Chapter 1
The Thermoelectric and Related Effects

Abstract This chapter defines the Peltier and Seebeck effects and introduces the concept of the thermocouple. It gives the relationships between the Peltier, Seebeck and Thomson coefficients. It also describes the related effects that appear in a magnetic field and defines the Hall, Nernst, Ettingshausen and Righi–Leduc coefficients.

1.1 Introduction

The first of the thermoelectric effects was discovered in 1821 by T.J. Seebeck. He showed that an electromotive force could be produced by heating the junction between two different electrical conductors. The Seebeck effect can be demonstrated by making a connection between wires of different metals (for example, copper and iron). The other ends of the wires should be applied to the terminals of a galvanometer or sensitive voltmeter. If the junction between the wires is heated, it is found that the meter records a small voltage. The arrangement is shown in Fig. 1.1. The two wires are said to form a thermocouple. It is found that the magnitude of the thermoelectric voltage is proportional to the difference between the temperature at the thermocouple junction and that at the connections to the meter.

Thirteen years after Seebeck made his discovery, J. Peltier, a French watchmaker, observed the second of the thermoelectric effects. He found that the passage of an electric current through a thermocouple produces a small heating or cooling effect depending on its direction. The Peltier effect is quite difficult to demonstrate using metallic thermocouples since it is always accompanied by the Joule heating effect. Sometimes one can do no better than show that there is less heating when the current is passed in one direction rather than the other. If one uses the arrangement shown in Fig. 1.1 the Peltier effect can be demonstrated, in principle, by replacing the meter with a direct current source and by placing a small thermometer on the thermocouple junction.

It seems that it was not immediately realised that the Seebeck and Peltier phenomena are dependent on one another. However, this interdependency was

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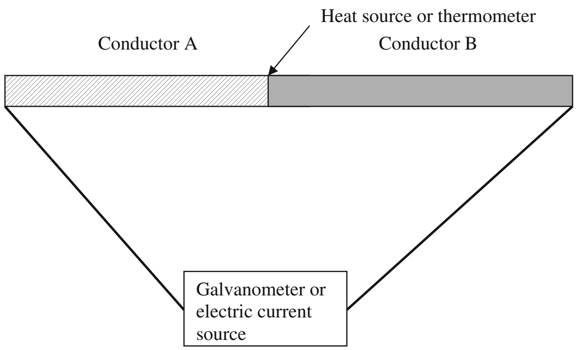


Fig. 1.1 Experiment to demonstrate the Seebeck and Peltier effects

recognised by W. Thomson (who later became Lord Kelvin) in 1855. By applying the theory of thermodynamics to the problem, he was able to establish a relationship between the coefficients that describe the Seebeck and Peltier effects. His theory also showed that there must be a third thermoelectric effect, which exists in a homogeneous conductor. This effect, now known as the Thomson effect, consists of reversible heating or cooling when there is both a flow of electric current and a temperature gradient.

The fact that the Seebeck and Peltier effects occur only at junctions between dissimilar conductors might suggest that they are interfacial phenomena but they are really dependent on the bulk properties of the materials involved. Nowadays, we understand that electric current is carried through a conductor by means of electrons that can possess different energies in different materials. When a current passes from one material to another, the energy transported by the electrons is altered, the difference appearing as heating or cooling at the junction, that is as the Peltier effect. Likewise, when the junction is heated, electrons are enabled to pass from the material in which the electrons have the lower energy into that in which their energy is higher, giving rise to an electromotive force.

Thomson's work showed that a thermocouple is a type of heat engine and that it might, in principle, be used either as a device for generating electricity from heat or, alternatively, as a heat pump or refrigerator. However, because the reversible thermoelectric effects are always accompanied by the irreversible phenomena of Joule heating and thermal conduction, thermocouples are generally rather inefficient.

The problem of energy conversion using thermocouples was analysed by Altenkirch [1] in 1911. He showed that the performance of a thermocouple could be improved by increasing the magnitude of the differential Seebeck coefficient, by increasing the electrical conductivities of the two branches and by reducing their thermal conductivities. Unfortunately, at that time, there were no thermocouples available in which the combination of properties was good enough for reasonably efficient energy conversion, although the Seebeck effect has long been used for the measurement of temperature and for the detection of thermal radiation. It was only in the nineteen-fifties that the introduction of semiconductors as thermoelectric materials allowed practical Peltier refrigerators to be made. Work on semiconductor thermocouples also led to the construction of thermoelectric generators with a high enough efficiency for special applications. Nevertheless, the performance of thermoelectric energy convertors has always remained inferior to that of the best conventional machines.

In fact, there was little improvement in thermoelectric materials from the time of the introduction of semiconductor thermoelements until the end of the twentieth century. However, in recent years, several new ideas for the improvement of materials have been put forward and, at last, it seems that significant advances are being made, at least on a laboratory scale. It is reasonable to expect that this work will soon lead to much wider application of the thermoelectric effects.

1.2 Relations Between the Thermoelectric Coefficients

We now define the Seebeck and Peltier coefficients and show how they are related to one another. For the time being we assume that the conductors are isotropic. We refer to the simple thermocouple shown in Fig. 1.2. Conductor A is joined at both ends to conductor B, the latter being divided into two parts so that, for example, a voltmeter can be inserted in the gap.

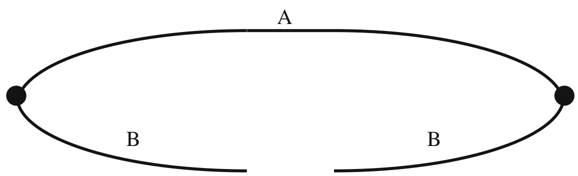
Suppose that a temperature difference ΔT is established between the two junctions and that the two free ends of conductor B are maintained at the same temperature. It will then generally be found that a potential difference V will appear between the free ends. The differential Seebeck coefficient, α_{AB}, is defined as the ratio of V to ΔT. Thus,

$$\alpha_{AB} = \frac{V}{\Delta T}. \tag{1.1}$$

α_{AB} is deemed to be positive if the electromotive force tends to drive an electric current through conductor A from the hot junction to the cold junction. It is noted that, particularly in older texts, the quantity that is now known as the Seebeck coefficient has often been called the thermoelectric power or the thermal EMF coefficient.

We define the differential Peltier coefficient, π_{AB}, for the same thermocouple by supposing that a source of EMF is connected across the gap in conductor B so as to drive a current around the circuit in a clockwise direction. The Peltier coefficient is

Fig. 1.2 Simple thermocouple



regarded as positive if the junction at which the current enters A is heated and the junction at which it leaves A is cooled. π_{AB} is equal to the ratio of the rate q of heating or cooling at each junction to the electric current I,

$$\pi_{AB} = \frac{q}{I}. \tag{1.2}$$

We note that it is much simpler to measure the Seebeck coefficient than the Peltier coefficient. Thus, whereas both quantities enter into the theory of thermoelectric energy conversion, it would be preferable if only one of them had to be specified. In fact, one of the Kelvin relations allows us express the Peltier coefficient in terms of the Seebeck coefficient. The relevant equation is

$$\pi_{AB} = \alpha_{AB} T. \tag{1.3}$$

The other Kelvin relation connects the Seebeck coefficient and the Thomson coefficient, τ, or, rather, the difference between the Thomson coefficients of the two conductors. The Thomson coefficient is defined as the rate of heating per unit length that results from the passage of unit current along a conductor in which there is unit temperature gradient. The appropriate Kelvin relation is

$$\tau_A - \tau_B = T\frac{d\alpha_{AB}}{dT}. \tag{1.4}$$

The Seebeck and Peltier coefficients are defined above for a pair of conductors whereas it would be much more convenient if their values could be given for a single material. In fact, the absolute Seebeck or Peltier coefficient becomes equal to the differential coefficient if the second material can be regarded as having zero absolute coefficients. This concept can be realised in practice by using a superconductor as the second material. It is reasonable to assign zero Seebeck or Peltier coefficients to a superconductor since the differential coefficients between all pairs of superconductors are zero.

Of course, there is no material that remains in the superconducting state at ordinary temperatures, so it might be thought that the absolute Seebeck coefficients of other materials can be obtained only at low temperatures. However, this is not the case. It is reasonable to write (1.4) in the form

$$\tau = T\frac{d\alpha}{dT} \tag{1.5}$$

for a single conductor. Thus, if the absolute Seebeck coefficient of a material at low temperatures is determined by connecting it to superconductor, one can then use (1.5) to find the value at higher temperatures after measuring the Thomson coefficient [2, 3]. This procedure has been carried out for the metal lead, which may be used as a reference material when determining the absolute coefficients for other substances.

In actual fact, most metals, like lead, have very small absolute values of the Seebeck coefficient compared with practical thermoelectric materials that are almost invariably semiconductors.

1.3 Effects in a Magnetic Field

Electric charges are subject to transverse forces when they travel in a magnetic field. Thus, the thermoelectric effects, like the other transport properties, become changed when a magnetic field is applied and there also appear some new phenomena. We need to discuss these so-called thermogalvanomagnetic effects since they can affect the performance of thermoelectric devices and can even lead to new methods of energy conversion.

As we shall demonstrate in the next chapter, the electric and thermal conductivities are properties that are of importance when we are calculating the performance of devices based on the Seebeck and Peltier effects. Both quantities become less on the application of a magnetic field, though the changes are very small unless the field is very strong and the mobility of the charge carriers is high. The Seebeck and Peltier coefficients, too, will change under the influence of a magnetic field, B.

Usually, the value of the Seebeck coefficient will be the same when the direction of the magnetic field is reversed but this is not always the case. Any difference between the values of the Seebeck coefficient upon reversal of the field is called the umkehr effect. The umkehr effect has been shown [4] to be very large for certain orientations of the semimetal bismuth.

Another consequence of the action of a magnetic field [5] is the need to modify the Kelvin relation (1.3). The modified equation is

$$\pi(B) = T\alpha(-B). \tag{1.6}$$

When a transverse magnetic field is applied to a current carrying conductor, an electric field appears in a direction perpendicular to both the current and B. This is the well-known Hall effect. The Hall effect is not immediately relevant to energy conversion but is a useful tool in explaining the behaviour of the charge carriers. Of more direct significance for energy conversion are the transverse Nernst and Ettinghausen effects.

The Nernst effect, like the Hall effect, manifests itself as a transverse voltage in a magnetic field but it depends on the longitudinal temperature gradient or heat flow rather than on a longitudinal electric current. The Nernst coefficient, N, is defined by the relation

$$|N| = \frac{\mathrm{d}V/\mathrm{d}y}{B_z \mathrm{d}T/\mathrm{d}x}. \tag{1.7}$$

Here d*V*/d*y* is the transverse electric field. The sign of the Nernst effect is given in Fig. 1.3, which illustrates all the transverse thermogalvanomagnetic phenomena. The sign of the Nernst effect does not depend on whether the charge carriers are positive or negative and, in this respect, it differs from the Hall effect.

The Ettingshausen and Nernst effects are related to one another in the same way as the Peltier and Seebeck effects. The Ettingshausen effect is a transverse temperature gradient that is the result of a transverse magnetic field and a longitudinal flow of electric current. The Ettingshausen coefficient, *P*, is defined by

$$|P| = \frac{\mathrm{d}T/\mathrm{d}y}{i_x B_z}, \tag{1.8}$$

where i_x is the longitudinal current density. As one might have expected, there is a thermodynamic relationship between the Nernst and Ettingshausen coefficients,

$$P\lambda = NT, \tag{1.9}$$

where λ is the thermal conductivity, which has to be included since the Ettingshausen coefficient is defined in terms of a temperature gradient rather than a heat flow.

To complete the transverse phenomena, there exists the Righi–Leduc effect, which is a transverse temperature gradient arising from a longitudinal heat flow. The Righi–Leduc coefficient, *S*, is given by

$$|S| = \frac{\mathrm{d}T/\mathrm{d}y}{B_z \mathrm{d}T/\mathrm{d}x}. \tag{1.10}$$

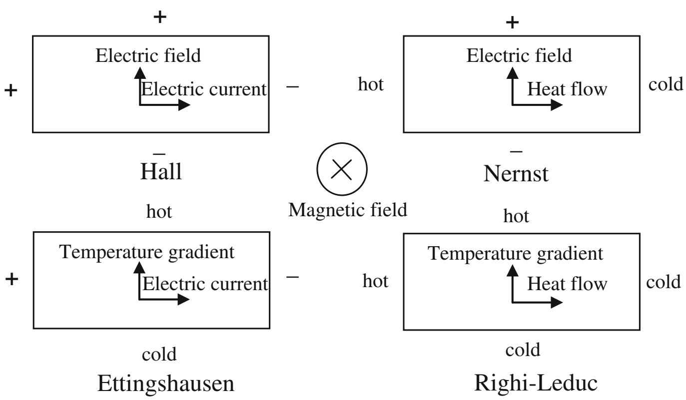


Fig. 1.3 The transverse thermogalvanomagnetic effects. When the effects are in the direction shown in the diagram, the coefficients are positive

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