Voltage Induced Across a Conductor In a Thermal Gradient

Albert E. Seaver & Brian P. Seaver
Nesperd Engineering
e-mail: aseaver@electrostatics.us & bseaver@nesperd.com

Abstract—**When a bar of electrically conductive solid material is thermally insulated except at its ends and is then heated to a temperature T_h at one end while it is held to a cooler temperature T_c at the other end, a linear thermal gradient ∇T develops along the length of the bar. If the bar has a free-electron charge density ρ then, since the hot end of the bar has expanded relative to the cold end, the free-electron charge density at the hot end will be lower than at the cold end due to this expansion. As a result, a charge density gradient $\nabla \rho$ is set up along the bar; and some of the free-electrons diffuse from the cooler temperature end towards the hotter temperature end of the bar. This diffusion results in a diffusion charge flux (current density) J_D which is controlled by the diffusion coefficient D. On the other hand, the movement of some free electrons to the hotter end results in an excess of free-electrons near the hotter end; and, since the counter-ions of the solid cannot move, an excess of positive charge occurs near the cooler end. This charge imbalance along the bar results in an electric field E along the bar and creates an E-field driven charge flux J_E which drives the free-electrons back towards the cooler end. Furthermore, the higher temperature at the hot end gives the free-electrons at the hotter end a slightly higher translational energy, and the thermal gradient ∇T sets up a thermal charge flux J_G which transports some of the higher energy free-electrons from the hotter to the colder end; and this transport is controlled by the thermophoresis coefficient G. However, if the bar is not electrically connected to its surroundings, the general charge flux equation requires that –in the steady state– the net electrical current density J must always be zero everywhere within the bar. Along the length of the bar this J = 0 restriction still allows free-electron movement as long as $J = 0 = J_E + J_D + J_G$ everywhere along the bar. In essence the temperature difference is responsible for both the thermal and concentration gradients which results in the movement of the free charges. The movement of the free charges in turn creates an E-field; but, since $E = -\nabla V$, a potential difference then exists along the length of the bar. In this paper the charge flux equation is used to explicitly determine the equation for the potential difference $\Delta V = V_h - V_c$ between the ends of the bar. The result shows that this potential difference is related to both the temperature difference $\Delta T = T_h - T_c$ between the ends of the bar and to the thermal expansion coefficient α of the bar. However, for temperature differences in the few 10s of degrees the potential difference is found to be independent of the properties of the bar; and the equation reduces to simply $\Delta V = k/q_e \, \Delta T$, where $k \approx 1.38 \times 10^{-23}$ J/K is Boltzmann's constant and $q_e \approx -1.6 \times 10^{-19}$ coulomb is the charge of an electron. At first glance the result seems to contradict the findings of thermocouple analysis which predicts each material has its own Seebeck coefficient $S = \Delta V/\Delta T$. The reason for the apparent difference is discussed.**

<div align="center">

I. INTRODUCTION

</div>

At a session of the Berlin Academy of Sciences on December 14, 1820 Thomas Johann Seebeck reported that a circuit made from two dissimilar metals with their junctions held at different temperatures (for example: T_h and T_c) would deflect a compass magnet [1]. Professor Hans Christian Oersted who earlier that year observed the magnetic effects of an electric current immediately realized that a current flowed in Seebeck's circuit; and it was the magnetic field from the current that deflected the compass magnet [1]. The generation of this current due to the temperature difference became the basis of the thermo-electric generator. It was also found that if the circuit were opened a voltage developed across the opened ends. This became the basis of the thermocouple, and the thermocouple voltage is (see discussion below) $\Delta V_t = (S_A - S_B)(T_h - T_c)$, where S_A and S_B are the Seebeck coefficients of metal A and B, respectively.

When the temperatures at both ends of the metals are the same, then no voltage occurs. This result indicates the cause of the measured voltage must be due to the thermal gradients within the metals.

The objective of the present paper is to examine the relationship between a temperature difference placed at the ends of a single conductor and the potential produced at its ends due to this temperature difference.

Unfortunately, at the present time no simple method has been devised to measure this voltage drop along a single metal conductor directly. The lack of such an experiment has required an indirect measurement using two dissimilar materials and requires an understanding of the Seebeck coefficient. However, when examined in this way, the results are only as accurate as the basic understanding of the physics of the Seebeck coefficient.

A. Indirect Analysis

Since a simple direct method to measure the voltage drop along a conductor in a thermal gradient has not yet been developed, an indirect method using the thermocouple voltage must be used. Hence, an understanding of the physics involved in the thermocouple voltage is required. The standard analysis is described as follows. If two dissimilar conductors A and B are connected together at their common end and held at a higher (or hot) temperature T_h while their other ends are each held at a cooler (or cold) temperature T_c, then there exists a common temperature difference $\Delta T = T_h - T_c$ across either of the two conductors A or B as shown in Fig. 1.
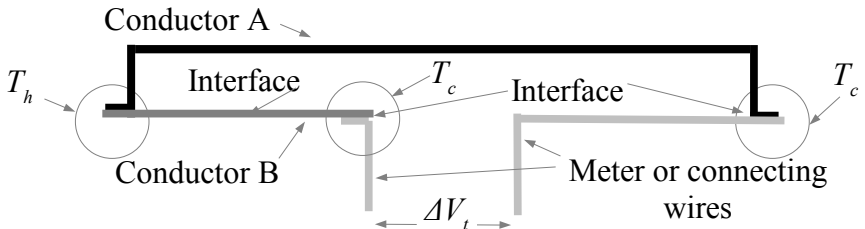
Fig. 1: General Diagram for a Thermocouple or Thermoelectric Generator

The incremental voltage change dV along an incremental distance dx of a conductor due to an incremental temperature change dT along that distance dx is found using the chain-rule by writing the equality $dV/dx = (dV/dT)(dT/dx) = S\, dT/dx$ where $S \equiv dV/dT$ is defined as the incremental Seebeck coefficient of the conductor. Next, using this definition of S and multiplying the equality on both sides by dx allows the equality itself to be written simply as $dV = S\, dT$. In general, $S = S(T)$, but for small temperature changes S is nearly independent of T; and, when this occurs, $dV = S\, dT$ can be integrated – starting from the cold end – along the full length of conductor A in Fig. 1 to yield $V_{hA} - V_{cA} = S_A (T_h - T_c)$. Defining $\Delta V_A = (V_{hA} - V_{cA})$ and $\Delta T = (T_h - T_c)$ as the voltage difference and temperature difference, respectively, between the ends of the conductor explicitly defines $S_A = \Delta V_A / \Delta T$ as the Seebeck coefficient of conductor A. Likewise, $dV = S\, dT$ can be integrated from the cold end along the full length of the conductor B to the hot end to yield $S_B = \Delta V_B / \Delta T$ as the Seebeck coefficient of conductor B. Hence, in Fig. 1 (if the two meter wires are absent) the voltage drop ΔV_t across the two open terminals (of A and B) starting from the cold end of conductor A, at potential V_{cA}, and ending at the cold end of conductor B, at potential V_{cB}, will be $\Delta V_t = \Delta V_A - \Delta V_B = V_{cB} - V_{cA} = (S_A - S_B)(T_h - T_c)$, where in this result it is assumed that $V_{hA} = V_{hB}$ at the (zero thickness) interface between A and B (see Section B2a below).

If the meter (or connecting) wires are now included in the circuit of Fig. 1, then the voltage drop along the wire on the right, from the cold end of the wire held at temperature T_c to the open end of the wire at temperature T_{Woe}, must be the same as the voltage drop along the wire on the left, from the cold end of the wire held at temperature T_c to the open end of the wire at temperature T_{Woe}. As a result, these two voltage drops will always cancel each other; so there is no effective voltage drop from the meter leads or connecting wires.

Experimentally T_c can be chosen, and T_h and ΔV_t can be measured, but still $\Delta V_t = (S_A - S_B)(T_h - T_c)$ is a single equation with two unknowns; namely, S_A and S_B. It is possible to change a conductor and repeat the measurements, but no matter how many different conductors are used, there will always be one more unknown than the number of equations. As a result it is customary to assign to platinum a Seebeck coefficient of zero ($S_{pt} = 0$) which then allows the equation $\Delta V_t = V_{cB} - V_{cA} = (S_A - S_{pt})(T_h - T_c)$ to give a measurement of the Seebeck coefficient of S_A at the temperature T_h. Most often T_c is chosen as 0°C (a convenient temperature found in an ice-water bath); so, the Seebeck coefficients are most often reported with a reference temperature at 0°C. For a platinum wire along B in Fig. 1 and $T_c = 0$°C the Seebeck coefficient of a metal placed along A in Fig. 1 can be found using the equation $S_A = \Delta V_t / [T_h(^0\text{C}) - 0^o\text{C}] = \Delta V_t / T_h(^0\text{C})$, where for $T_h > 0$°C at the hot end the current flows from the platinum to metal A when the sign of S_A is positive. For example, Kaye & Laby [2] list values of ΔV_t of several chemical elements relative to platinum (reported at $T = -100$°C and $T = +100$°C) from which the Seebeck coefficient can be calculated using $S_A = \Delta V_t / T(^0\text{C})$. Experimentally, the Seebeck coefficient is found to be somewhat temperature dependent; many metals have a positive S, but some are negative and a few (example: calcium) can change sign as the temperature changes [2].

For Internet enthusiasts interested in thermoelectrics, there is an open-access 8-lecture-series Short Course on Thermoelectrics given by the International Thermoelectric Society [3]. The second lecture by Vining [4] (see Section 8.2, p. 33.) gives the standard classical argument for a voltage drop across a conductor in a temperature gradient; namely, electrons at the hot end have more energy and thermally diffuse to the colder end making the hot end positive and giving rise to the voltage difference across the conductor. However, further considerations are needed because the resultant physics does not explain the experimentally measured values of *S*. Consequently, quantum physics arguments are brought into play [5]. Although progress using quantum physics has been advancing, to date no satisfactory explanation for the measured values of all the Seebeck coefficients has been presented.

B. Hidden Assumptions

1) Free-electrons

The first assumption in a classical physics discussion of metals is that every solid metal has some free-electrons. A free-electron is an electron that can be moved under the action of an applied force. In this paper it is also assumed that there are some free-electrons in all materials. For example, in the Drude model for a metal, valence electrons are assumed to be able to completely detach from their positive ions and form a free-electron gas. In the Drude model it is assumed that there is a free-electron associated with each atom of the metal and the number density *n* of the free-electrons is equal to the number density of the ions (or atoms), and the charge density ρ of the free-electrons is, therefore, quite large. However, this free-electron concept can be applied to any material. In a semiconductor the dopant atoms are assumed to each have a free-electron and the number density *n* of the free-electrons is equal to the number density of the dopant atoms. In an insulator a hopping mechanism is assumed to allow a few electrons to move; so, the number density *n* of the free-electrons is very small. The net result is even an insulator can be thought of as having free-electrons although due to its low number density *n,* and, hence, low charge density ρ, its electrical conductivity σ is so low as not to be measurable. The net result is that each material has a defined charge density *n* of free-electrons, and these free-electrons can be moved when subjected to the action of any force.

2) Constant equilibrium properties

The second assumption is that in thermodynamic equilibrium every metal can be described by a set of properties which are constant throughout the metal.

a) Zero thickness interface

Due to the constant equilibrium assumption above, it is implicitly assumed when two metals are connected together at a common interface and placed in thermodynamic equilibrium that both metals maintain their set of properties up to the common interface. This gives rise to the concept of a zero thickness interface with a jump in the properties occurring at the interface. The zero thickness interface implies $V_{hA} = V_{hB}$ at the interface and allows the voltage drops across the conductors to be simply additive when determining ΔV_t.

II. CHARGE FLUX EQUATION

In this Section II the charge flux equation will be summarized. Then in Section III the potential drop at the ends of a metal bar held in a temperature gradient will be discussed, (A) using the standard classical method, and then (B) adding a charge density gradient produced by the temperature gradient. Finally, after applying the results to a thermo-couple measurement system and finding that the results are insufficient to explain the Seebeck coefficient, a finite-thickness interface correction (C) is added to account for a potential at the interface.

This paper looks at finding the voltage drop ΔV along an isolated conductor due to a temperature difference ΔT along the conductor using the charge flux equation. What we present here gives twice the classical value found in [5]; but we argue that our result is correct, and is only part of the classical physics answer. We suggest that by including the potential drop across each finite-thickness interface that there may be no need to bring quantum mechanics into the picture.

In general, the charge flux equation gives the charge transport of multiple species across a unit area per unit time. In this paper, as is customary in a thermocouple analysis, only one specie – free-electrons – will be assumed to be the specie of interest. The charge flux equation can be developed based purely on the calculus of a gradient in any scalar quantity across a volume element [6]. However, – in the absence of magnetic affects – the charge flux equation has also been developed from a classical physics model of colli-sions [7]; when only electrons are free to move the charge flux equation [7] reduces to

$$\mathbf{J} = \sigma \mathbf{E} - D \nabla \rho - G \rho \nabla T \qquad \textbf{Electron Charge Flux} \qquad (1)$$

where σ is the electrical conductivity of the conductor, and based on the – free-electrons as the only specie capable of moving – assumption in this paper σ is due entirely to elec-tron conduction. In (1) $\mathbf{E}$ is the electric field at any point where $\mathbf{J}$ is evaluated. The other terms in (1) are as follows:

$$\rho = sqn = s_e qn = q_e n = \rho_e \qquad \textbf{Electron Charge Density} \qquad (2)$$

where the first equality is the general form and the next three can be used after it is de-termined that the specie under study is electrons. Specifically, s is the sign ($s = \pm 1$) of the charged specie (for electrons: $s = s_e = -1$), q is the charge on a positron $q \approx +1.6 \times 10^{-19}$ coulombs and n is the number density of the specie (here it is the free-electron number density) at the point where $\mathbf{J}$ is evaluated. Electron charge is often written as $q_e = s_e q \approx -1.6 \times 10^{-19}$ C. The electrical conductivity is

$$\sigma = s^2 qnb = s(sqn)b = s_e(s_e qn)b = s_e \rho_e b = -\rho_e b \qquad \textbf{Electrical Conductivity} \qquad (3)$$

where here again the first two equalities are the general form for a conductivity of a specie and the next three equalities can be used after it is determined that the specie under study is electrons. The mobility b of the electrons in the conductor is given by

$$b = q\tau/m \qquad \textbf{Electron Mobility} \qquad (4)$$

where τ is the average collision time and $m = m_e$ is the mass of the electron, $m_e \approx 9.109 \times 10^{-31}$ kg. The electron diffusion coefficient D and electron thermophoresis coefficient G are respectively given by

$$D=kTb/q \qquad \textbf{Electron Diffusion Coefficient} \qquad (5)$$

where $k \approx 1.38$ x 10^{-23} J/K is Boltzmann's constant, and T the temperature at the evaluation point and

$$G=kb/q=D/T \qquad \textbf{Electron Thermophoresis Coefficient.} \qquad (6)$$

A. Understanding the Charge Flux Equation

The charge flux equation (1) may look daunting at first view, but it is very easy to understand. First of all (1) is composed of three flux terms: namely, since $\mathbf{E} = -\nabla V$, a first term

$$\mathbf{J_E}=\sigma\,\mathbf{E}=-\sigma\,\nabla V =-s\,b\rho\,\nabla V \qquad \textbf{E-Field Charge Flux} \qquad (7)$$

due to the electric field $\mathbf{E}$ (or gradient in potential V) that may exist in the material, a second term

$$\mathbf{J_D}=-D\nabla\rho \qquad \textbf{Density Diffusional Charge Flux} \qquad (8)$$

due to any density gradient $\nabla\rho$ that may exist in the material, and a third term

$$\mathbf{J_G}=-G\rho\nabla T \qquad \textbf{Thermophoretic Charge Flux} \qquad (9)$$

due to any thermal gradient ∇T that may exist in the material. In its most condensed form (1) can be written with the aide of (7), (8) and (9) as

$$\mathbf{J}=\mathbf{J_E}+\mathbf{J_D}+\mathbf{J_G}. \qquad (10)$$

Since (10) is the charge flux at any point in space, (10) can be applied anywhere; so it is applicable not only along the length of a conductor in a thermal gradient, it is also applicable at an interface. Finally, it is at times useful to write (1) with every term containing ρ and ∇ so, with the aide of (7), (1) becomes

$$\mathbf{J}=-s\,b\rho\nabla V -D\nabla\rho-G\rho\nabla T \qquad \textbf{Electron Charge Flux.} \qquad (11)$$

Written as (11) it becomes immediately clear that there will be a charge flux whenever there is a gradient in V, ρ or T, and in all situations the magnitude of the flux will be dependent on ρ or the gradient of ρ. In what follows the usefulness of the charge flux equation as given by (1), (10) or (11) will be demonstrated.

III. DISCUSSION

Three different methods of looking at the physics of a thermal gradient along a conductor are presented in this discussion section.

A. Standard consideration: ∇T causes ∇V

This first method is the standard consideration that ∇T causes a thermal diffusion flux of the free-electrons and that this flux gives rise to a potential ∇V [4], [5]. The argument goes as follows: Consider a conductor held at one end by a hotter heat source and at the other end by a cooler heat sink. Ignore (in this standard consideration section) the fact that there is an expansion of the metal at the hotter end which would give rise to a small $\nabla\rho$ term. Ignoring (as was done in [4] and [5]) any $\nabla\rho$ the along the conductor the charge

flux equation (11) for the free-electrons in the steady state requires $\mathbf{J} = 0$ everywhere, so (11), with $\mathbf{J} = 0$ and the aide of (6), reduces to

$$\nabla V = -[k/(sq)]\nabla T \qquad \textbf{Electron Charge Flux: Ignores } \nabla\rho \textbf{ term.} \qquad (12)$$

If the change in temperature is only in the x direction, then (12) is simply

$$dV = -[k/(sq)]d\,T\,. \qquad (13)$$

Integration of (13) from T_c to T_h gives

$$\int_{V_c}^{V_h} dV \;\; = -\frac{k}{sq}\int_{T_c}^{T_h} dT$$

$$V_h - V_c \;\; = -\frac{k}{sq}\left(T_h - T_c\right). \qquad (14)$$

In this section the charge flux equation was used to explicitly determine the equation for the potential difference $\Delta V = V_h - V_c$ between the ends of the conductor whose ends are at a temperature difference $\Delta T = T_h - T_c$; and (14) is simply $\Delta V = k/q_e\,\Delta T$. Since $k \approx$ 1.38 x 10^{-23} J/K is Boltzmann's constant and $q_e = sq \approx$ -1.6 x 10^{-19} coulomb is the charge of an electron, $-k/(sq) = -k/q_e = +8.625$ x 10^{-5} eV/K = 86.3 μV/K. At first glance, the result seems to contradict the findings of thermocouple analysis which predicts each material has its own measured Seebeck coefficient $S = \Delta V/\Delta T$ whereas the Seebeck coefficient for metals is on the order of only a few μV/K. This result, based on Maxwell-Boltzmann statistics is consistent with the recent findings of Fujita and Suzuki [5] based on using Fermi-Dirac statistics; namely, they made the same assumption (ignored $\nabla\rho$) and argued both holes and electrons are important, so F-D statistics gave them ½ the value of (14).

B. New consideration: ∇T *causes both* $\nabla\rho$ *and* ∇V

To analyze an isolated conductor that is in a temperature gradient the full charge flux equation given by (1), (10) or (11) must be used. If the thermal gradient ∇T is only in the x direction, then concerns on ∇T, $\nabla\rho$ and ∇V will only be in the x direction. In the steady state no total charge flux can exist ($\mathbf{J} = 0$) and (11) is written as

$$0 = -s\rho b\frac{dV}{dx} - D\frac{d\rho}{dx} - G\rho\frac{dT}{dx}. \qquad (15)$$

But, using the chain-rule $\dfrac{d\rho}{dx} = \dfrac{d\rho}{dT}\dfrac{dT}{dx}$ (15) becomes

$$0 = -s\rho b\frac{dV}{dx} - D\frac{d\rho}{dT}\frac{dT}{dx} - G\rho\frac{dT}{dx} = -s\rho b\frac{dV}{dx} - \left(D\frac{d\rho}{dT} + G\rho\right)\frac{dT}{dx}. \qquad (16)$$

If a cubic volume of the metal is of length L_0 when at temperature T_0 and is heated to a temperature T then as noted in [8] (see p. F-117 in [8]) its length expands to $L \approx L_0\left[1 + \alpha\left(T - T_0\right)\right]$ where α is the coefficient of linear expansion. Furthermore, its volume is $Vol = L^3 = Vol_0\left[1 + \alpha\left(T - T_0\right)\right]^3 \approx Vol_0\left[1 + 3\alpha\left(T - T_0\right)\right]$ provided $T - T_0$ is small enough such that $\alpha\left(T - T_0\right) \ll 1$. If at temperature T_0 there are N free-electrons in the volume Vol_0, then when at temperature T the free-electron number density is $n = N/Vol$ and the free-electron charge density (2) will be

$$\rho = sqn = \frac{sqN}{Vol} \approx \frac{sqN}{Vol_0 \left[1 + 3\alpha\left(T - T_0\right)\right]} \approx \rho_0 \left[1 - 3\alpha\left[T - T_0\right]\right].$$ But a series expansion of

$$e^x = 1 + x + \frac{x^2}{2!} + \cdots$$ allows $$e^{-3\alpha(T - T_0)} = 1 - 3\alpha\left(T - T_0\right) + \frac{\left[-3\alpha\left(T - T_0\right)\right]^2}{2!} - \cdots$$ and, if

$3\alpha\left(T - T_0\right) \ll 1$,   then $\rho \approx \rho_0\left[1 - 3\alpha\left(T - T_0\right)\right] \approx \rho_0 e^{-3\alpha(T - T_0)}$.   As   a   result,

$$\frac{d\rho}{dT} \approx \frac{d\left[\rho_0 e^{-3\alpha(T - T_0)}\right]}{dT} \approx -3\alpha\rho$$ and (16) becomes

$$0 = -s\rho b \frac{dV}{dx} - \left(-3D\alpha\rho + G\rho\right)\frac{dT}{dx}. \tag{17}$$

Rearranging (17) gives

$$\frac{dV}{dx} = -\frac{1}{sb}\left(G - 3D\alpha\right)\frac{dT}{dx} = -\frac{G}{sb}\left(1 - 3\alpha\frac{D}{G}\right)\frac{dT}{dx} = -\frac{k}{sq}\left(1 - 3\alpha T\right)\frac{dT}{dx} \tag{18}$$

where (6) was used twice in the last step in (18). Multiplying both sides of (18) by dx and integrating from one end of the conductor at T_c to the other end at T_h gives

$$
\begin{aligned}
dV &= -\frac{k}{sq}dT + 3\frac{k}{sq}\alpha\, T dT \\
\int_{V_c}^{V_h} dV &= -\frac{k}{sq}\int_{T_c}^{T_h} dT + 3\frac{k}{sq}\alpha\int_{T_c}^{T_h} T dT \\
V_h - V_c &= -\frac{k}{sq}\left(T_h - T_c\right) + \frac{3}{2}\frac{\alpha k}{sq}\left(T_h^2 - T_c^2\right) \\
&= -\frac{k}{sq}\left(T_h - T_c\right) + \frac{3}{2}\frac{\alpha k}{sq}\left(T_h - T_c\right)\left(T_h + T_c\right) \\
&= -\frac{k}{sq}\left(T_h - T_c\right)\left[1 - \frac{3\alpha}{2}\left(T_h + T_c\right)\right].
\end{aligned}
\tag{19}
$$

Typical α values for the expansion of metals (see [2] Section 2.3.5) are typically in the range of $(10 - 20) \times 10^{-6}$/K. So, for $T_h \approx 100°C$ and $T_c = 0°C$ the brackets term in (19) is

$$1 - (3/2)\alpha\left(T_h + T_c\right) = 1 - (3/2)(20 \times 10^{-6}/K)(373.15 + 273.15\,K) = 1 - 0.0194$$ so the

error is less than 2% if the potential difference is given by (14) instead of (19).

From these results it can be stated, if a conductor is in a thermal gradient ΔT, then when the measured potential difference ΔV at the ends of the conductor is plotted against the thermal gradient ΔT a straight line of slope $k/q = 86.3$ μV/K will result (within an error of $< 2\%$ for a 100°C change in ΔT. However, this measurement of ΔV must be made without the conductor being connected to other materials or else the Seebeck effect will change the measurement. Unfortunately, to date no known simple and direct measurement technique exists.

However, if a thermocouple is made by two different conductors as depicted in Fig. 1 then using (19)

$$\Delta V_A = -\frac{k}{sq}\left(T_h - T_c\right)\left[1 - \frac{3}{2}\left(T_h + T_c\right)\alpha_A\right], \tag{20}$$

whereas

$$\Delta V_B = -\frac{k}{sq}(T_h - T_c)\left[1 - \frac{3}{2}(T_h + T_c)\alpha_B\right].$$ (21)

So the total voltage from T_{cA} to T_h and back to T_{cB} is

$$
\begin{aligned}
\Delta V_t &= \Delta V_A - \Delta V_B \\
&= -\frac{k}{sq}(T_h - T_c)\left[1 - \frac{3}{2}\alpha_A(T_h + T_c)\right] + \frac{k}{sq}(T_h - T_c)\left[1 - \frac{3}{2}\alpha_B(T_h + T_c)\right] \\
&= \frac{k}{sq}(T_h - T_c)\left[\frac{3}{2}\alpha_A(T_h + T_c)\right] - \frac{k}{sq}(T_h - T_c)\left[\frac{3}{2}\alpha_B(T_h + T_c)\right] \\
&= \frac{3}{2}\frac{k}{sq}(T_h - T_c)(T_h + T_c)(\alpha_A - \alpha_B) \\
&= -\frac{3}{2}\frac{k}{sq}(T_h - T_c)(T_h + T_c)(\alpha_B - \alpha_A).
\end{aligned}
$$ (22)

When platinum is chosen as the reference metal and defined as having a Seebeck coefficient of zero, the measured Seebeck coefficient becomes defined as $S = -\Delta V_t/\Delta T$. A comparison with (22) would imply

$$S = \frac{3}{2}\frac{k}{sq}(T_h + T_c)(\alpha_{pt} - \alpha) \qquad \textbf{Zero Thickness Interface.}$$ (23)

It is noted that (23) has a slight increasing temperature dependence (since temperatures are in kelvin), and $-k/(sq)$ is positive (since for free electrons s = –1), and (by default) (23) will give the Seebeck coefficient of zero for platinum. However, (23) does not account for the measured Seebeck coefficients. For example, (see [2] section 2.3.5 Thermal Expansion) for platinum $\alpha_{Pt} = 8.8 \times 10^{-6}$/K near room temperature whereas for copper $\alpha_{Cu} = 16.5 \times 10^{-6}$/K. So, for $T_h = 100°C$ and $T_c = 0°C$ (22) gives (recall: $\Delta V_t = V_{cPt} - V_{cCu}$)

$$\Delta V_t = \frac{3}{2} 86.3\,\mu V/K\,(100 - 0)(373.15 + 273.15)(8.8 - 16.5) \times 10^{-6} = -64.4\,\mu V \quad \text{which}$$

for copper over this 100°C change in ΔT gives $S_{cu} = +0.644$ µV/°C, since $V_{cCu} - V_{cPt} = V_{cCu} - 0 = -\Delta V_t$ when V_{cPt} is referenced to zero. The Seebeck coefficient using tabulated data from Kaye and Laby [2] gives $S_{cu} = +7.6$ µV/°C; so, the thermal gradient contribution only accounts for about 10% of the Seebeck coefficient of copper.

From the foregoing it is clear that although (19) or (20) would be needed to account for the potential drop across an electrically isolated conductor in a thermal gradient, (14) would be sufficient to describe the potential drop to within a few percent accuracy. However, if the voltage drop is being measured by adding a second conductor a thermocouple results and (22) must be used to predict the potential drop. However, (22) gives only a small fraction of the measured thermocouple voltage and not always the correct sign, so something else must be active to fully explain the thermocouple voltage. That something else is discussed below.

C. New consideration: Finite thickness interface has both $\nabla\rho$ and ∇V

Up until now in the analysis of Fig. 1 it has been assumed that the interface between the two conductors is of zero thickness. The zero thickness interface came about due to

the logic of James Clark Maxwell. His famous Maxwell's equations first appeared in their fully developed form in his renowned textbook [9]. Lesser known in this textbook was his struggle to decide how to define surface charge density (see Vol. 1, pp. 72-73 in [9]). He presented two possibilities. In one scenario he reasoned that charges had no mass and needed no depth to occupy the surface. In a second scenario he reasoned that if the charges had a mass then they would be required to occupy a depth of some finite thickness. He then argued that with the most sensitive instruments of his day no mass was ever detected when charges were placed on a surface; and, therefore, a zero thickness interface would be the best choice. Maxwell died in 1879, and it was not until almost 18 years after his death that J. J. Thomson discovered the electron had a mass and it was about 1000 times smaller that that of the hydrogen ion. It is reasonable to assume Maxwell would have changed his definition of surface charge density to that of having a finite thickness had he been privy to Thomson's information.

Now consider two materials A and B that have different characteristic or intrinsic free-charges densities ρ_{0A} and ρ_{0B}, respectively. Logic and reason indicate that if the two materials are connected together at an interface then there is an abrupt change in the free-charge densities at the interface; and a charge density gradient $\nabla\rho$ is set at the interface. Since free-electrons will move under the action of the diffusional force set up by the gradient, some of the free-electrons in the higher charge density material will diffuse across the interface and into the lower charge density material as described by (8). Because the ion associated with the free electron cannot move, this sets up and electric field **E** pointing from the higher to the lower free-charge density material. The electric field **E** drives some of the electrons back as described by (7) until an equilibrium is set up where the two charge fluxes (7) and (8) are equal everywhere in both materials. The details of this problem have been worked out elsewhere [10], [11]; across an interface of two conductors A and B held at temperature T the results reveal a finite thickness interface of a well defined thickness λ_{IFAB} [11] and an interfacial potential difference given by [10] as

$$V_{0A} - V_{0B} = -\frac{kT}{sq} \ln \frac{\rho_{0A}(T)}{\rho_{0B}(T)} \tag{24}$$

where ρ_{0A} and ρ_{0B} are the characteristic or intrinsic free-charges densities of the two materials beyond the thickness of the interface. For the thermocouple problem being studied in this paper, since only free electrons are the specie of interest, $s = -1$, and $-(kT)/(sq) = -(kT)/(q_e)$ is a positive quantity in (24).

An examination of (24) is quite revealing. If $\rho_{0A} > \rho_{0B}$, then free-electrons leave A and move into B at the interface leaving A positive with respect to B and resulting in $V_{0A} > V_{0B}$. This logic is clearly found in (24), since, if $\rho_{0A} > \rho_{0B}$ then the ln term is positive and hence $V_{0A} - V_{0B}$ will be positive. But, if $V_{0A} - V_{0B}$ is found to be positive in (24), then by logic V_{0A} must be more positive than V_{0B}.

On the other hand if $\rho_{0A} < \rho_{0B}$, then, the ln term is negative and a similar discussion ensues to reveal $V_{0B} < V_{0A}$.

In the authors' opinions it is this potential drop that occurs at an interface of two solid conductors that has been overlooked in the classical analysis of the thermocouple. An interfacial voltage drop described by (24) occurs at the hot junction as well as at each of

the cold junctions and each voltage drop contributes to the total voltage drop around the thermocouple loop.

To analyze the interfacial voltage drops across a thermocouple note in Fig. 1 that (24) indicate a voltage drop occurs across the cold interface or junction of metal A and the connecting wire of a magnitude

$$V_{0A} - V_{0W} = -\frac{kT_c}{sq} \ln \frac{\rho_{0A}(T_c)}{\rho_{0W}(T_c)}. \tag{25}$$

Likewise, a voltage drop occurs across the cold junction of metal B and the connecting wire of

$$V_{0B} - V_{0W} = -\frac{kT_c}{sq} \ln \frac{\rho_{0B}(T_c)}{\rho_{0W}(T_c)}. \tag{26}$$

So, if the voltage drops are added starting from the cold wire to the metal A interface, then, the sum of these voltage drops will be (25) minus (24) minus (26) where (24) is evaluated at T_h. Since (25) minus (26) have ln terms involving the connecting wires, and, since ln A/W – ln B/W → ln A/B, the voltage drop across all three interfaces will add to

$$\Delta V_{tIF} = V_{cB} - V_{cA} = \frac{kT_h}{sq} \ln \frac{\rho_{0A}(T_h)}{\rho_{0B}(T_h)} - \frac{kT_c}{sq} \ln \frac{\rho_{0A}(T_c)}{\rho_{0B}(T_c)}. \tag{27}$$

These interfacial voltage drops must be added to (22) to obtain the full voltage drop that occurs across the two connecting wires of Fig. 1. Furthermore, the charge densities in (27) must be determined at their specific temperatures.

Note in (27) that if $T_h \to T_c$ that $\Delta V_{tIF} \to 0$ even though, in general, the ln term is not zero. Thus, (27) implies that although there is a voltage drop across an interface at any temperature the sum of the voltage drops is zero if all the conductors are at the same temperature; a result that is found experimentally. Furthermore, if two solid conductors of the same material are connected together then $\rho_{0A} = \rho_{0B}$ and the ln terms are both zero so there is no interfacial voltage drop as would be expected. For a Pt-Cu thermocouple the addition of (27) gives –2.08 mV which must be added to the –64.4 µV due to the thermal gradient giving –2.14 mV and a Seebeck coefficient of 21.4 µV.

To create a thermocouple two different materials must be brought together to form an interface. In the early classical analysis presented above in Section IIIa and IIIb no special attention was paid to the interface. Instead the interface was treated simply as a zero thickness plane that defines the boundary between the two different conductors. However, it is well known that when two different uncharged materials are brought together and then separated that the materials often are charged to opposite polarities; and this phenomenon is known collectively as triboelectric charging or simply tribocharging [12]. Clearly, in tribocharging some charges moved across the contacting interface. As a result, some charge must have moved across the contacting area in a unit of time – that time being equivalent to the time of contact. When any two materials are brought together in contact, there is no prior indication as to weather the contact will be kept (to possibly make a thermocouple) or separated (to possibly produce tribocharging). As a result, there must be included in any complete thermocouple theory a consideration of **J** across each interface as well as the consideration that a temperature gradient ∇T will have on the physics of the problem.

IV.   CONCLUSIONS

The potential difference across an electrically isolated conductor in a thermal gradient has been analyzed, is given by (19) or (20), and involves α the coefficient of linear thermal expansion. However, because α is so small, the potential difference can be given by (14) with ≤ 2% error. However, measurement of this potential difference must be measured without introducing errors due to dissimilar metals in contact. This direct measurement has yet to be done. Instead, a thermocouple is used where one metal of the thermocouple is the metal of interest. An analysis using the charge flux equation reveals that (19) does not predict the full picture when compared to measured data. A new look at the classical analysis reveals that the potential drop across each interface must be taken into account when measuring with a thermocouple. This will be the subject of a future paper.

REFERENCES

[1] Enn Velmre, "Thomas Johann Seebeck (1770–1831) ," *Estonian Journal of Engineering*, Vol. 13, No. 4, 2007, pp. 276–282.

[2] G. W. C. Kaye and T. H. Laby, *Tables of Physical & Chemical Constants*, 1995, Available: http://www.kayelaby.npl.co.uk/general_physics/2_3/2_3_2.html

[3] K. I. Uemura, et. al., *SCT-93 Short Course on Thermoelectrics*, 1993, Available: http://www.its.org/sct93

[4] C. B. Vining, *Thermoelectric Fundamentals and Physical Phenomena*, 1993, Available: Lecture 2, http://www.its.org/sct93

[5] S. Fujita and A. Suzuki, "Quantum Theory of Thermoelectric Power (Seebeck Coefficient)," in *Electromotive Force and Measurement in Several Systems*, InTech, 2011, pp. 1-20.

[6] A. E. Seaver, "Multicomponent Transport Equations in Electrostatics," Proceedings of the ESA 1995 Annual Meeting, Rochester, NY, Morgan Hills, CA: Laplacian Press, 1995, pp. 193-209.

[7] A. E. Seaver, "Development of the charge flux equation using the contiguous collision averaging method," *J. Electrostat*, Vol. 46, No. , 1999, pp. 177-192.

[8] R. C. Weast, *CRC Handbook of Chemistry and Physics*, Boca Raton, Florida: CRC Press, 1981-82.

[9] J. C. Maxwell, *A Treatise on Electricity and Magnetism*, Vol. 1 and Vol. 2, New York: Dover, 1954.

[10] A. E. Seaver, "The Criteria for Interfacial Electro-Thermal Equilibrium," Proceedings ESA Annual Meeting 2005, University of Alberta, Edmonton, Alberta, Canada, Morgan Hills, CA: Laplacian Press, 2005, pp. 184-200.

[11] A. E. Seaver, "On Solid-Solid Interface Thickness," Proceedings of the ESA Annual Meeting on Electrostatics 2007, Purdue University, West Lafayette, IN, June 12-14, 2007, Cambria, CA: Laplacian Press, 2007, pp. 109-130.

[12] J. A. Cross, *Electrostatics: Principles, Problems and Applications*, Bristol: Adam Hilger, 1987.