## S10.D. Thermoelectricity

Read Reichl's introductory remarks.
See §4.3 of O.Madelung, "Introduction to Solid State Theory" for the conventional approach.

Thermal couple: temperature measuring device consisting of joining two different metal bars to form a closed circuit of two junctions.

As the name implies, the subject thermoelectricity deals with the transport of charge (or heat) caused by a temperature gradient (or electric field). It is exemplified by the following phenomena.

Seebeck effect: temperature difference across the junction of two different metals creates an electromotive force (EMF).

Peltier effect: electric current creates temperature difference between the two junctions of a thermal couple.

Thomson effect: heat is emitted or absorbed if a current is passed through a wire maintained at a temperature gradient.

These effects are easily explained by treating a metal as a neutral system consisting of a fluid of electrons moving in a background of immobile positive ions.

Let

$\mu_{\text{el}} = \mu_{\text{el}}(T)$ = chemical potential of electrons

$\mu_{\text{el}}^e = \mu_{\text{el}} - F\phi$ = electrochemical potential of electrons

$\phi$ = electric potential $\qquad$ $F$ = Faraday's constant

$\boldsymbol{J}_q$ = heat flux $\qquad$ $\boldsymbol{J}_{\text{el}}$ = electron flux

Since the thermoelectric effects usually involve two types of metal, temperature gradient, and electric field, we are dealing with an entropy production [see (10.179a)]

$$T\sigma = -\boldsymbol{J}_S \cdot \nabla_{\boldsymbol{r}} T - \boldsymbol{J}_{\text{el}} \cdot \nabla_{\boldsymbol{r}} \mu_{\text{el}}^e \qquad \text{[ molar version ]} \qquad (10.274)$$

$$= -\boldsymbol{J}_S \cdot \nabla_{\boldsymbol{r}} T - \boldsymbol{J}_{\text{el}} \cdot (\nabla_{\boldsymbol{r}} \mu_{\text{el}} - F\boldsymbol{E}) \qquad (10.274a)$$

which corresponds to the generalized Ohm's law

$$\begin{pmatrix} \boldsymbol{J}_S \\ \boldsymbol{J}_{\text{el}} \end{pmatrix} = -\begin{pmatrix} L_{SS} & L_{SE} \\ L_{ES} & L_{EE} \end{pmatrix} \begin{pmatrix} \nabla_{\boldsymbol{r}} T \\ \nabla_{\boldsymbol{r}} \mu_{\text{el}}^e \end{pmatrix} \qquad (10.275\text{-}6)$$

$$= -\begin{pmatrix} L_{SS} & L_{SE} \\ L_{ES} & L_{EE} \end{pmatrix} \begin{pmatrix} \nabla_{\boldsymbol{r}} T \\ \nabla_{\boldsymbol{r}} \mu_{\text{el}} - F\boldsymbol{E} \end{pmatrix} \qquad (10.276a)$$

The Onsager's relations require

$$L_{SE} = L_{ES}$$

Contact potential: potential difference across the junction of two different metals.

### S10.D.1. The Peltier Effect

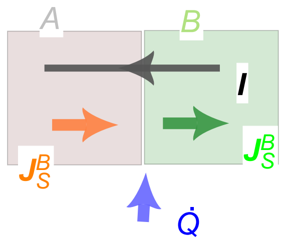


Fig.10.5a

Consider first a current passing from a metal wire of metal $A$ into another of metal $B$ [see Fig.10.5a]. If we keep a uniform temperature throughout the wires, $\nabla T = 0$, and (10.274-6) becomes, for each wire,

$$T\,\sigma = -\boldsymbol{J}_{\text{el}} \cdot (\nabla_{\boldsymbol{r}} \mu_{\text{el}} - F\boldsymbol{E})$$

$$\boldsymbol{J}_S = -L_{\text{SE}} (\nabla_{\boldsymbol{r}} \mu_{\text{el}} - F\boldsymbol{E})$$

$$\boldsymbol{J}_{\text{el}} = -L_{\text{EE}} (\nabla_{\boldsymbol{r}} \mu_{\text{el}} - F\boldsymbol{E})$$

$$\rightarrow \qquad \boldsymbol{J}_S = \frac{L_{\text{SE}}}{L_{\text{EE}}} \boldsymbol{J}_{\text{el}} = -\frac{L_{\text{SE}}}{F\,L_{\text{EE}}} \boldsymbol{I} \qquad (10.279\text{a})$$

where

$\boldsymbol{I} = -F\,\boldsymbol{J}_{\text{el}}$ = electric current density due to the electron flux.

The entropy transport parameter ( or Seebeck coefficient ) is defined as

$$S^* = \frac{J_S}{J_{\text{el}}} = \frac{L_{\text{SE}}}{L_{\text{EE}}} \qquad (10.279)$$

For two wires of the same uniform cross sections, all fluxes are perpendicular to the junction. Charge conservation demands

$$\boldsymbol{J}_{\text{el}}^A = \boldsymbol{J}_{\text{el}}^B = \boldsymbol{J}_{\text{el}}$$

so that (10.279a) gives

$$\boldsymbol{J}_S^A = S_A^*\,\boldsymbol{J}_{\text{el}} = -\frac{S_A^*}{F} \boldsymbol{I} \qquad\qquad \boldsymbol{J}_S^B = S_B^*\,\boldsymbol{J}_{\text{el}} = -\frac{S_B^*}{F} \boldsymbol{I}$$

Thus,

$$S_A^* \neq S_B^* \quad \rightarrow \quad \boldsymbol{J}_S^A \neq \boldsymbol{J}_S^B$$

$\rightarrow$ Heat is generated (or absorbed) at the junction

Let $\boldsymbol{I}$ be flowing from $B$ to $A$ and denote its magnitude as $I_{BA}$. Hence,

$$\boldsymbol{I} = I_{BA}\,\hat{\boldsymbol{n}}_{BA} \qquad \boldsymbol{J}_S^A = -\frac{S_A^*}{F} I_{BA}\,\hat{\boldsymbol{n}}_{BA} \qquad \boldsymbol{J}_S^B = -\frac{S_B^*}{F} I_{BA}\,\hat{\boldsymbol{n}}_{BA}$$

where $\hat{\boldsymbol{n}}_{BA}$ is the unit vector pointing from $B$ to $A$ across the junction.

If $|\boldsymbol{J}_S^B| > |\boldsymbol{J}_S^A|$, heat is absorbed at the junction. Let $\dot{Q}$ be the rate of heat absorption per unit area. Then

$$\dot{Q} = T\left(\boldsymbol{J}_S^B - \boldsymbol{J}_S^A\right) \cdot (-\hat{\boldsymbol{n}}_{BA}) = \frac{T}{F}(S_B^* - S_A^*)\,I_{BA} \qquad (10.279\text{b})$$

where $\dot{Q} \overset{>}{\underset{<}{}} 0$ means heat is $\begin{matrix}\text{absorbed}\\ \text{emitted}\end{matrix}$ at the junction.

Note that $\dot{Q}$ is a scalar with units

$$[\dot{Q}] = [\,\text{heat}/(\text{area} \cdot \text{time})\,]$$

Since the material labels are dummies, (10.279b) can be written in a more general form

$$\dot{Q} = \frac{T}{F}\left(S_j^* - S_k^*\right) I_{jk} \qquad j, k = A, B \qquad (10.279c)$$

for a junction with electric current flowing from metal $j$ to $k$.

The Peltier heat is defined as

$$\bar{\pi} \equiv \left(\frac{\dot{Q}}{I}\right)_{\nabla T = 0} \qquad (10.277)$$

= rate of heat absorption per unit area per unit electric current density

$$= \frac{T}{F}\left(S_j^* - S_k^*\right) \qquad \text{for } I_{jk} \qquad (10.280)$$

The Peltier coefficient $\Pi$ is defined by

$$\dot{Q} = \left(\Pi_j - \Pi_k\right) I \qquad (10.280a)$$

Comparing with (10.280) gives

$$\Pi_j = T\, S_j^* \qquad (10.280b)$$

which is known as Thomson's first relation.

The circuit for measuring the Peltier effect is shown in Fig.10.5b. The heat absorption directions are for the case $\dot{Q} > 0$, $S_B^* < S_A^*$.

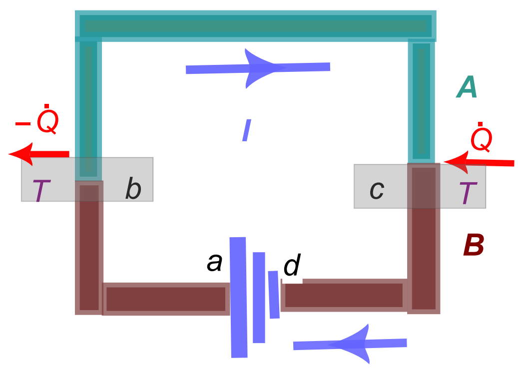


Fig.10.5b.

See Reichl's Fig.10.5 for the experimental configurations for measuring the Peltier effect.

## S10.D.2. The Seebeck Effect

A typical circuit for measuring the Seebeck effect is shown in Fig.10.6. The two junctions, $b$ & $c$, between the wires of different metals, $A$ & $B$, are kept at different temperatures $T$ & $T + \Delta T$. The circuit is open so that the potential at points $a$ & $d$ can be measured by a potentiometer at temperature $T_0$.

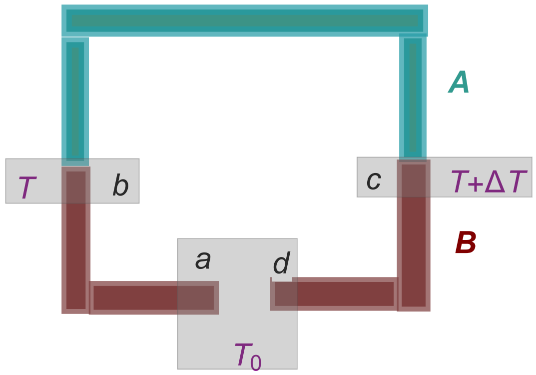


Fig.10.6.

Setting $\boldsymbol{J}_{\text{el}} = 0$ in (10.274-6) gives

$$T\,\sigma = -\,\boldsymbol{J}_S \cdot \nabla_{\boldsymbol{r}} T$$

$$\boldsymbol{J}_S = -L_{\text{SS}}\,\nabla_{\boldsymbol{r}} T - L_{\text{SE}}\,\nabla_{\boldsymbol{r}} \mu_{\text{el}}^e$$

$$0 = -L_{\text{ES}}\,\nabla_{\boldsymbol{r}} T - L_{\text{EE}}\,\nabla_{\boldsymbol{r}} \mu_{\text{el}}^e$$

→ $$\nabla_{\boldsymbol{r}} \mu_{\text{el}}^e = -\frac{L_{\text{ES}}}{L_{\text{EE}}}\,\nabla_{\boldsymbol{r}} T$$

$$= -\frac{L_{\text{SE}}}{L_{\text{EE}}}\,\nabla_{\boldsymbol{r}} T \qquad \text{[ Onsager's relations used. ]}$$

$$= -S^*\,\nabla_{\boldsymbol{r}} T \qquad \text{[ (10.279) used. ]} \qquad (10.281)$$

Integrating along the circuit from point $a$ to $d$ gives

$$\int_a^d d\,\boldsymbol{r} \cdot \nabla_{\boldsymbol{r}} \mu_{\text{el}}^e = \int_a^d d\,\mu_{\text{el}}^e = (\mu_{\text{el}} - F\,\phi)_a^d = -F\,(\,\phi_d - \phi_a) \qquad (10.282a)$$

$$= -\int_a^d d\,\boldsymbol{r} \cdot S^*\,\nabla_{\boldsymbol{r}} T \qquad \text{[ (10.281) used. ]}$$

$$= -\left[\int_a^b d\,T\,S_B^* + \int_b^c d\,T\,S_A^* + \int_c^d d\,T\,S_B^*\right]$$

$$= -\left[\int_{T_0}^T d\,T\,S_B^* + \int_T^{T+\Delta T} d\,T\,S_A^* + \int_{T+\Delta T}^{T_0} d\,T\,S_B^*\right]$$

$$= -\left[\int_{T+\Delta T}^T d\,T\,S_B^* + \int_T^{T+\Delta T} d\,T\,S_A^*\right]$$

$$= \int_T^{T+\Delta T} d\,T\,(S_B^* - S_A^*) \qquad (10.285)$$

→ $$\phi_{a\,d} = \phi_a - \phi_d = \frac{1}{F}\int_T^{T+\Delta T} d\,T\,(S_B^* - S_A^*) \qquad (10.286)$$

∴ $$\frac{d\,\phi_{a\,d}}{d\,T} = \frac{S_B^* - S_A^*}{F}$$

$$= \frac{\pi}{T} \qquad \text{[ (10.280) used. ]} \qquad (10.287)$$

Since (10.287) was obtained using Onsager's relations [see derivation of (10.281)], checking it against experimental data provides a test on the Onsager relations. Excellent agreement can be found in Reichl's Table 10.6.

## S10.D.3. Thomson Heat

Since the Thomson effect involves only one type of metal subject to both a temperature gradient and an electric field, (10.274-6) become

$$T\,\sigma = -\boldsymbol{J}_S \cdot \nabla_{\boldsymbol{r}} T + F \boldsymbol{J}_{\text{el}} \cdot \boldsymbol{E} \tag{10.288a}$$

which corresponds to the generalized Ohm's law

$$\begin{pmatrix} \boldsymbol{J}_S \\ \boldsymbol{J}_{\text{el}} \end{pmatrix} = -\begin{pmatrix} L_{\text{SS}} & L_{\text{SE}} \\ L_{\text{ES}} & L_{\text{EE}} \end{pmatrix} \begin{pmatrix} \nabla_{\boldsymbol{r}} T \\ -F\boldsymbol{E} \end{pmatrix} = \begin{pmatrix} -L_{\text{SS}} \nabla_{\boldsymbol{r}} T + L_{\text{SE}} F \boldsymbol{E} \\ -L_{\text{ES}} \nabla_{\boldsymbol{r}} T + L_{\text{EE}} F \boldsymbol{E} \end{pmatrix} \tag{10.288b}$$

Eliminating $\boldsymbol{E}$ gives

$$L_{\text{EE}} \boldsymbol{J}_S - L_{\text{SE}} \boldsymbol{J}_{\text{el}} = -(L_{\text{EE}} L_{\text{SS}} - L_{\text{SE}} L_{\text{ES}}) \nabla_{\boldsymbol{r}} T$$

$$\rightarrow \quad \boldsymbol{J}_S = \frac{L_{\text{SE}}}{L_{\text{EE}}} \boldsymbol{J}_{\text{el}} - \frac{\mathcal{L}}{L_{\text{EE}}} \nabla_{\boldsymbol{r}} T \qquad \mathcal{L} = L_{\text{EE}} L_{\text{SS}} - L_{\text{SE}} L_{\text{ES}} = \det \mathbb{L}$$

$$= S^* \boldsymbol{J}_{\text{el}} - \frac{\mathcal{L}}{L_{\text{EE}}} \nabla_{\boldsymbol{r}} T \tag{10.288c}$$

Putting this into the entropy balance equation

$$\frac{\partial s}{\partial t} + \nabla_{\boldsymbol{r}} \cdot \boldsymbol{J}_S = 0$$

$$\rightarrow \quad \frac{\partial s}{\partial t} = -S^* \nabla_{\boldsymbol{r}} \cdot \boldsymbol{J}_{\text{el}} - \boldsymbol{J}_{\text{el}} \cdot \nabla_{\boldsymbol{r}} S^* + \nabla_r \cdot \left( \frac{\mathcal{L}}{L_{\text{EE}}} \nabla_{\boldsymbol{r}} T \right)$$

where $s$ is the entropy density.

Since $S^*$ is a function of $T$, the 2nd term on the right corresponds to a heat generation

$$\dot{q} = -T \frac{d S^*}{d T} \boldsymbol{J}_{\text{el}} \cdot \nabla_{\boldsymbol{r}} T \tag{10.288d}$$

which is called the Thomson heat rate since it is non-zero only when both an electric current and temperature gradient are present (conditions for the Thomson effect).

The Thomson's coefficient $K$ is defined by

$$\dot{q} = -K\, \boldsymbol{J}_{\text{el}} \cdot \nabla_{\boldsymbol{r}} T \tag{10.288e}$$

Comparing with (10.288d) gives

$$K = T \frac{d S^*}{d T} \tag{10.288f}$$

which is known as the Thomson's second relation.

Consider a wire of length $L$ and cross section $A$. For small temperature difference $\Delta T$ between the ends of the wire, (10.288e) can be written as

$$\dot{q} = -K \frac{I}{A} \frac{\Delta T}{L}$$

$$\rightarrow \quad \dot{Q} = -K\, I\, \Delta T = \text{total heat rate of wire}$$

$$\sigma_A = \frac{1}{I} \lim_{\Delta T \to 0} \frac{\dot{Q}}{\Delta T}$$

$$= \frac{1}{I} \frac{d \dot{Q}}{d T} \tag{10.288}$$

is called by Reichl the Thomson heat.