Thermoelectric Effect Peltier Seebeck and Thomson

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Abstract: A simple model system is generated to derive explicit thermoelectric effect expressions for Peltier, Seebeck and, Thomson. The model applies an n-type semiconductor junction with two different charge-carrier concentration n_L and n_R. Peltier effect and Seebeck effect are calculated by applying a reversible closed Carnot cycle, and Thomson effect by the Boltzmann transport equation.

Peltier's heat rate for the electric current I is: $dQ/dt = (\Pi_A - \Pi_B)I$.

Peltier's coefficients calculated by the model are: $\Pi_A = kTln(n_L)$ $\Pi_B = kTln(n_R)$.

Seebeck's EMF of two junctions at different temperatures T_H and T_C is: $V = -S(T_H - T_C)$.

Seebeck's coefficient calculated by the model is: $S = k \ln(n_L/n_R)$.

Thomson's heat rate for the current density J is: $dq/dt = -K J \, \Delta T$.

Thomson's coefficient calculated by the model is: $K = (3/2)k$.

Peltier effect and Seebeck effect are reversible thermodynamic processes.

Thomson's (Kelvin's) second relation $K = T \, dS/dT$ does not comply with the calculated coefficients.

1. Background

The Peltier effect is the production or absorption of heat at a junction between two different conductors when electric charge flows through it [1]. The rate dQ/dt of heat produced or absorbed at a junction between conductors A and B is:

$$dQ/dt = (\Pi_A - \Pi_B)I, \tag{1}$$

where I is the electric current and Π_A, Π_B are Peltier's coefficients of the conductors.

The Seebeck effect is the production of EMF, electromotive force, with junctions of two different conductors. Two junctions connected back to back are held at two different temperatures T_H and T_C and an EMF V appears between their free contacts:

$$V = -S(T_H - T_C). \tag{2}$$

S is Seebeck's coefficient.

The Thomson effect is the production or absorption of heat along a conductor with temperature gradient ΔT when electric charge flows through it [1]. The heat dq/dt produced or absorbed along a conductor segment is:

$$dq/dt = -K J \Delta T, \tag{3}$$

where J is the current density, and K is Thomson's coefficient.
The three coefficients are related by Thomson relations (Kelvin relations).

$$\Pi = T S, \tag{4}$$

where: $\Pi = \Pi_A - \Pi_B$, and:

$$K = T dS/dT. \tag{5}$$

Reference [1] includes links to updated literature on thermoelectric effects.

Although these three main thermoelectric effects have been well known for a long time, it is difficult to find explicit expressions in the literature for their three coefficients in terms of more fundamental physical quantities, though some calculations do exist [2]. Advanced sources apply Onsager's theory of irreversible processes to calculate the coefficients in terms of Onsager's linear coefficients [3]-[5]. However, these coefficients are not more fundamental than the thermoelectric coefficients, and they are also difficult to find.

The purpose of this page is to generate a simple system and calculate for it explicit expressions of the thermoelectric coefficients.

Electrons in conductors occupy energy levels in pairs of opposite spins. Lower levels are fully occupied and upper levels are empty and the level population is determined by Fermi-Dirac statistics. In order to move in the conductor an electron that occupies some level must be scattered to an empty level. For this reason low energy electrons do not contribute to electric current because their nearby levels are all occupied. The Fermi level is the energy where the electron occupation probability is 0.5. Only electrons with energies near this level contribute to the current. The Maxwell-Boltzmann distribution of the electron velocity is not applicable in this case.

Semiconductor crystals are a special case [4], [6]. A fully occupied valence band is separated from an empty conduction band in these materials by a forbidden gap without energy levels in it. If the gap is large enough direct thermal excitation of electrons from band to band is negligible and the material will be an insulator. Introduction of donors to the material will add electrons to the conduction band and make it n-type. Acceptors will add holes to the valence band and make it p-type. A donor atom has an extra electron, compared to a crystal atom, at a level just below the bottom of the conduction band and it will be thermally transferred to the conduction band where it is free to move. An acceptor atom has one less electron just above the valence band. An Electron caught by the acceptor will leave a free moving hole in the valence band. Practically, if the donor level is shallow, then all the donors will be ionized in n-type material. So that the density of free moving electrons is equal to the donor density. Similarly, the density of free moving holes is equal to the acceptor density in p-type material.

If the doping levels are not too high the charge carrier density, either of electrons or holes, will be lower than the energy level density within the bands. Each carrier may be scattered to many neighboring empty levels so that practically it is a free particle. The Maxwell-Boltzmann velocity distribution will then be applicable to the carriers.

2. Contact Potential

Consider two pieces of n-type semiconductor with higher n_L and lower n_R electron densities, where n_L and n_R are equal to the corresponding donor densities. Therefore, these densities are temperature independent. If the two pieces are brought into contact to form a junction, electrons will start to diffuse from the left higher n_L to the right lower n_R density. The diffusion generates a space charge region, electric field, and potential difference V_c between the two pieces, that stops further electron diffusion. V_c is the contact potential. It is not directly measureable by a voltmeter, for example, because the voltmeter probes make their own contact potentials with the two ends of the junction. The sum of all the junction potentials is then zero.

If the two pieces are separated after being in contact, their capacity will drop, the voltage between them will go up and it will then be measureable. Methods that measure the contact potential are based on this phenomenon [7]-[8]. The contact potential is calculated in Appendix-B (27)):

$$e^{-eV_c/kT} = n_R/n_L, \tag{6}$$

or (28):

$$V_c = (kT/e)\ln(n_L/n_R). \tag{7}$$

e is the electron charge and k is Boltzmann's constant.

3. Charge Flow in a Semi-Conductor with Temperature Gradient

The electric current through a semi-conductor with a temperature gradient is calculated in appendix-C by applying Boltzmann transport equation. This equation yields expressions for the currents that are similar to Onsager's linear equations that relate forces to flows, but with the advantage that there are no unknown linear coefficients. If the charge carrier density does not depend on the position, then the electric current J_q will be (37):

$$J_q = \sigma[E - (k/2e)dT/dx], \tag{8}$$

where σ is the electrical conductivity (40) and E is the electric field.

For zero current (8) may be integrated to yield:

$$V = (k/2e)\Delta T. \tag{9}$$

By using the values of k and e a voltage gradient of 43 microvolt/degree, independent of the charge density, is developed between the cold and hot ends of the conductor.

4. Thermoelectric Effects

A. Peltier Effect: Heating or cooling a junction by electric current.

Carnot's original cycle involves heat transformation between a hot T_H bath and a cold T_C bath by a gas in a cylinder equipped with a moving piston. Heat partly flows from a hot bath to a cold bath, and partly is transformed to mechanical work in a reversible four step closed cycle. Carnot knew nothing about the chemical potential, not even about entropy, since both of them belonged to the far future in his time. Never the less, he correctly analyzed his cycle without these terms. At each step of the cycle macroscopic mechanical work of the moving piston is transformed to microscopic thermal movement of the gas particles by elastic collisions between the particles and the piston [9].

Similarly, the macroscopic electrical work of a power source is transformed in a junction to microscopic thermal heat by acceleration of charge carriers in the electric field. Electrons that cross a junction will be either slowed, or accelerated by a contact potential difference V_c according to the directions of their velocity vector relative the electric field. Thus, they will absorb or deliver an amount of heat eV_c to the junction, where V_c is given by eq. (7). Peltier coefficients (2) are then:

$$\Pi_A = kTln(n_L) \qquad \Pi_B = kTln(n_R). \qquad (10)$$

B. Seebeck Effect: Direct power generation from temperature difference.

Direct conversion of thermal to electrical energy is analyzed by applying the original Carnot method to a junction device operating in a reversible four step closed cycle. The "Carnot machine" shown in figure-1 has some resemblance to devices that are used to measure contact potential [7]-[8].
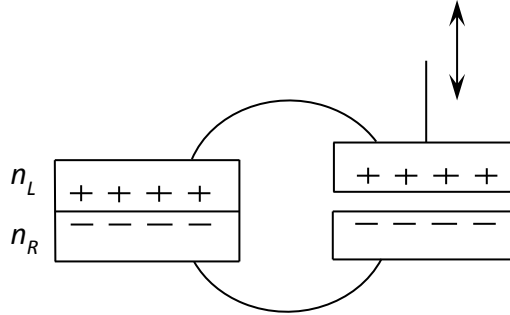

Fig. 1. A "Carnot machine" consists of two junctions connected in parallel, one with two semiconductors pieces with permanent contact, and one with two separated and moveable pieces. The distance between them is externally controlled.

Two junctions of semiconductors are connected in parallel. The two semiconductors are in permanent contact in the left junction and are separated and moveable in the right junction. The distance between the separated pieces is externally controlled. The connecting wires are made of the same semiconductor material so that there is only one contact junction in the device. The contact potential V_c within a junction is given by (7). Since the right junction parts are electrically charged, there will be attraction force between them. Changing the distance between them requires mechanical work. The machine operates in a four step cycle between a hotter heat-bath T_H and a colder heat-bath T_C.

In step-1 the machine is attached to the hot bath T_H. The right upper part moves down isothermally toward the lower part with a constant junction potential V_H. The increasing capacity of the right junction drives charge ΔQ_H that flows from the left contact junction that absorbs heat $\Delta Q_H = eV_H$ from the hot bath (Peltier effect). The pieces of the right junction perform equivalent work on the external force that hold them in place.

In step-2 the machine is separated from the hot bath T_H and the right upper part moves adiabatically further down toward the lower part. The machine cools down until the temperature drops to T_C of the cold bath. The junction potential drops from V_H to V_C.

In step-3 the machine is attached to the cold bath T_C. The upper part moves back isothermally with constant V_C and recedes from the lower part. The decreasing capacity of the right junction drives charge ΔQ_C that flows in the opposite direction to step-1. The flow through the left junction delivers heat $\Delta Q_C = eV_C$ to the cold bath (Peltier effect reversed direction) and the external force performs an equivalent work on the right junction.

In step-4 the machine is separated from the cold bath T_C. The upper part continues to move up adiabatically and the machine heats up until it reaches the temperature T_H of the hot bath. The junction potential goes up from V_C to V_H, its original state, and a full cycle is completed.

The adiabatic work done by the machine on the external force in step-2 is equal to the adiabatic work done by the external force on the machine in step-4. The EMF V of the machine is the work done by moving a unit charge in a complete closed cycle. This work is equal to the sum of step-1 and step-3 for a unit charge e. Using (7) the work will be:

$$eV = k(T_H - T_C)\ln(n_L/n_R). \tag{11}$$

Combining (7) and (11) yields Carnot's efficiency 1 - T_C / T_H. The Seebeck coefficient (1) is:

$$S = k \ln(n_L/n_R). \tag{12}$$

The coefficient S is a constant that does not depend on the temperature and the output EMF (2) is a linear function of the temperature difference.

Inserting Peltier and Seebeck coefficients (10), (12) into (4) verifies the first Thomson relation.

The Seebeck effect is discussed here with an n-type mono-carrier junction that has two different electron densities. The classical pn junction is very similar, except that the minority carrier density, i.e., the electron density in the p-type material, is weakly temperature dependent. A similar process with the pn junction is reversible, but it is not a closed cycle since electron-hole pairs are generated at some temperature and recombined at another temperature. As a result the contact potential will not be exactly according to (7) and the efficiency will not be exactly that of Carnot.

C. Thomson effect: Generation or absorption of heat in a current carrying conductor with a temperature gradient.

Since charge carriers in the model semiconductor are considered free particles, each carrier is associated with thermal energy (3/2) kT (appendix-A). Thus, when a particle moves from lower to higher temperature it will absorb heat from its vicinity, and when it moves the other way it will deliver heat to it.

When a charge carrier moves back and forth between two points with different temperatures, heat absorbed at the hotter point will be emitted at the colder point without any net charge flow, thus it contributes to heat conduction. When the net flow of charge carriers is not zero, as under the effect of an electric field, there will be net emission or absorption of heat along the conductor that depends on the flow direction. Thus, both thermal conduction and the Thomson effect are a result of changing the heat content of the charge

carriers as they move along the temperature gradient. Thermal conduction is the result of balanced carrier movement with zero average flow, and the Thomson effect is a result of a deviation from this balance.

The current density in a wire is $J = n\,v$, where n is the charge carrier density and v is its speed along the wire. During a time Δt, $J\Delta t$ carriers enter a wire segment at x where the temperature is $T(x)$, move a distance $\Delta x = v\,\Delta t$, and the same number leave it at $x + \Delta x$ where the temperature is $T(x + \Delta x)$. The average kinetic energy of a carrier is $(3/2)\,kT$, so that Δq, the amount of energy transferred in the wire segment Δx to its vicinity during Δt is:

$$\Delta q = (3/2)k(T(x + \Delta x) - T(x))J\Delta t. \tag{13}$$

The rate of heat flow to the vicinity is:

$$\Delta q/\Delta t = (3/2)kJ\Delta T. \tag{14}$$

So the Thomson coefficient is:

$$K = (3/2)k. \tag{15}$$

Figure-2 shows the classical configuration of two junctions at two different temperatures T_C and T_H connected back to back, and two wires, a and b, under temperature gradient of $T_H - T_C$.
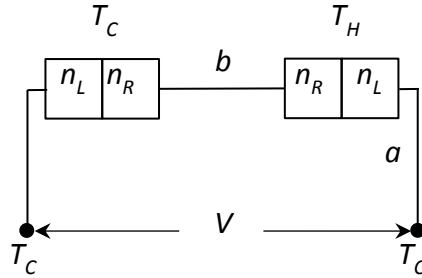

Fig. 2.   Two junctions at two different temperatures are connected back to back by conducting wires.

The EMF output voltage of the circuit is equal to the sum of the potential differences on the four segments. Wire-a is made of n_L material and wire-b is made of n_R material. According to (9) the voltage drop along the wires does not depend on the charge carrier concentration, so it is the same on both wires. Since the wires are under opposing temperature gradients, their potential differences will cancel. By using (7) the overall output voltage, $eV = k(T_H - T_C)\ln(n_L/n_R)$, is the same as that calculated for the reversible Seebeck effect in (11).

5. Conclusions

Charge flow within a conductor involves two irreversible processes where energy gained from the electric field is transferred to the conductor, heat conduction and Thomson heating. The Thomson effect takes place in a steady state system of heat flow rather than in an equilibrium system. However, reversing the current direction will reverse the direction of Thomson heat flow. This property is shared with a reversible process.

Seebeck's EMF varies linearly with the temperature difference and its corresponding coefficient is a constant that does not depend on the temperature. According to the second Thomson relation (5) there

should not be Thomson heat for a linear effect. But yet, when charge carriers enter a wire at a cold end, and leave it at a hot end, their heat content changes and they must cool it or absorb heat from its vicinity.

Thermoelectric effects in systems are much more complicated than the simple model presented here. In metals only electrons with energy within a few kT around the Fermi energy contribute to the current, and their number is strongly temperature dependent, mainly at low temperatures. In addition, their thermal energy is not that of free particles. Yet, Seebeck effect and Peltier effect are basically reversible thermodynamic processes. Discussing them in terms of non-equilibrium irreversible theories is meaningless.

Appendix A: Thermal Energy of a Particle

The average kinetic energy is calculated by summing all the squared velocities over all directions in space in a spatial angle of 4π determined by a declination angle θ, 0 to π, and azimuth angle of 2π. Each velocity is weighed by a distribution probability $f_0(x, v, \theta)$ [9]:

$$< v^2 >= \int f_0(x, v, \theta) \, |\boldsymbol{v}|^2 d^3\boldsymbol{v}, \tag{16}$$

where $v = |\boldsymbol{v}|$ and $d^3\boldsymbol{v} = 2\pi v^2 dv \, Sin(\theta)d\theta$.

Maxwell-Boltzmann distribution is:

$$f_0(v) = (m/2\pi kT)(3/2)e^{-mv^2/2kT}, \tag{17}$$

where the pre-exponential factor in (17), determined by the condition

$\int_0^\infty 4\pi v^2 f_0 \, dv = 1$, is applied to the calculation of $<v^2>$. By transforming to a dimensionless variable $x = (m/2kT)^{1/2}v$, and using the integrals in appendix D :

$$< v^2 >= 4\pi \int f_0(v)v^4 dv = 3kT/m. \tag{18}$$

The average kinetic energy is:

$$m < v^2 >/2 = (3/2)kT. \tag{19}$$

Appendix B: Contact Potential

It is assumed that the junction is perpendicular to the x-direction, and that the depth of the space charge layer in it is small compared to the electron's mean free path. The thermal velocity of electrons on the left side must have a minimal component v_x in order to overcome the potential barrier and cross to the right side: $(1/2)mv_x^2 > eV_c$. Electrons on the right side do not have a barrier for crossing back to the left. An electron that crosses the junction from left to right, will be slowed by the electric field and lose energy eV_c. This energy will be thermally regained from its vicinity. An electron moving in the opposite direction will be accelerated by the field and thermally deliver the field-gained energy to its vicinity.

The current density through the contact will be:

$$J_n = \int_{v_x>v_0} f_0(v)v_x \, d^3v + \int_{v_x<0} f_0(v)v_x \, d^3v \quad = J_n^2 - J_n^1, \tag{20}$$

where: $v_0 = (2eV_c/m)^{1/2}$.

It is convenient to use here Cartesian coordinates $d^3v = dv_x dv_y dv_z$. By inserting the Maxwell-Boltzmann distribution (17) the current will be:

$$J_n^2 = n_L (\frac{m}{2\pi kT})^{3/2} \int_0^\infty e^{\alpha_z} dv_z \int_0^\infty e^{\alpha_y} dv_y \int_{v_0}^\infty e^{\alpha_x} v_x dv_x \tag{21}$$

$$J_n^1 = n_R (\frac{m}{2\pi kT})^{3/2} \int_{-\infty}^0 e^{\alpha_z} dv_z \int_{-\infty}^0 e^{\alpha_y} dv_y \int_{-\infty}^0 e^{\alpha_x} v_x dv_x \tag{22}$$

where: $\alpha_i = -mv_i^2/(2kT)$, $i = x, y, z$.

Using the formulas in appendix-D, the integrals will be:

$$\int_0^\infty e^{\alpha_i} dv_i = (\pi kT/m)^{1/2}, \tag{23}$$

$$\int_{v_0}^\infty e^{\alpha_x} v_x dv_x = (kT/m)e^{-eV_c/kT}, \tag{24}$$

$$\int_{-\infty}^0 e^{\alpha_x} v_x dv_x = (kT/m). \tag{25}$$

The overall current will be:

$$J_n = J_n^2 - J_n^1 = (kT/8\pi m)^{1/2} n_L (e^{-eV_c/kT} - n_R/n_L). \tag{26}$$

For equilibrium, $J_n = 0$, the potential difference at the contact will be:

$$e^{-eV_c/kT} = n_R/n_L, \tag{27}$$

or:

$$V_c = (kT/e) \ln(n_L/n_R). \tag{28}$$

If an external voltage source V is connected to the system, and the voltage falls on the junction, the current will be:

$$J_n = (kT/8\pi m)^{(1/2)} n_L (e^{e(V-V_c)/kT} - n_R/n_L), \tag{29}$$

or, by (28):

$$J_n = (kT/8\pi m)^{(1/2)} n_R (e^{eV/kT} - 1). \tag{30}$$

This formula is the *I–V* diode equation.

Appendix C: Charge Flow within a Conductor with Temperature Gradient
The charge flow within a conductor is calculated by application of Boltzmann transport equation. A temperature gradient along the x-coordinate is assumed.

$f(x, v)$ is a non-equilibrium distribution function that determines the probability of a particle within a system to be at some place x and to have some local thermal velocity $\boldsymbol{v}$. The Boltzmann transport equation expresses this global non-equilibrium distribution in terms of local equilibrium distributions $f_0(x, v)$. The equation enables application of properties of equilibrium systems to the study of a non-equilibrium system. The linear transport equation is:

$$f(x, v, \theta) = f_0(x, v) - l\, Cos(\theta)[(\partial f_0/\partial x) + (\boldsymbol{a}/v)(\partial f_0/\partial v)]\,, \tag{31}$$

where l is the mean free path, $\boldsymbol{v}$ is the velocity vector, $v = |\boldsymbol{v}|$, and θ is the vector direction relative to the x-coordinate. $\boldsymbol{a}$ is the acceleration due to external force. For example, $\boldsymbol{a} = e\,\boldsymbol{E}\,/\,m$, where $\boldsymbol{E}$ is the electric field, e is the particle charge and m is its mass. Equation (31) is obtained from the classical linear transport equation [9] by replacing the relaxation time $\tau = l\,/\,v$.

The currents: A particle moving with a velocity $\boldsymbol{v}$ will cross a plane section of the conductor at x during a time Δt if its distance from the plane is less than $vCos(\theta)\Delta t$. The particle current through a unit cross section at x is obtained by summing all the velocities in all directions (spatial angle of 4π). Each velocity weighed by the distribution probability:

$$J_n = \int n(x)f(x, v, \theta)vCos(\theta)\, d^3v\,, \tag{32}$$

where $d^3v = 2\pi v^2 dv\, Sin(\theta)d\theta$. Substitution of the distribution function (31) into (32) yields the current:

$$J_n = -(4\pi l/3)[(eE/m)\int n(x)(\partial f_0/\partial v)v^2\, dv + \int n(x)(\partial f_0/\partial x)v^3\, dv], \tag{33}$$

where the f_0 contribution in (33) is zero, and the trigonometric integral is $\int Cos(\theta)\, Sin(\theta)\, d\theta = 2/3$.

Since the energy associated with each particle is $(1/2)mv^2$ the energy current will be, by a similar calculation:

$$J_u = -(4\pi l/3)[(eE/m)\int n(x)(\partial f_0/\partial v)v^4\, dv + \int n(x)(\partial f_0/\partial x)v^5\, dv]. \tag{34}$$

The currents will now be calculated by applying the Maxwell-Boltzmann distribution (17). Since (by (17)), $\partial f_0/\partial v = -(mv/kT)f_0$, the particle current will be:

$$J_n = -(4\pi l/3)[(eE/kT) - (d/dx)][n(x)\int (f_0)v^3\, dv)]. \tag{35}$$

Or, by transforming to a dimensionless variable $x = (m/2kT)^{1/2}v$, and using the integrals in appendix D:

$$J_n = [4l/3/(2\pi m)^{1/2}][eEn/(kT)^{1/2} - d(n(kT)^{1/2})/dx]. \tag{36}$$

Assuming that the charge density does not depend on the position, the current will be:

$$J_n = [(4l/3)/(2\pi m)^{1/2}](1/kT)^{1/2}n[eE - (1/2)d(kT)/dx]. \tag{37}$$

The charge current will be $J_q = eJ_n$. A similar calculation yields the energy current:

$$J_u = 2[(4l/3)/(2\pi m)^{1/2}][(kT)^{1/2}eEn - d(nkT)^{3/2}/dx], \tag{38}$$

or, by combining (36) and (38):

$$J_u = 2kTJ_n - 2[(4l/3)/(2\pi m)^{1/2}]nkT^{1/2}d(kT)/dx. \tag{39}$$

Equation (39) expresses the energy current as a sum of two terms. The first is convection, the energy associated with the particle flow, and the second is heat conduction, which is proportional to the temperature gradient and independent of the particle current.

Equations (36), (39) may be applied to calculate the diffusivity, electrical and thermal conductivity, and to verify the Wiedemann-Franz law and Einstein relations.

For example, the electrical conductivity σ, defined by $J_q = eJ_n(dn/dx = 0, dT/dx = 0) = \sigma E$, is:

$$\sigma = [(4l/3)/(2\pi m)^{1/2}]e^2n/(kT)^{1/2}. \tag{40}$$

Equations (36), (38) are similar to Onsager's linear equations that relate forces to flows, but have the advantage that they do not include unknown linear coefficients like Onsager's. The values of these coefficients may be obtained by comparing the two sets of equations.

Appendix D: Integrals

$$\int_0^\infty x^n e^{-a^2x^2} dx = \Gamma(n + 1/2)/2a^{n+1}. \tag{41}$$

Γ is the gamma function:

$$\Gamma(n) = (n - 1)! \tag{42}$$

$$\Gamma(x + 1) = x\Gamma(x) \tag{43}$$

$$\Gamma(x)\Gamma(x + 1/2) = \Gamma(2x)\pi^{1/2}/2^{2x-1} \tag{44}$$

$$\Gamma(1/2) = \pi^{1/2} \tag{45}$$

$$\Gamma(3/2) = (1/2)\pi^{1/2} \tag{46}$$

$$\Gamma(5/2) = (3/4)\pi^{1/2} \tag{47}$$

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On the web: February 2014.

Note added on August 2017:

From Wikipedia "Thermoelectric Effect", Talk: note 34:

[34 I defy anyone to find the Thomson (Kelvin) Relations anywhere in Thomson's writings.](#)

"I defy anyone to find the Thomson (Kelvin) Relations in Thomson's writings. They may be based upon equations in "On The Dynamical Theory Of Heat," but look throughout his complete works and you will not find the Relations. I have been unable to find any discussions of them in late 19th and early 20th Century writings on thermoelectrics, either. They do not seem to emerge until around the time that Lars Onsager introduced his work on reciprocal relations in the 1930's. The Relations appear to grow out of 20th Century work in thermodynamics and discussion of the Thomson Relations takes off from there." …

Michael Spry

By the author:
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Links:

1. Thermodynamics Research Laboratory,
   http://www.uic.edu/~mansoori/Thermodynamics.Educational.Sites_html
2. Thermodynamik - Warmelehre, http://www.schulphysik.de/thermodyn.html
3. The Blind Men and the Elephant
4. My Spin on Lunacy
5. Five Weeks in a Balloon
6. The first man I saw
7. "Faster, Faster!"
8. Perfection can't be rushed
9. The man higher up
10. Brains
11. The First-Class Passenger
12. other