get

$$\mathbf{j}_{Q_E} = \frac{L_{22}}{T^2} \nabla T \quad \text{with} \quad \kappa_E = \frac{L_{22}}{T^2}. \tag{1.53}$$

1.7.4.2 Coupled Processes

Let us now consider the TE coupling in more detail. In the absence of any particle transport, the basic expression is already known since it is given by Eq. (1.50). We now define the Seebeck coefficient as the ratio between the two forces, electrochemical gradient and temperature gradient, then the Seebeck coefficient expression is given by

$$-\frac{1}{e}\,\nabla\mu_{\mathrm{e}} \equiv \alpha\nabla T = \mathbf{E}_{|j=0} \tag{1.54}$$

for the electric field relation. By using Eq. (1.50), we finally find for Seebeck

$$\alpha = \frac{1}{eT}\frac{L_{12}}{L_{11}}. \tag{1.55}$$

If we consider now an isothermal configuration, we can derive the expression of the coupling term between current density and heat flux, which is nothing more than the Peltier coefficient

$$\mathbf{j} = eL_{11}\left(-\frac{1}{T}\nabla\mu_{\mathrm{e}}\right), \quad \mathbf{j}_Q = L_{21}\left(-\frac{1}{T}\nabla\mu_{\mathrm{e}}\right), \tag{1.56}$$

we get

$$\mathbf{j}_Q = \frac{1}{e}\frac{L_{12}}{L_{11}}\,\mathbf{j}, \tag{1.57}$$

and the Peltier coefficient Π is given by

$$\mathbf{j}_Q = \Pi\,\mathbf{j}, \quad \Pi = \frac{1}{e}\frac{L_{12}}{L_{11}}. \tag{1.58}$$

As one can see, we have the equality

$$\Pi = \alpha T.$$

The close connection between Peltier and Seebeck effects is illustrated by this compact expression. In a later section, we show that a similar connection can be derived for the Thomson effect. From a fundamental point of view, this shows that all of these effects are in fact different expressions of the same quantity, called the “entropy per carrier,” defined by Callen [323, 324]. It will be considered first, followed by the definitions of the transport parameters.

1.7.5
The Entropy Per Carrier

By using a classical approach of thermodynamic cycle, we can consider a carrier traveling through the different step of the Carnot cycle. With focus on the two adiabatic branches of the thermodynamic cycle, it appears that a certain amount of entropy is driven from the hot reservoir to the cold one, but also from the cold reservoir to the hot side. In this convective process, the carrier acts as if it was carrying some entropy. Let us derive this by considering the entropy flux density. From the heat flux density expression, we can write

$$\mathbf{j}_S = \frac{1}{T}\left[L_{21}\left(-\frac{1}{T}\nabla\mu_e\right) + L_{22}\nabla\left(\frac{1}{T}\right)\right]. \tag{1.59}$$

According to Ohm's law, see Eq. (1.48), it can be simplified into

$$\mathbf{j}_S = \frac{L_{21}}{TeL_{11}}\,\mathbf{j} + \frac{1}{T}L_{22}\nabla\left(\frac{1}{T}\right). \tag{1.60}$$

We see here that the entropy flux contains two terms, one with an electrochemical origin and the other with a thermal origin. The first term shows that a fraction of the entropy is transported by the flux of carriers. Then the entropy transported per carrier (or per particle) is given by

$$S_N = \frac{L_{21}}{TL_{11}}. \tag{1.61}$$

We remark that the Seebeck coefficient is directly proportional to S_N since we have

$$S_N = e\alpha. \tag{1.62}$$

It is important to note that the entropy per particle is a fundamental parameter from which all the TE effects derive. Nevertheless, the reader should take care not to attribute a specific entropy to each carrier. Since thermodynamics never considers isolated particle but only a large number of particles, the definition of the entropy per particle refers to an averaged property of the fermion gas, as a statistical definition. This is also valid for the $S_N = e\alpha$ expression where the Seebeck effect cannot be reduced to the direct summation of the individual contribution of the carriers. As an illustration, one can see that S_N is a function of the electrical conductivity through the term L_{11} and the conductive models, similarly to the Drude model [325–327], cannot be derived at the scale of a carrier, with the attribution of a specific electrical conductivity to each carrier.

1.7.6
Kinetic Coefficients and Transport Parameters

By using the entropy per carrier S_N defined in Eq. (1.62), we can obtain now a complete correspondence between the kinetic coefficient and the transport parameters. We have

L_{11}	$L_{12} = L_{21}$	L_{22}
$\frac{T}{e^2}\sigma_T$	$\frac{T^2}{e^2}\sigma_T S_N$	$\frac{T^3}{e^2}\sigma_T S_N^2 + T^2\kappa_J$

and the Onsager expressions become

$$\mathbf{j} = -\sigma_T\left(\frac{\nabla\mu_\mathrm{e}}{e}\right) + \frac{\sigma_T S_N T^2}{e^2}\,\nabla\left(\frac{1}{T}\right), \tag{1.63}$$

$$\mathbf{j}_Q = -T\sigma_T S_N\left(\frac{\nabla\mu_\mathrm{e}}{e}\right) + \left(\frac{T^3}{e^2}\sigma_T S_N^2 + T^2\kappa_J\right)\nabla\left(\frac{1}{T}\right). \tag{1.64}$$

Finally, we distinguish between the thermal conductivity under zero electrochemical gradient and under zero particle transport,

$$\kappa_E = \frac{L_{22}}{T^2}, \quad \kappa_J = \frac{1}{T^2}\left(\frac{L_{11}L_{22} - L_{21}L_{12}}{L_{11}}\right), \tag{1.65}$$

leading to the equality

$$\kappa_E = T\alpha^2\sigma_T + \kappa_J. \tag{1.66}$$

It should be mentioned here that the present description only considers the electronic gas contribution to the thermal conductivity. An additional contribution κ_{lat} arises from the lattice.

By inserting Eq. (1.63) into Eq. (1.64) and using $\mathbf{E} = -{}^{\nabla\mu_e}/_e$ and the local expansion $\nabla({}^1/_T) = -{}^1/_{T^2}\nabla T$, the "classical" constitutive relations

$$\mathbf{j} = \sigma_T\mathbf{E} - \sigma_T\ \alpha\nabla T \qquad \text{and} \qquad \mathbf{j}_Q = \alpha T\mathbf{j} - \kappa_J\nabla T \tag{1.67}$$

are reproduced, see also [328]. Then, it follows that $\mathbf{E} = \alpha\nabla T + \varrho\ \mathbf{j}$ with electrical resistivity $\varrho = {}^1/_{\sigma_T}$.

1.7.7
The Dimensionless Figure of Merit *zT*

We have seen from the kinetic matrix $[L]$ that the off-diagonal terms represent the coupling between the heat and the electrical fluxes. The question is now to consider the way to optimize a given material in order to get an efficient heat pump driven by an input electric current or an efficient TE generator driven by the heat flow supplied. The procedure can be derived for both applications, but we propose here to consider a thermogenerator application.

Let us first look at the optimization of the fluxes. Since a TE material is an energy conversion device, the more heat flows into the material, the more electrical power may be produced. In order to achieve this, we expect a large thermal conductivity for the material. Unfortunately, this will also lead to a very small temperature difference and, consequently, small electrical output voltage and power. This configuration can be called the short-circuit configuration since the fluxes are maximized and the potential differences are minimized.

Now we consider the coupled processes from a potential point of view. In order to obtain a larger voltage, the material should exhibit a large temperature difference. Then the thermal conductivity of the material should be as small as possible, leading to a very small heat flux and, consequently, again, a small electrical power output. This configuration can be called the open-circuit configuration since the potential differences are maximized and the fluxes are minimized.

It is worth noticing that both short-circuit and open-circuit configurations lead to a nonsatisfactory solution. Moreover, they are in contradiction since the thermal conductivity is expected to be maximal in the short-circuit configuration and minimal in the open-circuit one! This contradiction can be resolved if we consider the expression of the thermal conductivities previously given by Eq. (1.66), that is,

$\kappa_E = T\alpha^2\sigma_T + \kappa_J$. Since it is established under zero current, the κ_J corresponds to the open-circuit configuration while κ_E corresponds to the short-circuit configuration. From the previous developments, see Eq. (1.66), we expect $\frac{\kappa_E}{\kappa_J}$ to be maximal in order to obtain the maximal output electrical power. Then we can write

$$\frac{\kappa_E}{\kappa_J} = 1 + zT \tag{1.68}$$

with the figure of merit zT defined by

$$zT = \frac{\alpha^2\sigma_T}{\kappa_J} T. \tag{1.69}$$

This relation was also found by Zener, see [50].

As one can notice from Eq. (1.68), the zT term should be maximal in order to obtain an optimal material. The TE properties of the material are summarized in the zT expression, firstly proposed by Ioffe [36]. zT enables a direct measurement of the quality of the material for practical applications, and the figure of merit is clearly the central term for material engineering research.

At first glance, the presence of the temperature in the expression of the figure of merit may be strange since T is not a material property, but an intensive parameter, which partly defines the working conditions. Nevertheless, one should notice that, in terms of thermodynamic optimization, the material properties are negligible without considering the available exergy of the working system. This is achieved by introducing the temperature in the expression of the figure of merit, which provides a reference to the exergy evaluation.

1.8
Heat and Entropy

Let us consider the coupled Onsager expressions:

$$\mathbf{j} = -\sigma_T \left(\frac{\nabla\mu_{\mathrm{e}}}{e}\right) + \frac{\sigma_T S_N T^2}{e^2}\,\nabla\left(\frac{1}{T}\right), \tag{1.70}$$

$$\mathbf{j}_Q = -T\sigma_T S_N \left(\frac{\nabla\mu_{\mathrm{e}}}{e}\right) + \left[\frac{T^3}{e^2}\sigma_T S_N^2 + T^2\kappa_J\right]\,\nabla\left(\frac{1}{T}\right). \tag{1.71}$$

We can combine both equations to get

$$\mathbf{j}_Q = T\,S_N\mathbf{j} + T^2\kappa_J\,\nabla\left(\frac{1}{T}\right), \tag{1.72}$$

where we identify a conductive term, proportional to $\nabla\left(\frac{1}{T}\right)$, and a “Peltier” term, proportional to $\mathbf{j}$:

$$q_\kappa = T^2\kappa_J\nabla\left(\frac{1}{T}\right) = -\kappa_J\nabla T, \tag{1.73}$$

$$q_\pi = T\frac{S_N}{e}\,\mathbf{j}. \tag{1.74}$$

This Peltier heat transported because of the TE effects results in the effect commonly attributed to Peltier: the heat observed at an inhomogeneous junction due to the TE effects.

1.8.1
Volumetric Heat Production

The volumetric heat production can be estimated from the total energy flux

$$\mathbf{j}_E = \mathbf{j}_Q + \frac{\mu_\mathrm{e}}{e}\,\mathbf{j}.$$

According to energy and particle conservation, we have, under steady state,

$$\nabla \cdot \mathbf{j}_E = 0 \quad \text{and} \quad \nabla \cdot \mathbf{j} = 0. \tag{1.75}$$

Then,

$$\nabla \cdot \mathbf{j}_Q = -\frac{\nabla \mu_\mathrm{e}}{e} \cdot \mathbf{j}.$$

Since the electrical field is $\mathbf{E} = -\frac{\nabla \mu_\mathrm{e}}{e}$, we find

$$\nabla \cdot \mathbf{j}_Q = \mathbf{E} \cdot \mathbf{j}. \tag{1.76}$$

This summarizes the possible transformation of the energy since it shows that heat can be produced by the degradation of the electrochemical potential μ_e and that electrical power can also be extracted from heat.

1.8.2
Entropy Production Density

If we consider the entropy flux density, we can calculate the entropy production ν_S from

$$\nu_S = \nabla \cdot \mathbf{j}_S = \nabla \left(\frac{\mathbf{j}_Q}{T}\right) = \nabla \left(\frac{1}{T}\right) \cdot \mathbf{j}_Q + \frac{1}{T}\,\nabla \cdot \mathbf{j}_Q$$

to get

$$\nu_S = \nabla \left(\frac{1}{T}\right) \cdot \mathbf{j}_Q - \frac{\nabla \mu}{eT} \cdot \mathbf{j}. \tag{1.77}$$

As shown earlier, the entropy production is due to nonisothermal heat transfer and electrical Joule production. The previous expression can be rewritten in the form

$$\nu_S = \nabla \left(\frac{1}{T}\right) \cdot \mathbf{j}_E + \nabla \left(-\frac{\mu_\mathrm{e}}{T}\right) \cdot \mathbf{j}_N. \tag{1.78}$$

In this form, we obtain the illustration of one major result of the Onsager description: The total entropy production is given by the summation of the force–flux products,

$$\nu_S = \nabla \cdot \mathbf{j}_S = \Sigma\, \overrightarrow{\text{force}} \cdot \overrightarrow{\text{flux}}. \tag{1.79}$$

This is a very general result of the Onsager theory. When deriving the entropy production according to Onsager kinetic expressions, the constraint of minimal entropy production leads to a final expression where the overall entropy production is directly given by the sum of the products of forces and fluxes.

1.8.3
Heat Flux and the Peltier–Thomson Coefficient

In the previous sections, we considered the volumetric heat transformation from the calculation of the divergence of the heat flux $\nabla \cdot \mathbf{j}_Q$. We now propose to analyze its different terms. First, by elimination of the electric field $\mathbf{E}$ from the previous set of equations, we get

$$\mathbf{j}_Q = \alpha T \mathbf{j} - \kappa_J \nabla T, \tag{1.80}$$

and the divergence of the heat flux becomes

$$\begin{aligned}\nabla \cdot \mathbf{j}_Q &= \nabla \cdot (\alpha T \mathbf{j} - \kappa_J \nabla T) \\ &= T\mathbf{j} \cdot \nabla\alpha + \alpha\ \nabla T \cdot \mathbf{j} + \alpha T\ \nabla \cdot \mathbf{j} + \nabla \cdot (-\kappa_J \nabla T),\end{aligned} \tag{1.81}$$

where we find four terms, which can be identified:

- $\alpha T \nabla \cdot \mathbf{j}$: equals zero due to particle conservation,
- $T\mathbf{j} \cdot \nabla\alpha$: "Peltier–Thomson" term,
- $\mathbf{j} \cdot \alpha \nabla T = \mathbf{j} \cdot (\mathbf{E} - \mathbf{j}/\sigma_T) = \mathbf{j} \cdot \mathbf{E} - j^2/\sigma_T$: electrical work production and dissipation,
- $\nabla \cdot (-\kappa_J \nabla T)$: change in thermal conduction due to heat produced or absorbed.

To sum up, the sources of the heat flux are

$$\nabla \cdot \mathbf{j}_Q = T\ \mathbf{j} \cdot \nabla\alpha + \mathbf{j} \cdot \mathbf{E} - \frac{j^2}{\sigma_T} - \nabla \cdot (\kappa_J \nabla T). \tag{1.82}$$

Most of these terms are common, but less intuitive is the Peltier–Thomson term, which is now considered.

1.8.4
The Peltier–Thomson Term

Now we show that the $T\mathbf{j} \cdot \nabla\alpha$ term contains both the Thomson contribution (local temperature gradient effect) and the Peltier contribution (isothermal spatial gradient effect). By using the equivalence $\Pi = \alpha T$, we obtain

$$T\mathbf{j} \cdot \nabla\alpha = T\mathbf{j} \cdot \nabla\left(\frac{\Pi}{T}\right) = T\mathbf{j} \cdot \left(\frac{1}{T}\nabla\Pi - \frac{1}{T^2}\Pi\nabla T\right) = \mathbf{j} \cdot (\nabla\Pi - \alpha\nabla T). \tag{1.83}$$

Then, the traditional separation of the Peltier and Thomson contribution is artificial since they both refer to the same physics of the gradient of the entropy per particle, temperature-driven gradient or spatially driven gradient. The isothermal configuration leads to the Peltier expression, meanwhile a spatial gradient leads to the Thomson result.

- Pure Peltier, isothermal junction between two materials:

$$\mathbf{j} \cdot (\nabla \Pi - \alpha \nabla T) = \mathbf{j} \cdot (\nabla \Pi),$$

- Thomson, homogeneous material under temperature gradient:

$$\mathbf{j} \cdot (\nabla \Pi - \alpha \nabla T) = \mathbf{j} \cdot \left(\frac{\mathrm{d}\Pi}{\mathrm{d}T} - \alpha \right) \nabla T = \tau \mathbf{j} \cdot \nabla T, \tag{1.84}$$

  with

$$\nabla \Pi = \frac{\mathrm{d}\Pi}{\mathrm{d}T} \nabla T \qquad \text{and} \qquad \tau = \frac{\mathrm{d}\Pi}{\mathrm{d}T} - \alpha, \tag{1.85}$$

and the heat flux divergence takes the form

$$\nabla \cdot \mathbf{j}_Q = \tau \mathbf{j} \cdot \nabla T + \mathbf{j} \cdot \mathbf{E} - \frac{j^2}{\sigma_T} - \nabla \cdot (\kappa_J \nabla T). \tag{1.86}$$

If we consider a configuration where $\kappa_J \neq f(T)$, then Eq. (1.86) reduces to

$$\nabla \cdot \mathbf{j}_Q = \tau \mathbf{j} \cdot \nabla T + \mathbf{j} \cdot \mathbf{E} - \frac{j^2}{\sigma_T} - \kappa_J \nabla^2 T. \tag{1.87}$$

As one can notice, the Peltier and Thomson terms both refer to the gradient $\nabla\alpha$. It is worth noticing that the isothermal configuration for the Peltier expression and the temperature gradient configuration for the Thomson effect correspond to specific chosen conditions. With another set of conditions, one can obtain other definitions. For example, Peltier heat can be considered to be absorbed or released inside the active material due to the position-dependent Seebeck coefficient. It is then referred to as *"distributed Peltier effect"* or *"extrinsic Thomson effect"* [329–331].

1.8.5
Local Energy Balance

By using the expression $\nabla \cdot \mathbf{j}_Q = \mathbf{E} \cdot \mathbf{j}$, see Eq. (1.76), the local energy balance can be expressed from Eq. (1.87) [332]:

$$\nabla \cdot \mathbf{j}_Q - \mathbf{E} \cdot \mathbf{j} = \kappa_J \, \nabla^2 T + \frac{j^2}{\sigma_T} - \tau \mathbf{j} \cdot \nabla T = 0. \tag{1.88}$$

It should be noticed that this derivation does not need any assumption concerning the behavior of the system, whether in equilibrium or not. In the case of transient configuration, the energy balance equation should be corrected using $\varrho_{\mathrm{md}} \, C_\mu$, where C_μ is the heat capacity (thermal mass, thermal capacity) and ϱ_{md} is the mass density:

$$\begin{gathered} \varrho_{\mathrm{md}} \, C_\mu \, \frac{\partial T}{\partial t} + \nabla \cdot \mathbf{j}_Q = \mathbf{E} \cdot \mathbf{j} \longrightarrow \\ \kappa_J \nabla^2 T + \frac{j^2}{\sigma_T} - \tau \mathbf{j} \cdot \nabla T - T \, \mathbf{j} \cdot (\nabla \alpha)_T = \varrho_{\mathrm{md}} \, C_\mu \, \frac{\partial T}{\partial t}. \end{gathered} \tag{1.89}$$

In this form, the local energy balance has the general form of a continuity equation [54]. Besides the classical terms of heat equation due to Fourier heat transfer, see [333], there are contributions due to Joule's heat, Thomson heat, and distributed Peltier heat, which lead to a general form of heat equation in the framework of thermoelectricity.

One-dimensional models are often used, see, for example, [15, 334, 335]. Even in one dimension, the addition of time dependence can induce additional effects. For example, the spatial separation of Peltier cooling from Joule heating enables additional transient cooling when a cooler is pulsed [336, 337], see also Section 4.2. The reader may find some more information and insights about transient effects in thermoelectricity in Refs [46, 308, 309, 338–349] and in Chapter 4 of this book.

1.9
The Thermoelectric Engine and Its Applications

In a first approach, as usually carried out for traditional steam engines, only the fluid is considered and the walls of the enclosure containing this fluid are not taken into account. These contributions of the walls to the global efficiency are not considered, neither the boiling walls of the steam engine nor the lattice vibrations (phonons) of the TE material. Then we have a similar picture of the two systems, not only for the fluid (steam or electronic gas) but also for the thermal leak (boiling walls or lattice vibrations) as symbolically shown in Figure 1.16.

For every thermodynamic engine, the TE can work as a generator or a consumer. As a thermoelectric generator (TEG), the engine is driven by the entering heat flux and converts a fraction of it into electrical power through an electric current. As a receptor, the engine is driven by an electric current and acts as a pump for the heat flux. Two modes can be distinguished when operated as a consumer, a thermoelectric pump for heating or cooling. Heating and cooling modes are defined with a unique description. The difference comes from the useful part of the system that should be cooled or heated. In the cooling mode, we refer to a thermoelectric cooler (TEC), and in the heating mode, we refer to thermoelectric heater (TEH) (Figure 1.14).

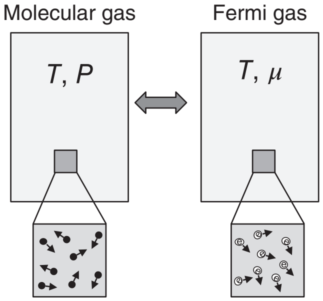

Figure 1.14 Comparison between steam and thermoelectric engine.

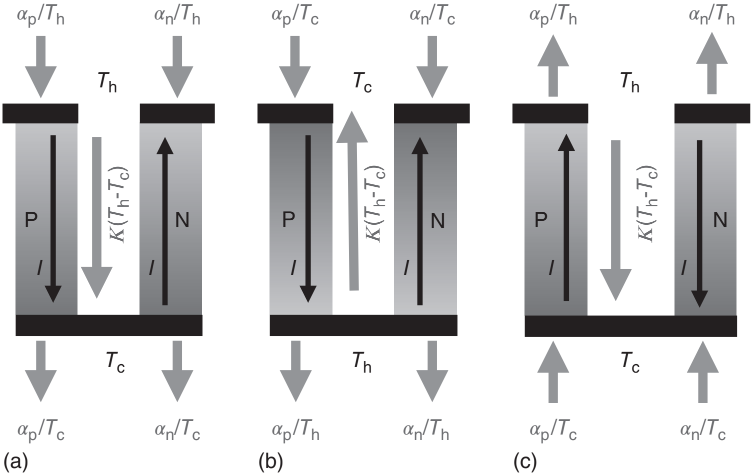

Figure 1.15 Thermoelectric applications: (a) thermogenerator (TEG), (b) TE cooler (TEC), (c) TE heater (TEH), see Figure 1.18 for details.

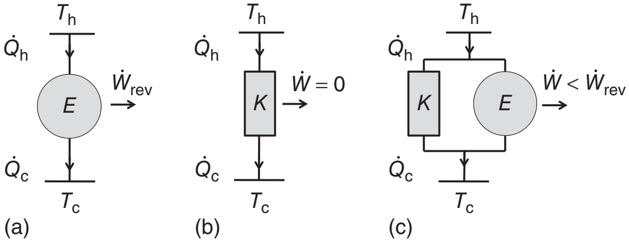

Figure 1.16 Thermodynamic system: (a), reversible; (b) fully dissipative, (c) reversible in parallel with a pure leakage. The latter case obtains a correct model of the thermodynamic fluid and its convective contribution (*E*), and the leakages, lattice and conductive contribution of the fluid (*K*).

Since heat flux and electric current are coupled, it is not possible to separate these three modes strictly, and, in fact, a thermogenerator also acts as a heat pump. On the other hand, a TEC can be understood as a TEG working with an electric current larger than its short-circuit current. All three configurations are summarized in Figure 1.15, where the thermal processes are shown in gray and the electrical processes in black.

As we observe, and regardless of the working mode, the efficiency of the engine is reduced by the presence of a heat leak. As a consequence, materials with very low lattice thermal conductivity are highly required for TE applications.

Let us consider now a sample of TE material where one end is maintained at temperature T_h and the other at temperature T_c with $T_h > T_c$. If we consider the Fermi gas inside the sample, then we achieve from elementary statistical arguments a large velocity combined with a small gas density at the hot end and a small velocity combined with a large gas density at the cold end. It should be noted that since heat flows from the hot to the cold end, the system cannot be considered under equilibrium conditions although the averaged carrier flux is zero: particles move from the cold to the hot side and from the hot to the cold side, but the two counter-directed fluxes are equal since the cell is closed. We also see that the gradient of carrier density is directly driven by the temperature gradient. Since the carriers are charged particles, we obtain an electrochemical potential difference, commonly called voltage difference, which is induced by the application of a temperature difference. This illustrates the coupling of the electrochemical potential gradient and the temperature. Next, since the averaged carrier flux is zero, but heat is transported at the same time, we obtain the same values of particle fluxes from the hot to the cold side and from the cold to the hot side. From this observation, we can conclude that heat and carrier fluxes are coupled. While being very simple, this description contains the main contributions to TE processes. In the ideal, reversible case without entropy production, this would be a Carnot cycle containing two “isothermal” processes of heat exchange at the hot and cold sides, and two “adiabatic” processes of noninteracting motion from the hot to the cold side and from the cold to the hot side.

Actually, since the TE process is not ideal, we can then estimate the principle sources of entropy of the working system that are the nonisothermal heat transfer and the nonadiabatic travel of the carriers from cold to hot terminals and from hot to cold terminals. This entropy production in the nonadiabatic branches is due to the collisions between carriers and the interactions with the crystal lattice of the material. Nonideal situations are shown in Figure 1.16. In the case of a reversible system (case a), the entropy flux is conserved so we have ${}^{\dot{Q}_\mathrm{h}}/_{T_\mathrm{h}} = {}^{\dot{Q}_\mathrm{c}}/_{T_\mathrm{c}}$. The output power is then given by $\dot{W}_\mathrm{rev} = \dot{Q}_\mathrm{h} - \dot{Q}_\mathrm{c} = \eta_\mathrm{C}\dot{Q}_\mathrm{h}$ where $\eta_\mathrm{C} = (1 - T_\mathrm{c}/T_\mathrm{h})$ is the Carnot efficiency. In the case of a fully dissipative system (case b), we have $\dot{Q}_\mathrm{h} = \dot{Q}_\mathrm{c}$, then $\dot{W} = 0$. For most of the systems, we have the configuration (c) and the output power is strictly smaller than $\dot{W}_\mathrm{rev}$. Finally, let us stress again that the current description does not explicitly mention the atoms of the crystal lattice that provide parasitic thermal conduction due to phonons or other thermal conduction mechanisms. This is due to the Onsager description, which follows the so-called linear response theory where the linear-response Fourier’s law is used. Fourier’s law is valid for thermal conduction due to phonons as well as electrons and is therefore included in the phenomenological description. If these two processes are independent, then it is common to describe the thermal conductivity in the absence of carrier transport as $\kappa_J = \kappa_\mathrm{el} + \kappa_\mathrm{lat}$, where κ_el is the electronic contribution and κ_lat is the lattice contribution.

1.10

Thermodynamics and Thermoelectric Potential

Until now, we have not really taken into account the working conditions of the TE system. Similarly to any working engine, a TE device should be correctly driven in order to provide work in the best conditions. Then a precise control of the applied thermodynamic potentials (or fluxes) is needed in order to get correct use of the potentialities of the TE material. Since the TE process implies the coupling of the heat flux and electric current, these two fluxes should be driven optimally. This important question has been addressed by Snyder et al. in 2002/2003. They derived two key parameters of the "compatibility approach": the relative current and the TE potential [350, 351]. Both are reduced variables that can be used as a mathematical basis to analyze the local performance of TE material related to the working conditions.

1.10.1
Relative Current, Dissipation Ratio, and Thermoelectric Potential

The relative current density is defined by the ratio of electrical current density j to purely conductive fraction of the heat flux q_κ

$$u = -\frac{j^2}{\kappa \nabla T \cdot \mathbf{j}} \qquad \text{or} \qquad \frac{1}{u}\mathbf{j} = -\kappa \nabla T. \tag{1.90}$$

Note the writing of the ratio on the basis of two vectors $\mathbf{j}$ and $\mathbf{q}_\kappa = -\kappa \nabla T$.

Instead of using relative current density u, one could have introduced the dimensionless function r defined by

$$r = \frac{1}{u\alpha T} = \frac{-\kappa \nabla T \cdot \mathbf{j}}{j^2 \alpha T} = \frac{-\kappa \nabla T \cdot \mathbf{n}}{j \alpha T}, \tag{1.91}$$

which represents the ratio of dissipative to reversible heat fluxes. In the last term, we assume parallel (or antiparallel) fluxes with flow direction $\mathbf{n} = \mathbf{j}/j$.

In this and in section 1.10.2, we write some formulae both in terms of u and as function of r; in the latter case, they may appear more transparent.

Another possible variant was published by Kedem and Caplan [352], who described two coupled flows by their "degree of coupling functions." This approach reduces both the TE flows and forces to dimensionless numbers, an approach that is very similar to that applied in numerical fluid dynamics where dimensionless numbers (e.g., the Prandtl number) are used for nondimensionalizing the field equations [353] Such an approach had been firstly proposed by Clingman [273] in 1961, using a dimensionless heat flux c. For a detailed introduction of the ratios r and c, we refer to Chapter 5, Section 5.8.

From the point of view of local equilibrium thermodynamics, all local flows are considered as dependent on quasistatic local intensive variables. By relating this to the relative current, we must state that u is a function of the "potentials" T and μ_e in general. However, since the coupling between T and μ_e is weak (but nonzero) in the available TE materials (see Section 1.5.5), it is possible under certain conditions to focus on $u(T)$ as achieved in the compatibility approach, see Chapter 5 of this book.

From Eq. (1.80), the total heat flow $\mathbf{q}$ becomes

$$\mathbf{q} = \alpha T\,\mathbf{j} + \frac{\mathbf{j}}{u} = (1+r)\,\alpha T\,\mathbf{j} =:\ \Phi\,\mathbf{j} \quad \text{with}$$
$$\Phi = \alpha T + \frac{1}{u} = (1+r)\,\alpha T, \tag{1.92}$$

where Φ is the “thermoelectric potential” [351, 354]. Equation (1.92) points to the coupling of the two potentials Φ and T because we find

$$y(\Phi, T) = \frac{1}{u(\Phi, T)} = \Phi - \alpha T = r\alpha T. \tag{1.93}$$

Note that $y = 1/u$ can be defined as relative heat flux (as, e.g., achieved by Sherman *et al.* [271]).

The previous definitions make it clear that the TE coupling in isotropic media is described by

$$\mathbf{j} = \frac{1}{\Phi}\,\mathbf{q} = u\,\mathbf{q}_\kappa \quad \text{with} \quad \mathbf{q}_\kappa = r\alpha T\,\mathbf{j}, \tag{1.94}$$

whereby we generally assume parallelity of electric current and heat flow.24) The fact that the total heat and carrier fluxes are directly connected by the TE potential is fundamental since it allows us to derive the principle results of the thermodynamics of thermoelectricity directly from it. According to the previous definitions, the volumetric heat production ν_q becomes (with $\nabla \cdot \mathbf{j} = 0$)

$$\nu_q = \nabla \cdot \mathbf{q} = \nabla \cdot (\Phi\,\mathbf{j}) = \nabla\Phi \cdot \mathbf{j} = \mathbf{j} \cdot \nabla\left(\alpha T + \frac{1}{u}\right) = \mathbf{j} \cdot \nabla[(1+r)\,\alpha T]. \tag{1.95}$$

Note that $\nabla \cdot \mathbf{q} = \mathbf{j} \cdot \mathbf{E}$, see Eq. (1.76), and $\mathbf{E} = -{}^{\nabla\mu}/_{e}$, see Eq. (1.47). Then, we find

$$\mathbf{E} = \nabla\Phi = -{}^{\nabla\mu_e}/_{e} \implies \mu = -e\,(\Phi - \Phi_0), \tag{1.96}$$

which means that the electric field $\mathbf{E}$ can be calculated on a phenomenological level from the gradient of the TE potential Φ, or alternatively, by the negative gradient $-{}^{\nabla\mu_e}/_{e}$ when referring to a TE system by taking into account its chemical nature or solid-state physics. For details, we recommend the reading of Domenicali’s review [107].

Since the heat production term $\mathbf{j} \cdot \nabla\left(\frac{1}{u}\right)$ directly reduces the efficiency, it now becomes evident that the maximum efficiency coincides with the minimization of $\nabla({}^{1}/_{u})$. This is obtained for a specific value of $u_{\text{opt}} = s$, where s is called the “compatibility factor” (see the next section). For optimization of r and thermodynamic aspects of compatibility, see Section 5.8.

By considering the entropy flux, we obtain $\mathbf{j}_S = \frac{1}{T}(\alpha T + {}^{1}/_{u})\mathbf{j} = {}^{\Phi}/_{T}\mathbf{j}$, and the expression of the volumetric entropy production becomes

$$\nu_S = \nabla \cdot \mathbf{j}_S = \mathbf{j} \cdot \nabla\left(\frac{\Phi}{T}\right) = \frac{\nu_q}{T} + \mathbf{q} \cdot \nabla\left(\frac{1}{T}\right) = \mathbf{j} \cdot \nabla[(1+r)\,\alpha\ ]. \tag{1.97}$$

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24) A more general definition of u seems possible when writing the relative current density in terms of fluctuating currents, which are indeed 3D. In this context, particle and heat flow should be considered in an anisotropic medium where the material parameters are tensors, see, for example, [355].

This expression is in agreement with the Onsager formulation of the entropy production as the summation of the flux–force products, see Eq. (1.78), which here reduces to a single product since Φ is a compact expression of the thermodynamic potentials. For a given material, the TE potential enables a direct measurement of the total volumetric heat and entropy production by the respective degradation of Φ and ${}^{\Phi}/_{T}$ at a preset current flux $\mathbf{j}$.

1.10.2
Local Reduced Efficiency and Thermoelectric Potential of TEG, TEC, and TEH

Following [289, Section 9.2.2, 335], we can conclude that the local performance of an infinitesimal segment of a TE element can be defined as

$$\eta_{\mathrm{loc}} = \frac{\mathrm{d}T}{T}\,\eta_{\mathrm{r}} \quad \text{and} \quad \varphi_{\mathrm{loc}} = \frac{T}{\mathrm{d}T}\,\varphi_{\mathrm{r}}, \tag{1.98}$$

where ${}^{\mathrm{d}T}/_{T}$ is the infinitesimal Carnot cycle factor for TEG and ${}^{T}/_{\mathrm{d}T}$ is the one for TEC. As the Carnot process is a reversible one, the reduced "efficiencies"[25] η_{r} and φ_{r} play the role of an "irreversibility factor," which at least measures the distance to reversibility for both TEG and TEC due to a nonperfect TE engine. Such considerations were first published by E. Altenkirch [99, 100, 102].

The reduced efficiency of a TEG η_{r} is defined as the ratio of the products of conjugated forces and fluxes [351], where we have to pay attention to the fact that the electrical power production in a volume $\mathrm{d}V$ is given by the production density $\pi_{\mathrm{el}} = \mathbf{j}\cdot\mathbf{E}$, also denoted as differential electrical power. Note that the net differential power *output* is given by $-\pi_{\mathrm{el}}$, see Section 5.4 and [357–359]. By using Eqs. 1.76 and 1.43, we obtain $\mathbf{j}\cdot\mathbf{E} - T\nu_S = {}^{1}/_{T}\mathbf{q}\cdot\nabla T = \mathbf{j}_S\cdot\nabla T$, and with $\mathbf{j}\cdot\mathbf{E} = \nabla\cdot\mathbf{q} = \mathbf{j}\cdot\nabla\Phi$ and $\mathbf{j}_S = {}^{\Phi\ \mathbf{j}}/_{T}$, we finally obtain

$$\eta_{\mathrm{r}} = \frac{\mathbf{j}\cdot\mathbf{E}}{\mathbf{j}_S\cdot\nabla T} = \frac{\pi_{\mathrm{el}}}{\pi_{\mathrm{el}} - T\nu_S} = \frac{1}{1 - \frac{T\nu_S}{\pi_{\mathrm{el}}}} = \frac{1}{1 + \frac{T\nu_s}{|\pi_{\mathrm{el}}|}} \implies \eta_{\mathrm{r}} = \frac{T}{\Phi}\,\frac{\nabla\Phi\cdot\mathbf{j}}{\nabla T\cdot\mathbf{j}}, \tag{1.99}$$

which coincides with Clingman's result [273] and corresponds to the reduced variation of the TE potential ${}^{\nabla\Phi}/_{\Phi}$ when changing the other potential ${}^{\nabla T}/_{T}$, which is coherent with a general definition of the efficiency of a nonequilibrium thermodynamic process of coupled fluctuating parameters. The reduced efficiency expression can be rewritten from u and Φ expressions, that is, with $u = \frac{1}{\phi - T\alpha}$, $\frac{\nabla\Phi\cdot\mathbf{j}}{\nabla T\cdot\mathbf{j}} = \alpha(1 - \frac{\alpha}{z}u) = \alpha\left(1 - \frac{1}{rzT}\right)$, $u = -\frac{z}{\alpha^2}\frac{\nabla\Phi\cdot\mathbf{j}}{\nabla T\cdot\mathbf{j}} + \frac{z}{\alpha}$ and $\frac{1}{r} = zT\left(1 - \frac{1}{\alpha}\frac{\nabla\Phi\cdot\mathbf{j}}{\nabla T\cdot\mathbf{j}}\right)$, respectively, see, for example, [289, 351]. The result is for TEG

$$\eta_{\mathrm{r}} = \frac{1 - \frac{u\alpha}{z}}{1 + \frac{1}{u\alpha T}} = \frac{1 - \frac{\alpha}{z(\Phi - \alpha T)}}{1 + \frac{z(\Phi - \alpha T)}{\alpha zT}} = \frac{\alpha T}{\Phi}\left[1 - \frac{1}{zT\left(\frac{\Phi}{\alpha T} - 1\right)}\right] = \frac{1 - \frac{1}{rzT}}{1 + r}. \tag{1.100}$$

---

[25] In References [335, 356] reduced efficiencies $\eta_{\mathrm{r}}^{(\mathrm{g})} \equiv \eta_{\mathrm{r}}$, $\eta_{\mathrm{r}}^{(\mathrm{c})} \equiv \varphi_{\mathrm{r}}$ are introduced for both TEG and TEC, respectively.

This classical expression of the reduced efficiency presents a maximum for the compatibility factor $u_{\mathrm{opt}} = s$ given as follows. Also, the optimal dissipation ratio can be derived: curve sketching $\frac{\mathrm{d}}{\mathrm{d}r}\,\eta_{\mathrm{r}}(r) = 0$ by means of an algebra tool gives

$$r_{\mathrm{opt}} = \frac{1 \pm \sqrt{1 + zT}}{zT}. \tag{1.101}$$

It is worth noticing that

$$r_{\mathrm{opt}} = \frac{1 \pm \sqrt{1 + zT}}{zT} = \frac{1}{-1 \pm \sqrt{1 + zT}},$$

that is, there is no contradiction to Eq. (5.60) in Section 5.8.

An analogous approach can be found for the reduced coefficient of performance of a TEC, φ_{r}. As a consequence of the underlying TE effects (which are inverse to each other, and similar are the definitions of the global performance parameters, efficiency η and coefficient of performance φ),[26] the reduced coefficient of performance φ_{r} is inversely defined:

$$\varphi_{\mathrm{r}} = \frac{\mathbf{j}_S \cdot \nabla T}{\mathbf{j} \cdot \mathbf{E}} = \frac{\pi_{\mathrm{el}} - T\nu_S}{\pi_{\mathrm{el}}} = 1 - \frac{T\nu_S}{\pi_{\mathrm{el}}} = \frac{\Phi}{T}\,\frac{\nabla T \cdot \mathbf{j}}{\nabla \Phi \cdot \mathbf{j}}. \tag{1.102}$$

For a direct comparison of TEG and TEC, we recommend a unified 1D model for both generator and cooler single elements [335]. Note that $u(T)$ differs only by sign if TEG and TEC are operated at reversed boundary temperatures, but otherwise in the same working conditions. For this case of directly comparing TEG and TEC, we find formally $\varphi_{\mathrm{r}} = 1/\eta_{\mathrm{r}}$, and the reduced efficiencies present a maximum for $u = s$; where s is the compatibility factor [351], $u_{\mathrm{opt}} = s^{(\mathrm{g})} = \frac{\sqrt{1+zT}-1}{\alpha T}$ of a TEG, but $u_{\mathrm{opt}} = s^{(\mathrm{c})} = \frac{-\sqrt{1+zT}-1}{\alpha T}$ of a TEC.

The reduced efficiency and local coefficient of performance are defined as functions of u in their ranges of typical use ($0 \le u \le 2\, s^{(\mathrm{g})}$ for TEG and $2\, s^{(\mathrm{c})} \le u \le 0$ for TEC). Note that the signs of the compatibility factors depend on whether a p-type leg or an n-type leg (or element) is considered.

In the special situation of maximum local TEG efficiency ($u = s^{(\mathrm{g})} > 0$) and maximum local TEC coefficient of performance ($u = s^{(\mathrm{c})} < 0$), the two values are formally equivalent,

$$\eta_{\mathrm{r,opt}} = \varphi_{\mathrm{r,opt}}^{-1} = \frac{\sqrt{1 + zT} - 1}{\sqrt{1 + zT} + 1} < 1,$$

as η_{r} and φ_{r} are local irreversibility factors. Note that the COP of a device is allowed to exceed 1, but there is a limit for the local optimum of this quantity as the respective Carnot limit cannot be exceeded by η and φ. The aforementioned relation shows again that zT is a thermodynamic material quantity determining the maximum irreversibility factor that is the same for both interrelated TE effects, that is, Seebeck and Peltier effects.

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[26] We follow Sherman's notation here and use φ instead of COP in TEC formulae.

The equivalent optimal TE potential is given by

$$\Phi_{\text{opt}}^{(\text{g/c})} = \alpha T + \frac{1}{s^{(\text{g/c})}} = \alpha T \left[\frac{\sqrt{1+zT}}{\sqrt{1+zT} \mp 1} \right] = (1 + r_{\text{opt}})\, \alpha T, \tag{1.103}$$

where the minus sign applies for TEG, but the plus sign for TEC. Comparing with Eq. (1.92), we find once again that

$$r_{\text{opt}} = \frac{1}{-1 \pm \sqrt{1+zT}}.$$

Note that dissipation is negligible for both TEG and TEC in the limit $zT \to \infty$. Furthermore, we find

$$\eta_{\text{r,opt}} = \left(2\frac{\Phi_{\text{opt}}^{(\text{g})}}{\alpha T} - 1 \right)^{-1} \quad \text{and} \quad \varphi_{\text{r,opt}} = 2\frac{\Phi_{\text{opt}}^{(\text{c})}}{\alpha T} - 1. \tag{1.104}$$

Since the maximum reduced efficiency coincides with the minimal entropy production, we conclude that the optimal value of the TE potential, Φ_{opt}, defines the best working conditions for the system. Therefore, it is obvious that an optimal value Φ_{opt} is correlated to an optimal ratio between dissipative and reversible heat flux given by $u_{\text{opt}} = s$, or, more precisely, by an optimal dissipation ratio r (see also Section 5.8). A detailed discussion for the TEG is presented in Refs [354, 360].

The total efficiency η and the total coefficient of performance φ, respectively, of a finite generator and a cooler element are obtained by summing up the local contributions based on the reduced efficiency all over the TE element in an integral sense, see Eqs. (5.4) and (5.5). The particular case of maximum performance of an infinitely staged[27] TEG and TEC has been investigated by Sherman *et al.* [271, 361]. By considering the expressions 1.99, 1.100 and 1.102, we can now plot the reduced coefficient of performance $\varphi_r = \eta_r^{-1}$ as a function of the reduced variable $\xi = \frac{\Phi}{\alpha T} = 1 + r$ (which is identical to Clingman's "dimensionless heat flux" c introduced in Chapter 5, see Eq. (5.44)). The general expression is then

$$\varphi_{\text{r}} = \frac{\xi}{1 - \frac{1}{zT(\xi - 1)}}.$$

Note that this formula is equivalent to Eq. (1.100). This expression can now be plotted for all the different working modes of the TE engine, see Figure 1.17. The plot can be separated into three zones, corresponding, respectively, from right to left, to the TEG, TEC, and finally TEH mode. As previously described, the optimal working conditions are obtained for $\varphi_{\text{r,opt}} = 2\,\frac{\Phi_{\text{opt}}}{\alpha T} - 1 = 2\xi_{\text{opt}} - 1 = 2\,r_{\text{opt}} + 1$.

The resulting reduced efficiencies and coefficient of performances are sprayed around this optimal line. As expected, there is an optimal $\varphi_{\text{r,opt}}$ value for the TEG

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[27] The device (or TE element) is broken up into an infinite number of stages. Note that the terms "perfectly infinitely staged element" and "self-compatible element" introduced next can be used synonymously.

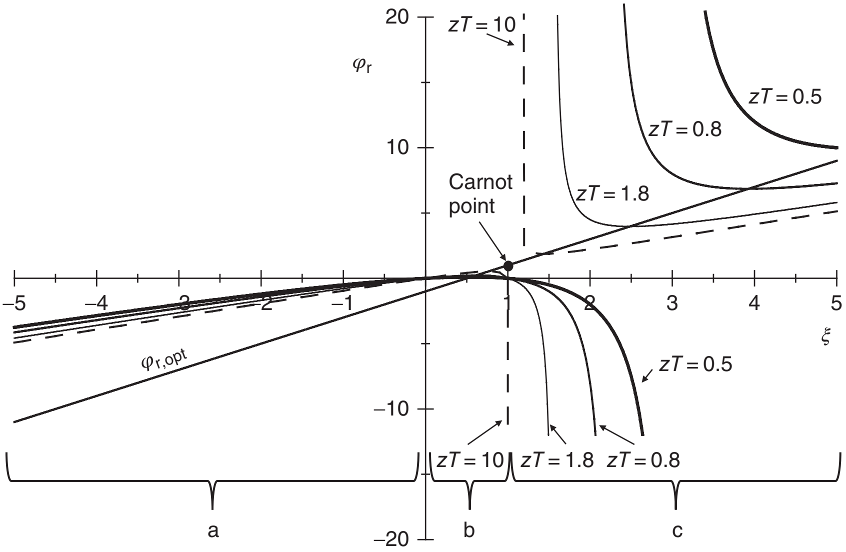

Figure 1.17 ϕ_r plot versus ξ for three different values of zT. Three different modes appear: (a) TEH mode, (b) traditional TEC mode, (c) TEG mode. The optimal working conditions are also given.

and TEC mode, corresponding to the maximal efficiency of a TEG and the maximal coefficient of performance of a TEC, respectively. When zT increases, these two optimal values becomes closer and closer. At the extreme we find the Carnot configuration, given by $zT \rightarrow \infty$, which leads to the condition $\varphi_r = \xi = 1$. In this case, the curve reduces to a single point of coordinates $(1, 1)$. There is a vertical asymptote passing through the "Carnot point," separating the TEG from the TEC mode.[28] The location of the Carnot point, exactly in between the two modes, means that the Carnot engine, as a reversible engine, may work with no distinction, as a generator or a receptor as depicted in Figure 1.18. It is worth noticing that the TEG and TEH modes are separated by a zone where the Peltier flux only counterbalances the conduction flux. This zone can be understood as a *regulation zone* of the conductive flux. The generator and receptor mode can also be considered using the classical, but extended current–voltage plot.

1.10.3
Thermoelectric Potential and Nonequilibrium Thermodynamics

We begin with the discussion of the Gibbs free energy G of an open one-component system, which is characterized by the thermodynamic variables T, p, N, and we recall known facts: Gibbs free energy is proportional to the numbers of particle, $G = \mu_c\, N$, with μ_c being the chemical potential.

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[28] From a practical point of view, a TEC can be understood as a TEG working at a current value larger than its short-circuit current.

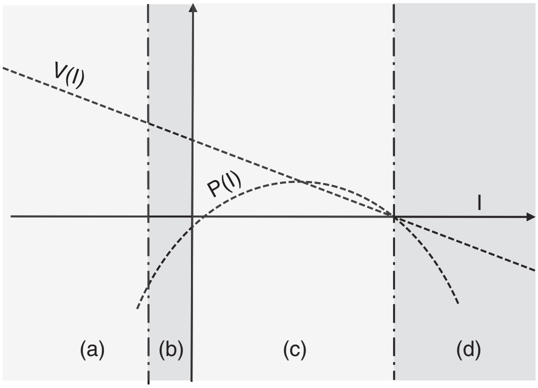

Figure 1.18 Current–voltage response. TEH: (a), Regulation: (b), TEG: (c), TEC: (d).

In the infinitesimal limit, changes of G due to energy and particle exchange are given by

$$\mathrm{d}G(T, p, N) = -S\ \mathrm{d}T + V\ \mathrm{d}p + \mu_\mathrm{c}\ \mathrm{d}N. \tag{1.105}$$

The thermodynamics of adding one particle to the system was first investigated in Vining's paper in 1997 [328]. Since Vining did not focus on compatibility, he used a capacity matrix formalism by taking into consideration the coupling between thermal and electric transport. Such an approach may be considered obsolete because the relative current density u and the TE potential $\Phi = \alpha T + {}^1\!/_u$ automatically include this coupling. Moreover, there is no continuity between a thermostatic description and a nonequilibrium thermodynamic description; in a more formal way, there is no continuity between the capacity matrix and the matrix of kinetic coefficients.

We consider now a stationary nonequilibrium state maintained by a total energy flux $\mathbf{j}_E$. For the description of such systems, the fundamental relation of classical equilibrium thermodynamics

$$\mathrm{d}S = \frac{1}{T}\ (\mathrm{d}U + p\,\mathrm{d}V - \mu_\mathrm{c}\ \mathrm{d}N) \tag{1.106}$$

is extended to thermodynamically nonequilibrium systems, and it is supposed that the transformation between two different states (characterized by one of the state functions S, U, F, H, G) is performed by a sequence of quasi-stationary states.

Here we show that the internal energy U is also suitable for describing the state of TE systems operating out of equilibrium; G and U are interconnected by Legendre transformations

$$G = U + p\ V - S\,T \quad \Rightarrow \quad \mathrm{d}U = T\ \mathrm{d}S - p\,\mathrm{d}V + \mu_\mathrm{c}\ \mathrm{d}N. \tag{1.107}$$

Note that the relation for $\mathrm{d}U$ is of particular importance because it is based on the differentials of the extensive values only.

To specify the changes in U for a TE system, we consider the relationship between the TE potential Φ and the total energy flux or the internal energy.

According to the first law of thermodynamics, the expression of the total energy flux $\mathbf{j}_E$, heat flux $\mathbf{j}_Q$, and particles flux $\mathbf{j}_N$ is given by $\mathbf{j}_E = \mathbf{j}_Q + \mu_\mathrm{e}\, \mathbf{j}_N$, where μ_e is here the electrochemical potential, and $\mathbf{j} = e\, \mathbf{j}_N$. Since $\mathbf{j}_Q = \Phi\, \mathbf{j} = e\, \Phi\, \mathbf{j}_N$, see Eq. (1.92), we obtain for the total energy flux

$$\begin{aligned}\mathbf{j}_E &= \mathbf{j}_Q + \mu_\mathrm{e}\, \mathbf{j}_N = (e\Phi + \mu_\mathrm{e})\mathbf{j}_N = \left(e\alpha T + \mu_\mathrm{e} + \frac{e}{u}\right) \mathbf{j}_N \\ &= (e\alpha T + \mu_\mathrm{e})\, \mathbf{j}_N + \frac{1}{u}\, \mathbf{j} = (e\alpha T + \mu_\mathrm{e})\, \mathbf{j}_N - \kappa\, \nabla T. \end{aligned} \tag{1.108}$$

Note that Eq. (1.108) separates the heat transported by the carriers (first term) and the Fourier heat occurring in any material (second term).

Applying energy and particle conservation, that is, $\nabla \cdot \mathbf{j}_E = 0$ and $\nabla \cdot \mathbf{j}_N = 0$, the nabla calculus directly gives $\nabla(e\, \Phi + \mu_\mathrm{e}) \cdot \mathbf{j}_N = 0$. This equation is fulfilled if $\nabla(e\, \Phi + \mu_\mathrm{e}) \perp \mathbf{j}_N$ or, alternatively, if

$$\nabla(e\, \Phi + \mu_\mathrm{e}) = 0 \quad \Rightarrow \quad e\, \Phi + \mu_\mathrm{e} = \text{const.} \quad \text{resp.} \quad \mu_\mathrm{e} = -e\, (\Phi - \Phi_0). \tag{1.109}$$

Equation (1.109) has already been discussed in Section 5.8.

Obviously, Eq. (1.108) contains irreversible heat conduction via u as part of the TE potential $\Phi = \alpha T + {}^{1}\!/_{u}$, that is, we have $\Phi \rightarrow \alpha T$ in the limit of a reversible process management. By definition of the specific heat under constant volume in a quasistatic description (index "qs")

$$C_V = \frac{\delta Q_\mathrm{rev}}{\mathrm{d}T} \simeq \frac{\delta Q_\mathrm{qs}}{\mathrm{d}T}, \tag{1.110}$$

the correct relation within the framework of equilibrium thermodynamics is (with $\mathrm{d}V = 0$)

$$\mathrm{d}U(T,N) = \delta Q_\mathrm{rev} + \delta W = C_V\, \mathrm{d}T + (e\alpha T + \mu_\mathrm{e})\, \mathrm{d}N, \tag{1.111}$$

where $\left(\frac{\partial U}{\partial N}\right)_T = (e\alpha T + \mu_\mathrm{e})$ is the fraction of the internal energy related to the carrier transport. Note that both the electrical and the thermal balance are influenced when adding a charged particle to the TE system. By comparing Eq. (1.111) with $\mathrm{d}U = T\, \mathrm{d}S + \mu_\mathrm{e}\, \mathrm{d}N$, we obtain

$$\mathrm{d}S = \frac{C_V}{T}\, \mathrm{d}T + e\alpha\, \mathrm{d}N, \tag{1.112}$$

which means that any change in entropy is caused by two effects: one is heat accumulation (or restitution by C_V) and the second is due to the transport of entropy by the variation of the number of carriers.

From Eq. (1.111), we find for the difference between two equilibrium states

$$\triangle U = \int \mathrm{d}U = \int C_V\, \mathrm{d}T + \int (e\alpha T + \mu_\mathrm{e})\, \mathrm{d}N = U_2 - U_1, \tag{1.113}$$

irrespective of the "path" between them. Usually, the transformation between these two states is performed by a sequence of quasi-stationary states, but we should keep in mind that such a strategy (lastly a "kinematic" description) cannot give us an answer to the system's driving forces, neither it gives insight into the system's evolution, which is governed by entropy-based principles.

Following Prigogine's principle of minimal entropy production, we clearly observe that there is a specific path that is used by the system, under constraints, to produce less entropy. This had been firstly investigated by Sherman *et al.* [271] and Clingman [273]. By applying the compatibility approach together with thermodynamic arguments, we can state additionally that minimum entropy production is obtained when the TE potential Φ takes a specific optimal value. There is no doubt that Φ is the correct potential for the description of the TE applications TEG, TEC, and TEH by taking into account heat conduction as an irreversible process in TE materials.

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