Important Definitions for Thermoelectricity

Seebeck Effect (1822)
"When two dissimilar conductors, A & B, constitute a circuit, a current will flow as long as the junctions of the two conductors are at different temperatures."

\[ \alpha = \frac{dE}{dT} \]

A is positive to B if electrons flow from A to B at the colder junction

Peltier Effect (1834)
"When an electric current flows across a junction of two dissimilar conductors, heat is liberated or absorbed."

\[ P = \frac{dQ}{dI} \]

If electrons flow from A to B at the hotter junction, heat is liberated at the hot junction and absorbed at the cold junction
**Question:** Can we tell which Junction will absorb or release heat due to the Peltier effect?

\[ \alpha = \frac{dE}{dT} \]

The direction of the electron flow [which is opposite to the current flow by convention] at the hot junction in a Seebeck series is from the metal occuring later in the series to the metal occuring earlier in the series.

Bi, Ni, Co, Pd, Pt, Cu, Mn, Hg, Pb, Sn, Au, Zn, Cd, Fe, Sb, Te.

For example, if A=Cu and B=Fe, then the electron flow is as pictured.

For the Peltier effect (where \( Q \) is the heat absorbed):

\[ P_{AB} = \frac{dQ}{dI} \]

The direction of the Seebeck electron flow is opposite to the electrons flowing from the battery. (Otherwise we would have an unstable situation).

\[ P_{AB} \text{ is positive if } A \text{ is positive to } B \]

\[ P_{AB} = -P_{BA} \]
Important Definitions for Thermoelectricity

**Thompson Effect**

"The change of heat content of a single conductor of unit cross section when a quantity of electricity flows along it through a temperature gradient of 1°K"

![Diagram of single conductor with temperature gradient and current flow](image)

$$\sigma = \frac{(dQ/dI) \cdot (1/dT)}{P}$$

Electrons flowing against the thermal gradient will absorb energy whereas electrons flowing down the thermal gradient will lose energy
Thermoelectric Conversion

Seebeck found that the thermally induced emf, $E_{th}$, is related to the thermoelectric power, $\varepsilon$, as follows;

$$
\varepsilon = \left( \frac{dE_{th}}{dT} \right)
$$

The Seebeck coefficient, $\alpha_{xy}$, for materials x, and y is;

$$
\alpha_{xy}(T) = \left( \frac{dE_{xy}}{dT} \right) = \varepsilon_x(T) - \varepsilon_y(T)
$$

Want to combine high Seebeck coefficient with low electrical resistivity and low thermal conductivity.

Note the relationship between Seebeck ($\alpha$), Peltier ($P$), and Thompson ($\sigma$) effects.

$$
\alpha = \frac{dP_{ab}}{dT} + (\sigma_b - \sigma_a)
$$

Operating principles of thermoelectric converter (3 Figures)
The induced voltage is (with no current);

\[ V = \alpha_{n,p} \left( T_H - T_L \right) \]

where \( \alpha_{n,p} = |\alpha_n| + |\alpha_p| \)

Adding a load, \( L \)

\[ V_L = \alpha_{n,p} \left( T_H - T_L \right) - (R_n + R_p)I \]

The p leg total internal resistance is;

\[ R_p = \frac{r_p}{A_p} \]

and similarly for the n leg.

The total power output is;

\[ W_L = R_L I^2 \]

Using Kirchhoff’s law to calculate the current;

\[ \frac{\alpha_{n,p} \left( T_H - T_L \right)}{(R_L + \frac{R_p}{A_p} + R_n)} \]

We define the efficiency of the thermoelectric unit as

\[ \eta_{TE} = \frac{W_L}{Q_{in}} \]
The thermal power input, $Q_{in}$, consists of three components:

1.) Direct Heat Conduction Across the Semiconductor Elements,
2.) Thermal energy required to compensate for the Peltier cooling at the hot shoe,
3.) Minus the Joule heating in the load

Note that it is assumed that half the Joule heating occurs at each junction.

Substituting:

$$
\kappa_{p,n} = \frac{k_{pn} A_{pn}}{l_{pn}}
$$

we find that

$$
Q_{in} = (\kappa_p + \kappa_n)(T_H - T_L) + \alpha_{n,p} I T_H - \frac{(R_p + R_n) I^2}{2}
$$

Defining

$$
m = \frac{R_L}{(R_p + R_n)}
$$

Then

$$
\eta_{TE} = \eta_{th} \cdot \eta_{mat}
$$

where;

$$
\eta_{th} = \frac{(T_H - T_L)}{T_H} \text{(Carnot)}
$$

and
\[\eta_{\text{mat}} = \left[ \left( m + 1 \right) - \frac{\eta_{\text{th}}}{2} + \frac{(m + 1)^2 \left( R_p + R_n \right) \left( \kappa_p + \kappa_n \right)}{\alpha_{n,p}^2 T_H} \right] \]

This term must be minimized, i.e.,

\[
d \left[ (R_p + R_n) \left( \kappa_p + \kappa_n \right) \right]^2 = 0
\]

When this is done,

\[m_{\text{opt}} = \sqrt{1 + Z \bar{T}}\]

Where

\[\bar{T} = \left( \frac{T_H + T_L}{2} \right)\]

and

\[Z = \frac{\left( |\alpha_n| + |\alpha_p| \right)^2}{\left[ \sqrt{\kappa_n R_n} + \sqrt{\kappa_p R_p} \right]^2}\]
at the optimum conditions

\[
(\eta_{TE})_{opt} = \eta_{th} \frac{(m_{opt} - 1)}{\left(\frac{T_L}{T_H} + m_{opt}\right)}
\]

If the p and n type materials have the same thermal conductivities and electrical resistivities, then the figure of merit becomes;

\[
Z = \frac{\alpha^2}{k\rho}
\]

Typical Figure of Merit Values @ 300°K

<table>
<thead>
<tr>
<th>Material</th>
<th>Seebeck Coeff.</th>
<th>FOM(Z)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metals</td>
<td>5 µV/°K</td>
<td>3 x 10^{-6} °K</td>
</tr>
<tr>
<td>Semicond.</td>
<td>200 µV/°K</td>
<td>2 x 10^{-3} °K</td>
</tr>
<tr>
<td>Insulators</td>
<td>1000 µV/°K</td>
<td>5 x 10^{-17} °K</td>
</tr>
</tbody>
</table>
A SIMPEL THERMOCOUPLE CIRCUIT—DEPICTING THE SEEBECK EFFECT

Fig. 5.27 A simple thermocouple circuit—depicting the Seebeck effect.
Fig. 5.28  Operating principle of the thermoelectric converter [2].
Fig. 5.29  Idealized thermoelectric converter [1].
Fig. 5.30  Figure-of-merit of selected thermoelectric materials
FIG. 3-4—Properties of 95% GeTe + 50% Bi₂Te₃
Silicon-Germanium Alloys at Room Temperature

Thermal Conductivity (Watt/cm°C) vs. Atomic % Silicon

- Silicon (Si)
- Germanium (Ge)
<table>
<thead>
<tr>
<th>Metal</th>
<th>ohm-cm</th>
<th>$\alpha$ ($\mu$V/$^\circ$C)</th>
<th>Carrier Concentration ($cm^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>1330</td>
<td>$-176$</td>
<td>$5.8 \times 10^{16}$</td>
</tr>
<tr>
<td>Sn</td>
<td>1300</td>
<td>$-163$</td>
<td>$6.4 \times 10^{18}$</td>
</tr>
<tr>
<td>Ge</td>
<td>1200</td>
<td>$-174$</td>
<td>$5.9 \times 10^{18}$</td>
</tr>
<tr>
<td>Fe</td>
<td>1080</td>
<td>$-186$</td>
<td>$5.3 \times 10^{18}$</td>
</tr>
<tr>
<td>Co</td>
<td>1130</td>
<td>$-172$</td>
<td>$6.1 \times 10^{18}$</td>
</tr>
<tr>
<td>Ni</td>
<td>1200</td>
<td>$-178$</td>
<td>$5.7 \times 10^{18}$</td>
</tr>
<tr>
<td>Ni</td>
<td>1355</td>
<td>$-168$</td>
<td>$6.3 \times 10^{18}$</td>
</tr>
<tr>
<td>Pt</td>
<td>1300</td>
<td>$-179$</td>
<td>$5.6 \times 10^{18}$</td>
</tr>
<tr>
<td>Mg</td>
<td>1120</td>
<td>$-178$</td>
<td>$5.7 \times 10^{18}$</td>
</tr>
<tr>
<td>Nb</td>
<td>1920</td>
<td>$-146$</td>
<td>$\sim 8 \times 10^{18}$</td>
</tr>
<tr>
<td>Nb</td>
<td>2050</td>
<td>$-141$</td>
<td>$\sim 9 \times 10^{18}$</td>
</tr>
<tr>
<td>Bi</td>
<td>1600</td>
<td>$-99$</td>
<td>$\sim 2 \times 10^{19}$</td>
</tr>
<tr>
<td>Bi</td>
<td>1450</td>
<td>$-126$</td>
<td>$\sim 1 \times 10^{19}$</td>
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<tr>
<td>Au</td>
<td>10.5</td>
<td>$+142$</td>
<td>$\ldots \ldots$</td>
</tr>
<tr>
<td>Au</td>
<td>9.9</td>
<td>$+253$</td>
<td>$\ldots \ldots$</td>
</tr>
<tr>
<td>Ag</td>
<td>206</td>
<td>$+204$</td>
<td>$5.5 \times 10^{18}$</td>
</tr>
<tr>
<td>Ag</td>
<td>207</td>
<td>$+15.6$</td>
<td>$\ldots \ldots$</td>
</tr>
<tr>
<td>Cu</td>
<td>60.5</td>
<td>$+413$</td>
<td>$4.7 \times 10^{17}$</td>
</tr>
<tr>
<td>Cu</td>
<td>54.5</td>
<td>$+404$</td>
<td>$\ldots \ldots$</td>
</tr>
<tr>
<td>In</td>
<td>350</td>
<td>$-223$</td>
<td>$\ldots \ldots$</td>
</tr>
<tr>
<td>In</td>
<td>720</td>
<td>$-216$</td>
<td>$\ldots \ldots$</td>
</tr>
<tr>
<td>Al</td>
<td>239</td>
<td>$+16.5$</td>
<td>$\ldots \ldots$</td>
</tr>
<tr>
<td>Zn</td>
<td>208</td>
<td>$+227$</td>
<td>$\ldots \ldots$</td>
</tr>
<tr>
<td>Zn</td>
<td>185</td>
<td>$+257$</td>
<td>$\ldots \ldots$</td>
</tr>
<tr>
<td>Cd</td>
<td>60</td>
<td>$+59$</td>
<td>$\ldots \ldots$</td>
</tr>
<tr>
<td>Cd</td>
<td>85</td>
<td>$+196$</td>
<td>$\ldots \ldots$</td>
</tr>
</tbody>
</table>
TABLE 4-2—Absolute thermoelectric power (ATP) of some elements (microvolts per degree C) (adapted with permission from N. Cusack and P. Kendall in Proceedings of the Physical Society, Vol. 72, 1958, p. 898. copyright by the Institute of Physics. Techno House, Redcliffe Way, Bristol BS1 6NX, England).

<table>
<thead>
<tr>
<th>Temperature, K</th>
<th>Cu</th>
<th>Ag</th>
<th>Au</th>
<th>Pt</th>
<th>Pd</th>
<th>W</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>1.19</td>
<td>0.73</td>
<td>0.82</td>
<td>4.29</td>
<td>2.00</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>200</td>
<td>1.29</td>
<td>0.85</td>
<td>1.34</td>
<td>-1.27</td>
<td>-4.85</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>273</td>
<td>1.70</td>
<td>1.38</td>
<td>1.79</td>
<td>-4.45</td>
<td>-9.00</td>
<td>0.13</td>
<td>4.71</td>
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<tr>
<td>300</td>
<td>1.84</td>
<td>1.51</td>
<td>1.94</td>
<td>-5.28</td>
<td>-9.99</td>
<td>1.07</td>
<td>5.57</td>
</tr>
<tr>
<td>400</td>
<td>2.34</td>
<td>2.08</td>
<td>2.46</td>
<td>-7.83</td>
<td>-13.00</td>
<td>4.44</td>
<td>8.52</td>
</tr>
<tr>
<td>500</td>
<td>2.83</td>
<td>2.82</td>
<td>2.86</td>
<td>-9.89</td>
<td>-16.03</td>
<td>7.53</td>
<td>11.12</td>
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<tr>
<td>600</td>
<td>3.33</td>
<td>3.72</td>
<td>3.18</td>
<td>-11.66</td>
<td>-19.06</td>
<td>10.29</td>
<td>13.27</td>
</tr>
<tr>
<td>700</td>
<td>3.83</td>
<td>4.72</td>
<td>3.43</td>
<td>-13.31</td>
<td>-22.09</td>
<td>12.66</td>
<td>14.94</td>
</tr>
<tr>
<td>1000</td>
<td>5.36</td>
<td>7.95</td>
<td>3.85</td>
<td>-17.86</td>
<td>-31.18</td>
<td>17.57</td>
<td>17.16</td>
</tr>
<tr>
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<td>9.06</td>
<td>3.88</td>
<td>-19.29</td>
<td>-34.21</td>
<td>18.53</td>
<td>17.08</td>
</tr>
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<td>...</td>
<td>3.78</td>
<td>-22.06</td>
<td>-40.27</td>
<td>19.53</td>
<td>15.92</td>
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<td>...</td>
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<td>-23.41</td>
<td>-43.30</td>
<td>19.60</td>
<td>14.94</td>
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<td>1600</td>
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<td>...</td>
<td>...</td>
<td>-26.06</td>
<td>-49.36</td>
<td>18.97</td>
<td>12.42</td>
</tr>
<tr>
<td>1800</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>-28.66</td>
<td>-55.42</td>
<td>17.41</td>
<td>9.52</td>
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<td>...</td>
<td>...</td>
<td></td>
<td>12.01</td>
<td>4.30</td>
</tr>
<tr>
<td>2400</td>
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<td>...</td>
<td>...</td>
<td>...</td>
<td></td>
<td>8.39</td>
<td>2.87</td>
</tr>
</tbody>
</table>

Fig. 8.27 Changes in the electrical resistivity and Seebeck coefficient of $n$-type SiGe thermoelectric material with time [24].
FIG. 14-11. Material efficiency as a function of $T_1$, for the case $T_2 = 300^\circ\text{K}$. 

- $Z_{\text{opt}} = 5 \times 10^{-3}$
- $Z_{\text{opt}} = 10^{-3}$
FIG. 14-12. Variation of thermal efficiency with $T_1$ and $Z_{opt}$ for a thermoelectric converter and a Carnot cycle, for the case $T_2 = 300^\circ\text{K}$. 
POWER CONVERSION SYSTEMS

CONVERTERS

DIRECT

THERMOELECTRIC
- Pb-Te
- Si-Ge
- SiGe-GaP
- SELENIDE
- ADVANCED

THERMIONIC
- IN-CORE
- OUT-CORE

DYNAMIC

BRAYTON
- SUPER ALLOY
- REFRACTORIES
- CERAMICS

RANKINE
- ORGANIC
- POTASSIUM

STIRLING
- PHILLIPS
- FREE PISTON