The Fundamentals of Thermoelectrics

A bachelor's laboratory practical

Contents

1 An introduction to thermoelectrics

Thermoelectric effects involve a fundamental interplay between the electronic and thermal properties of a system. These effects are most often observed by measuring electrical quantities (voltage and current) induced by thermal gradients. While not as straightforward to measure, electrical voltages and currents can induce heat flow. Electrically induced heat flow generates a temperature gradient and should not be confused with Joule heating. The two primary thermoelectric effects are the Seebeck effect and the Peltier effect, which when combined with the laws of thermodynamics, can be used to derive all other thermoelectric effects [1]. When a conductive material is subjected to a thermal gradient, charge carriers migrate along the gradient from hot to cold; this is the Seebeck effect. In the open-circuit condition, charge carriers will accumulate in the cold region, resulting in the formation of an electric potential difference (see Fig. 1).

The Seebeck effect describes how a temperature difference creates charge flow, while the Peltier effect describes how an electrical current can create a heat flow. Electrons transfer heat in two ways: 1) by diffusing heat through collisions with other electrons, or 2) by carrying internal kinetic energy during transport. The former case is standard heat diffusion, while the latter is the Peltier effect. Therefore, the Seebeck effect and the Peltier effect are the opposite of one another.

Since the initial discovery of thermoelectric effects in the early 1800s, a solid theoretical foundation has been developed. The Seebeck and Peltier effects can be combined with Ohm's law and standard heat conduction into

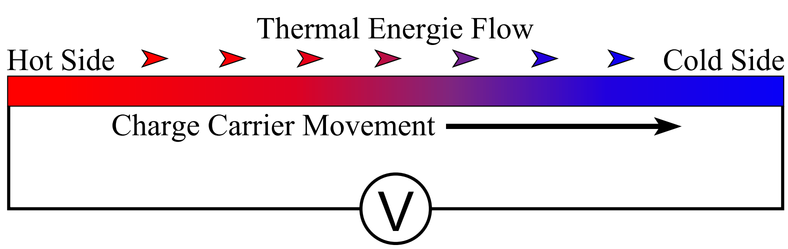

Figure 1: Charge carriers flow in response to a temperature gradient. The resulting charge imbalance creates a potential difference that can be measured using a voltmeter.

a single mathematical expression to describe the total voltage, $V = V_{\text{el}} + V_{\text{th}}$, and total heat flux, $\dot{Q} = P_{\text{el}} + P_{\text{th}}$, created by an electrically induced current, I_{el}, and temperature gradient, ΔT. In the linear response regime, the relationship is

$$\begin{pmatrix} V \\ \dot{Q} \end{pmatrix} = \begin{pmatrix} R & S \\ \Pi & -\kappa \end{pmatrix} \begin{pmatrix} I_{\text{el}} \\ \Delta T \end{pmatrix}, \tag{1}$$

where the matrix contains phenomenological thermoelectric coefficients. The two diagonal terms of this matrix are the "pure" coefficients, that is, the electrical resistance, R, and the thermal conductance, κ, which describe pure electrical and thermal effects separately. The two off-diagonal terms are the "mixed" coefficients relating electrical and thermal phenomena. The Seebeck coefficient, S, mandates the voltage produced by ΔT. Note that ΔT also induces a current, I_{th}, and the total current is $I = I_{\text{el}} + I_{\text{th}}$. Formally, the Seebeck coefficient is defined when $I = 0$, so that,

$$S = \lim_{\Delta T \to 0} \left. \frac{V}{\Delta T} \right|_{I=0}. \tag{2}$$

The corresponding thermovoltage, V_{th}, is also defined in the open-circuit condition:

$$V_{\text{th}} = S\Delta T|_{I=0}. \tag{3}$$

The well-known V_{el} from Ohm's law is the current-induced electric voltage defined by

$$V_{\text{el}} = I_{\text{el}} R|_{\Delta T=0}. \tag{4}$$

Therefore, the total voltage, V, is the sum

$$V = RI_{\text{el}} + S\Delta T = V_{\text{el}} + V_{\text{th}}. \tag{5}$$

Heat flows against ΔT (from hot to cold) according to Fourier's law of heat conduction, $P_{\text{th}} = -\kappa \Delta T$. The thermal conductance, κ, is defined formally as

$$\kappa = \lim_{\Delta T \to 0} - \left. \frac{\dot{Q}}{\Delta T} \right|_{I=0}. \tag{6}$$

The Peltier coefficient, Π, quantifies the heat flux, $P_{\text{el}} = \Pi I_{\text{el}}$, carried by I_{el} when $\Delta T = 0$. Analogous to κ, Π is defined by

$$\Pi = \left. \frac{\dot{Q}}{I_{\text{el}}} \right|_{\Delta T=0}. \tag{7}$$

Using an Onsager relation [2, 3], which results from the second law of thermodynamics, S and Π are related by

$$\Pi = ST, \tag{8}$$

for a system at temperature T. This is known as the (second) Thomson relation.

In the closed-circuit condition, ΔT gives rise to the thermocurrent, I_{th}, given by

$$I_{\mathrm{th}} = \frac{V_{\mathrm{th}}}{R} = \frac{S\Delta T}{R}. \tag{9}$$

The total current is the sum of the electrically and thermally induced currents

$$I = I_{\mathrm{el}} + I_{\mathrm{th}} = \frac{V_{\mathrm{el}} + V_{\mathrm{th}}}{R} = \frac{V}{R}, \tag{10}$$

where Eq. (5) has been used. The above equations form the complete theoretical foundation of elementary thermoelectric effects. In this lab practical, you will measure the thermoelectric coefficients of a semiconductor device.

2 The thermocouple

The first thermoelectric setup introduced in the lab practical is the thermocouple. This simple device consists of two conductors, A and B, which are connected at one end held at temperature T_1. Meanwhile, the voltage difference between conductors A and B is measured at the opposite end held at temperature T_2. The thermocouple is shown in Fig. 2. When $\Delta T = T_2 - T_1 \neq 0$, each conductor produces a themovoltage $V_\mathrm{A} = S_\mathrm{A}\Delta T$ and $V_\mathrm{B} = S_\mathrm{B}\Delta T$, where S_A and S_B are the respective Seebeck coefficients of conductors A and B. Therefore, the measured voltage difference between the two conductors is

$$V_\mathrm{AB} = V_\mathrm{A} - V_\mathrm{B} = S_\mathrm{A}\Delta T - S_\mathrm{B}\Delta T = S_\mathrm{AB}\Delta T, \tag{11}$$

where $S_\mathrm{AB} = S_\mathrm{A} - S_\mathrm{B}$ is the effective Seebeck coefficient of the conductor pair. Note that while S_A and S_B are intrinsic material properties of the conductors, S_AB is an effective Seebeck coefficient that describes the thermoelectric performance of a composite device.

Thermocouples are used regularly as thermometers by calibrating the response voltage, V_AB, based on known temperatures. Typically T_2 is maintained at room temperature, while T_1 is varied while measuring V. This is the most practical choice because the voltmeter can remain at room temperature. Once calibrated, a measurement of V_AB provides the temperature T_1. The K-type thermocouple (chromel–alumel) is the most common commercial thermocouple with a sensitivity of approximately $V_\mathrm{AB} = 41\,\mu\mathrm{V}/^\circ\mathrm{C}$ [4].

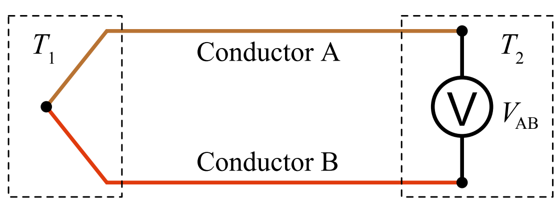

Figure 2: Two conductors, A and B, span a temperature gradient, $\Delta T = T_2 - T_1$, maintained by the local temperatures T_1 and T_2. The two thermovoltages established within each conductor produce a net thermovoltage, V_AB.

3 The Peltier device

Peltier devices are named so because, typically, they are used as a heat pump based on the Peltier effect. In this case, a constant current, I_{el}, is driven through the Peltier device, and the Peltier effect generates a temperature difference, $\Delta T \propto P_{\mathrm{el}} = \Pi I_{\mathrm{el}}$.

3.1 n- and p-type Peltier elements

When a semiconductor is used as a thermoelectric material, its majority charge carriers (electrons or holes) determine the electrical behaviour. For example, when n- and p-type semiconductors are biased in the same direction, their charge carriers flow in opposite directions. As a result, n- and p-type Peltier elements create opposite temperature gradients (see Fig. 3).

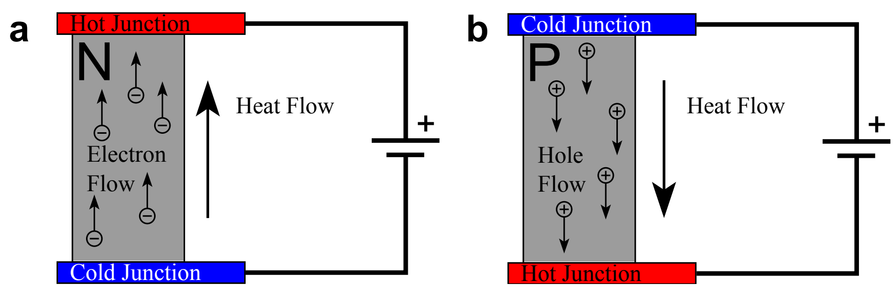

Figure 3: n-type versus p-type Peltier elements. a) An n-type semiconductor is biased externally creating an electrical current. The negative carriers (electrons) carry heat from bottom to top via the Peltier effect. b) The positive carriers (holes) within a p-type semiconductor–biased in the same direction as (a)–pump heat in the *opposite* direction, that is, from top to bottom.

3.2 Commercial Peltier devices

A single Peltier element can be used to produce electrical power (via the Seebeck effect) or to pump heat (via the Peltier effect). In either application, the power output of a single Peltier element is generally not sufficient for realistic situations. To increase their power, commercial Peltier devices are composed of many n-type and p-type semiconductor Peltier elements. The individual elements are connected in series using metallic junctions. As a result of this, the junctions between the semiconductors do not form a barrier potential, as they would do in a p-n diode, and charge carriers flow freely in both directions. In a Peltier device, the individual elements are arranged so that the n- and p-type heat flow in the same direction (see Fig. 4).

A complete Peltier device architecture is shown in Fig. 5. It consists of two electrically insulating ceramic plates sandwiching a series of p-n pairs joined by copper. This design provides a large surface area improving heat pumping for cooling and heating applications. Waste heat absorption and electrical power production (via the Seebeck effect) also benefit from the increased surface area.

3.3 Electrical power production

Though primarily used as heat pumps, Peltier devices nonetheless generate a thermovoltage, V_{th}, when subjected to a temperature gradient, ΔT. An electrical current, I will flow if the Peltier device is connected to a load resistor, R_{load}. In this case, the Peltier device converts heat energy to electrical energy quantified by the dissipated power, $P = IV_{\mathrm{load}}$, where V_{load} is the voltage drop across the load resistor.

In the laboratory, P can be determined by measuring I and V_{load}. The Peltier device is not an ideal voltage source; therefore, its internal resistance, R_{I}, must be included in the analyses of power data. Furthermore, R_{I} is typically on the order of a few tens of Ohms. Therefore, the resistance of the ammeter, R_{a}, cannot be ignored.

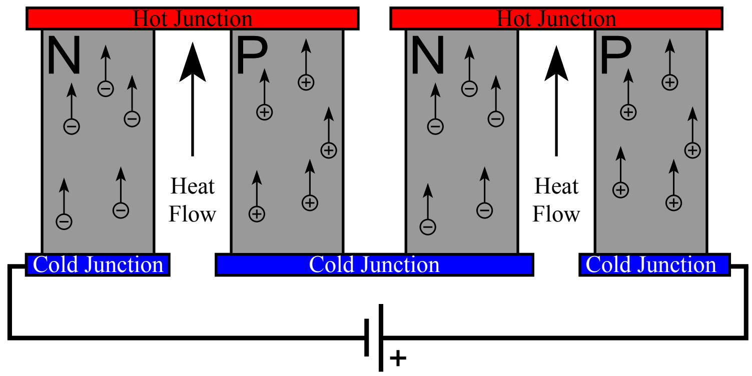

Figure 4: A series of alternating n- and p-type semiconductor elements, which pump heat from bottom to top when a voltage is applied.

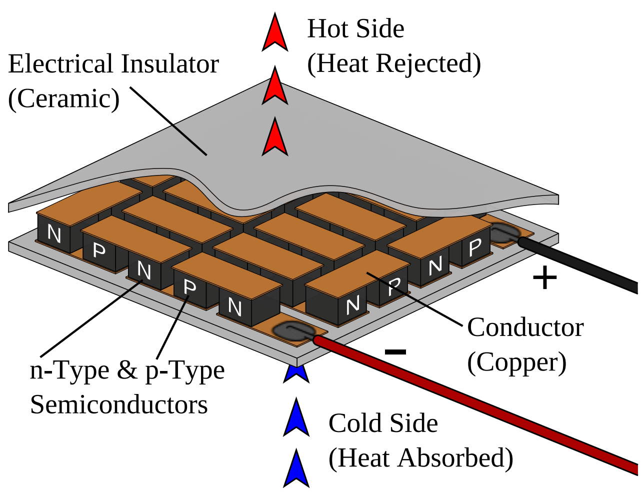

Figure 5: The design of a commercial Peltier device. Sandwiched between two ceramic insulators, alternating n- and p-type semiconductors elements are arranged across a plain and are connected in series electrically with copper junctions. When current is supplied to the Peltier device, heat is pumped from one surface to the other.

3.4 Thermal conductance

When current, I, flows through the Peltier device, heat flow $P_{\mathrm{el}} = \Pi I$ generates a temperature difference, ΔT. In response, heat conducts from the hot to the cold side of the Peltier device given by $P_{\mathrm{th}} = -\kappa \Delta T$. The electrical power dissipated in the Peltier device (that is, the Joule heat) is $P_{\mathrm{J}} = RI^2$, where R is the resistance of the Peltier device. P_{J} flows into both sides of the Peltier device. Finally, heat P_{air} flows from the hot side to the surrounding environment. These heat flows are shown in Fig. 6.

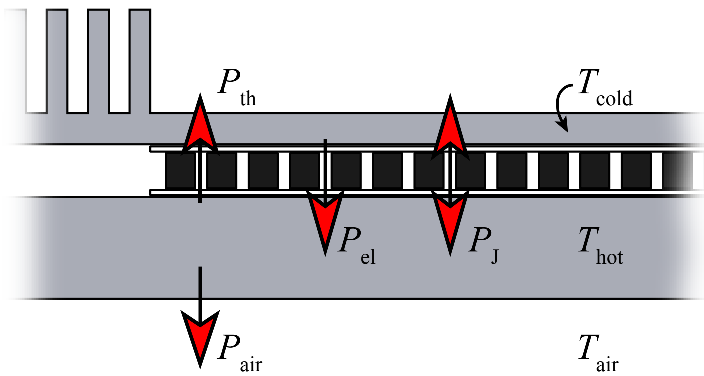

Figure 6: Heat flows in the Peltier device. Current, I, flowing through the Peltier device pumps heat $P_{\mathrm{el}} = \Pi I$ and generates the temperature gradient, $\Delta T = T_{\mathrm{hot}} - T_{\mathrm{cold}}$. In the opposite direction as P_{el}, heat flux P_{th} conducts through the Peltier device from hot to cold. Joule heat, P_{J}, flows into both sides of the Peltier device. Heat P_{air} conducts from the heat block to the surrounding air at temperature T_{air}.

A number of simplifications and approximations can be made to reduce the complexity of these heat flows during measurements. The first simplification is to perform the experiments in the open-circuit regime where $I = 0$. Therefore $P_{\mathrm{el}} = P_{\mathrm{J}} = 0$. The approximations are to assume that $T_{\mathrm{cold}} \approx T_{\mathrm{air}}$ and that $P_{\mathrm{air}} \approx 0$. These assumptions are fulfilled when ΔT is small and when the heat block is thermally insulated.

In this situation, only P_{th} affects the heat content of the hot block because T_{cold} is constant. The heat stored in the heat block is $Q_{\mathrm{hot}} = mcT_{\mathrm{hot}}$, where $m = 0.22\,\mathrm{kg}$ is the mass of the heat block, and $c = 897\,\mathrm{J/(kg\,K)}$ is the heat capacity of aluminium. The rate equation for the heat flow is

$$P_{\mathrm{th}} = \dot{Q}_{\mathrm{hot}} = mc\dot{T}_{\mathrm{hot}} = -\kappa T_{\mathrm{hot}}$$

Starting from a temperature $T_{\mathrm{hot}}\left(t = t_0\right) = T_0$, the hot block cools according to

$$\dot{T}_{\mathrm{hot}}\left(t\right) = \frac{\kappa}{mc}\left(T_0 - T_{\mathrm{hot}}\left(t\right)\right). \tag{12}$$

4 Laboratory procedure

4.1 Measurements with the thermocouples

Three metallic conductors are supplied in the lab: 1) phosphor-bronze, 2) copper, and 3) constantan. Each conductor is contained inside a stainless steel tube with BNC connections at both ends. The Seebeck coefficients for these materials are not very large. Therefore, a liquid nitrogen (LN_2) dewar is supplied to provide a large temperature difference between LN_2 at $T_{\mathrm{LN}} \simeq 77\,\mathrm{K}$ and room temperature ($T_{\mathrm{RT}} \simeq 297\,\mathrm{K}$). The supplied thermometer can be used to monitor the room temperature ends of the tubes, but T_{LN} does not need to be measured. See Fig. 7 for a schematic of the measurement.

Thermocouple measurement procedure:

1. Measure and record the room temperature resistance of each conductor individually.
2. Combine the conductors together in pairs and measure the three thermovoltages using the LN_2 dewar.
3. Determine the three effective Seebeck coefficients:
   (a) $S_{\text{C-Cu}}$ for constantan and copper.
   (b) $S_{\text{PB-Cu}}$ for phosphor-bronze and copper.
   (c) $S_{\text{C-PB}}$ for constantan and phosphor-bronze.

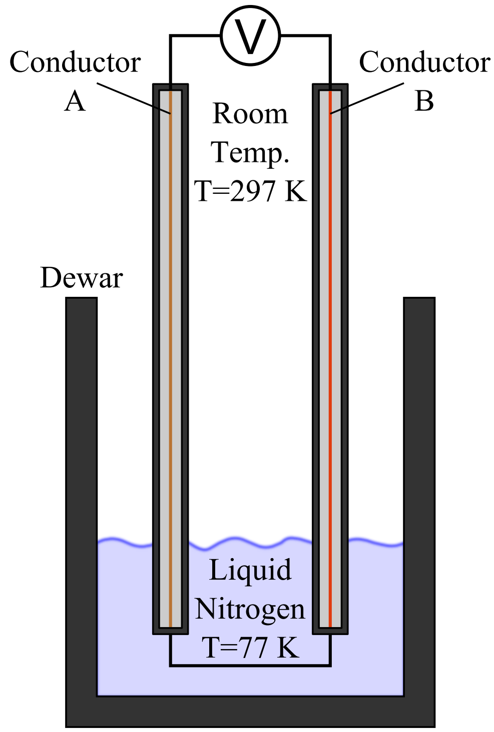

Figure 7: The two conductors, A and B, are enclosed inside two stainless steel tubes. They are connected together at one end and submerged in LN_2 dewar to cool them to $T_{\mathrm{LN}} \simeq 77\,\mathrm{K}$. The other ends remain at room temperature ($T_{\mathrm{RT}} \simeq 297\,\mathrm{K}$), and the voltage difference between the conductors is measured with a voltmeter.

4.2 Measurements with the Peltier device

The Peltier setup in the lab consists of a commercial Peltier device placed between two aluminium heat reservoirs as shown in Fig. 8. The "hot" reservoir is an aluminium block covered with thermal insulation. The "cold" reservoir is an aluminium block machined with cooling fins. A fan can be placed on the cold reservoir to improve its cooling power. This is recommended because it helps stabilize the temperature gradient.

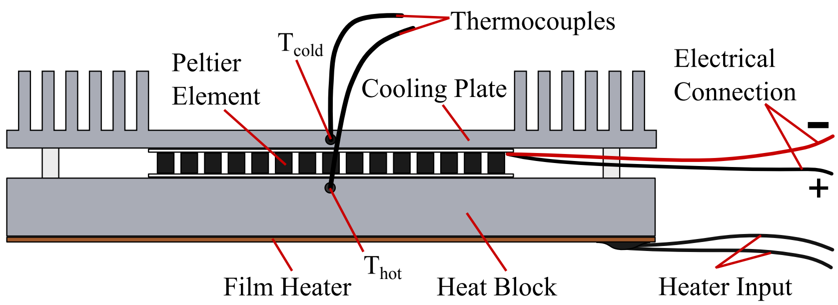

Figure 8: A schematic of the Peltier laboratory setup. The Peltier device is mounted between two aluminium masses. The bottom heat block can be heated with the film heater by applying a current to the heater inputs. The cooling plate on top can be cooled with the fan (not shown). The dual-channel thermometer probes (thermocouples) are inserted into two holes for measuring the temperature difference, $\Delta T = T_{\rm hot} - T_{\rm cold}$. The electrical connections of the Peltier device are used to apply and measure voltage and current.

4.2.1 Warm-up procedure

Before you start, get everything ready to record time-dependent data. Ideally you will record T_{cold}, T_{hot}, and V_{th} simultaneously. This is done best by heating *slowly* so that values do not change rapidly. You will measure ΔT with the two thermocouples embedded in the Al masses. Digital multimeters are available to measure electrical properties. The thermometer and the multimeters have a "hold" feature for pausing the measurements. This can help when recording time-dependent data.

1. Connect the thermometer probes and a voltmeter to the electrical connections of the Peltier device.
2. Place the fan on the cold block and turn it on.
3. Apply 12 V to the heater film. About 1 A of current will flow.
4. Measure T_{cold}, T_{hot}, and V_{th} as the system heats up.
5. It can take 30 min before the temperatures stabilize.

4.2.2 Constant temperature measurements

1. While waiting for the temperatures to stabilize, measure all the resistor values, R_{load}, in the circuit box and measure, R_{a}, the resistance of the ammeter.
2. Connect the circuit diagram as shown in Fig. 9. Make sure the voltmeter spans **both** the load resistor and the ammeter.
3. Once the temperatures have stabilized, record ΔT.
4. Measure V and I as a function of all R_{load} values.
5. Measure V and I when $R_{\text{load}} = 0$, that is, only use R_{a}.
6. Measure $V = V_{\text{th}}$ at $I = 0$, that is, V when $R_{\text{load}} = \infty$.
7. Measure ΔT again to see if there was a temperature drift.

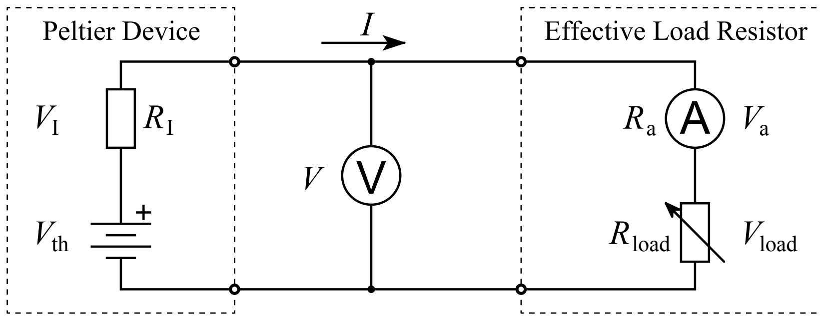

Figure 9: The circuit diagram for a Peltier device when connected to an electrical load. In addition to the internal resistance of the Peltier device, R_I, the setup includes a variable load resistance, R_load, and the resistance of the ammeter R_a. The temperature gradient generates the internal thermo-voltage, V_th. Voltages V_I, V_a, and V_load are created across resistances, R_I, R_a, and R_load, respectively. An ammeter is used to measure the current, I. A voltmeter is used to measure the voltage drop, V, across the total effective load resistance, $R_\mathrm{a} + R_\mathrm{load}$.

4.2.3 Cool-down procedure

While the system cools down, you will measure the thermal conductance.

1. Return the system to the open-circuit condition used during the warm-up procedure. That is, disconnect the ammeter and use only the voltmeter.

2. Get ready to measure time-dependent data.

3. Disconnect the film heater and start recording T_cold, T_hot, and V_th as the system cools down. This can take more than 30 min.

5 Data analysis

In your lab report you should discuss your results as well as observations that you deem relevant. Your data should be presented in an appropriate manner–that is, analyze your raw data and present it in an informative way. State and justify your assumptions. In addition, address following points (which will help you to analyze your data).

5.1 Thermocouple data analysis

1. How is the sign of the Seebeck coefficient determined?

2. You measured the three effective Seebeck coefficients, $S_{\text{C-Cu}}$, $S_{\text{PB-Cu}}$, and $S_{\text{C-PB}}$. Can you deduce the three intrinsic Seebeck coefficients S_{C}, S_{Cu}, and S_{PB}? Why or why not?

3. Is there a correlation between the measured resistances and the measured Seebeck coefficients?

4. Which of S_{C}, S_{Cu}, and S_{PB} should be the largest?

5.2 Peltier device data analysis

5.2.1 Time-dependent data

1. Using the warm-up and cool-down data, plot V_{th} as a function of $\Delta T = T_{\text{hot}} - T_{\text{cold}}$.

2. Fit the data with a linear function and extract the Seebeck coefficient.

3. Plot T_{hot} and T_{cold} as a function of time, t, measured during the cool-down.

4. Solve Eq. (12) and use it to fit your T_{hot} versus t cool-down data.

5. What is κ from the fit?

5.2.2 Power data

1. Calculate the measured Seebeck coefficient $S = V_{\text{th}}/\Delta T$, and compare it to the value found using your time-dependent data.

2. Collect the measured I-V pairs (including V_{th} at $I = 0$), and plot measured I as a function of measured V. Include a linear fit of this I-V data.

3. Extract I_{th} from the linear fit. Why cannot I_{th} be measured?

4. Using your I-V data, plot power, $P = IV$, as a function of V.

5. Derive a theoretical expression for P as a function of V, and use it to fit your data.

6. Had you measured a second set of I-V data using a 20 % larger value of ΔT, how would P versus V differ? This question is best answered with a sketch.

7. Plot P as a function of $R = R_{\text{a}} + R_{\text{load}}$, omitting the $R_{\text{load}} = \infty$ data point.

8. Derive a theoretical expression for P as a function of R, and use it to fit your data.

9. From the fit, what is the maximum power, P_{max}? At what value of R is P_{max} found? What is special about this value of R?

10. How does the measured maximum power, P_{max}, compare to the product of V_{th} and I_{th} from above?

11. What is the theoretical relationship between P_{max} and $I_{\text{th}}V_{\text{th}}$?

12. Two Peltier architectures are shown in Fig. 10 and 11 as alternatives to the architecture in Fig. 4. What are the advantages and disadvantages of these two alternative designs?

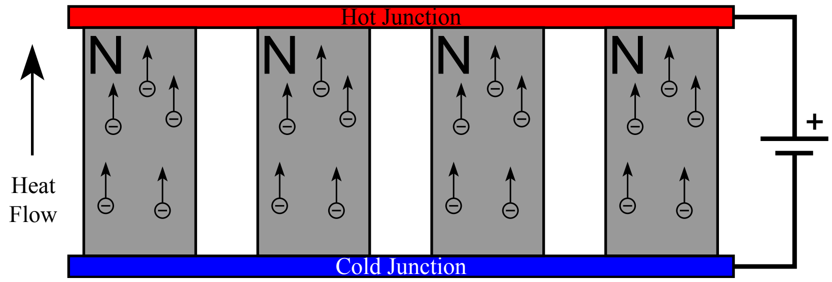

Figure 10: n-type Peltier elements are connected in parallel electrically.

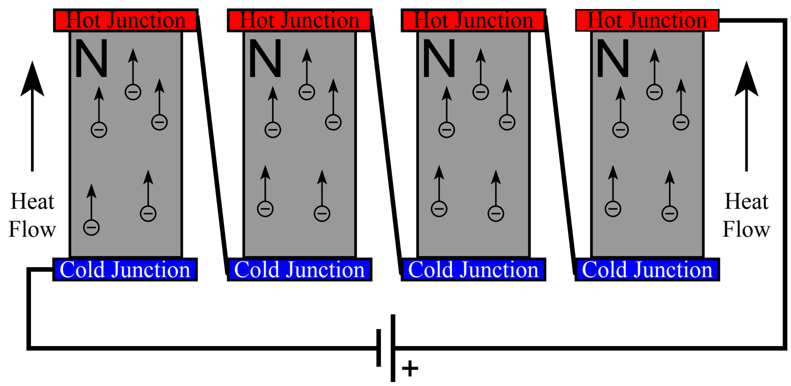

Figure 11: n-type Peltier elements are connected in series electrically.

5.3 Error Analysis

1. Of the two techniques used to measure the Seebeck coefficient of the Peltier device, which one is more accurate?
2. What is the main source of error of the time-dependent measurements?
3. Based on the assumptions used to derive Eq. (12), is your measured value of κ a lower bound or an upper bound for the true value of κ? Why?
4. What is the main source of error of the power measurements?
5. For measured values, such as P and V_{th}, how can the error be quantified?

References

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