

Applying Classical Physics and MOC to Predict the Output of a Thermocouple

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Abstract—A metal thermocouple (TC) consists of two dissimilar metal wires bonded together at one end and individually connected to measurement leads at the two open ends. When the bonded end of the wires is placed at a temperature different from that of the measurement lead ends, a voltage appears across the measurement leads. Classical physics, when used to predict the voltage expected from the thermal gradient found in the wires, does not account for the measured voltage. Due to this failure of classical physics, quantum physics has been brought into play to explain the details of TC physics, and –over the last half century– quantum physics has been the direction taken in TC theory. Unfortunately, to date no theory has been developed that predicts the output voltage of a TC over its useful temperature range. Presently all classical theories examine the temperature gradient and ignore the three interfaces that exist –one at the TC bond and two others where contact is made to the measurement leads. This seems justified because many years ago, and based on the best experimental data available at the time, James Clerk Maxwell (1831-1879) in his famous book titled “*A Treatise on Electricity and Magnetism*” suggested that charge at an interface did not occupy any space. Therefore, surface charge density could be defined as existing on a surface having zero thickness. This allowed a material's electrical conductivity to be defined as a single constant throughout the material. The concept of a zero-thickness interface also gave credence to Ohm's Law. Furthermore, thermodynamics is based on the assumption that each material has a well-defined set of temperature dependent properties that completely define the state of the material at any temperature. In the classical approach to treating TC physics, Ohm's Law is modified to account for the temperature variation; but nothing of consequence happens at the zero-thickness interfaces. As a result, it would appear that classical physics truly fails to describe TC physics, unless something has been overlooked. Fortunately, that something can be described as Maxwell's Other Choice (MOC). Maxwell chose the zero-thickness electrical interface because no mass change was detected when objects were charged; so, it was assumed that charge had no mass. Maxwell clearly stated if charge had mass that the zero-thickness electrical interface would be incorrect and a finite-thickness electrical interface would be needed. This finite-thickness electrical interface was MOC. Almost two decades after Maxwell's death it was discovered that charge had a mass and, hence, size; so MOC is the proper way to describe charge at an interface. Using MOC to describe an interface allows for the possibility of a finite charge density gradient to exist across an interface which in turn would give rise to a potential difference across an interface. In this paper it is shown when a modified Drude model and the full charge flux equation are used to study a metal TC that interfacial potential differences occur; and, when these potentials are taken into account, this classical physics model gives a

reasonable theory predicting the TC voltage over most of the useful temperature range for all the popular (i.e., Type B, E, J, K, N, R, S and T) thermocouples.

I. INTRODUCTION

A junction between two materials is known as an interface. For example, the inside of a glass half full of water has three interfaces: a water-glass interface, a water-air interface, and a glass-air interface. On the other hand, the water has only two interfaces: the water-glass interface, and the water-air interface.

A thermocouple (TC) –shown in Fig. 1– is a device used to measure temperature and has three interfaces of importance; these interfaces each being held at a constant temperature as depicted by the three circles in Fig. 1. The TC consists of two conductive but dissimilar materials (Conductor 1 and Conductor 2 in Fig. 1) connected at a common end –creating one interface– and placed at a position where the temperature T is to be measured; for example: $T = T_h$ in Fig. 1. The other end of each conductor is connected to a lead and held at a known “reference” temperature; for example: T_c in Fig. 1. These leads are the input to a voltmeter which measures the voltage ΔV_i shown in Fig. 1. The two conductors when connected together are referred to as a thermocouple or simply as a couple. If the difference between the temperature being measured and the reference temperature is ΔT , where for example: $\Delta T = T - T_c$ in Fig. 1, then the TC voltage in Fig. 1 is given by $\Delta V_i = S \Delta T$ where S is the Seebeck coefficient of the two-conductor couple and is named after Thomas Johann Seebeck (1770–1831) who discovered the effect [1].

A. MFC, MOC, the Interface and the TC Interfaces

When studying electrical affects in materials, the contribution of the interface is often ignored. This is mainly due to the observations of James Clerk Maxwell (1831-1879). When Maxwell was writing his famous book titled *A Treatise on Electricity and Mag-*

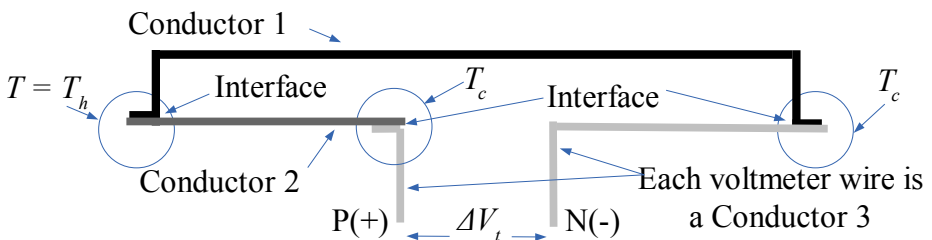


Fig. 1: General Diagram for a Thermocouple. Two metal wires are joined together at a junction, and this junction is placed at a temperature of interest designated as T_h . The two wires and connecting junction –the junction is usually a weld– is known collectively as a thermocouple (TC) but is also referred to as a couple. When the open ends of a couple are held at a reference temperature T_c and connected to a voltmeter, the reading of the voltmeter ΔV_i can be used to determine the temperature T provided that the Seebeck coefficient $S(T)$ of the couple is known, where $\Delta V_i = S(T) (T - T_c)$. The Seebeck coefficient is essentially the slope of the voltage-temperature curve. Although $S(T)$ can be nearly constant over a wide temperature range as in Fig. 6, usually it is not, as in Fig. 5 and Fig. 7.



Fig. 2: Photo of a Thermocouple Weld. Picture shows the two thermocouple wires and the spherical bead.

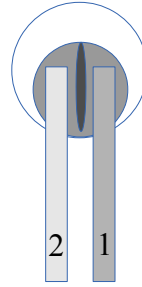


Fig. 3: Schematic of the interior of a bead. The interior has a (dark) fusion zone and a (lighter) heat-affected zone just like the weld depicted and described in Fig. 2.

netism [2] he was faced with the problem of how to electrically define charge at an interface.

Maxwell postulated, if charge had no mass then it had no size, and hence, there would be no need to assign a thickness to the interface. Because the most sensitive measurement instruments of his time could not detect any change of mass to an object when the object was charged, he reasoned electricity had no mass; and a zero-thickness electrical interface could, therefore, be used to describe charge at an interface (see [2] Vol 1, p. 72). This zero thickness interface postulate –which here is called *Maxwell's First Choice* (MFC)– has survived to this day.

However, Maxwell also postulated, if charge had a mass then it also had a size, and there must be an electrical thickness to an interface within which the charges would reside ([2] Vol 1, p. 72). This finite-thickness interface will be defined here as *Maxwell's Other Choice* (MOC), but he chose not to investigate it further, since, as stated above, no mass had ever been detected. In 1897, some 18 years after Maxwell's death, J. J. Thomson discovered the electron as a particle having charge and mass. Had Maxwell lived past the time of the electron's discovery, it is clear from his writings that he then would have immediately infused MOC into the study of electrical phenomenon at an interface.

This paper addresses only metallic thermocouples where the two wire interface is a weld, but the results should also be applicable to highly doped semiconductor thermocouples in simple physical contact. The connecting junction of the two wires is usually a welded interface like the one shown in Fig. 2, and has a slightly more complicated interfacial structure consisting of several zones as depicted in Fig. 3. A TC has three interfaces; namely, one within each of the three constant temperature circles shown in Fig. 1.

The normal assumption in classical TC analysis is to assume each junction is always in an isothermal region; so, the contribution to the thermocouple voltage is zero, and the junction does not play a role other than joining the wires [3]. This assumption is not made here; instead it is argued that the key to understanding the Seebeck coefficient and

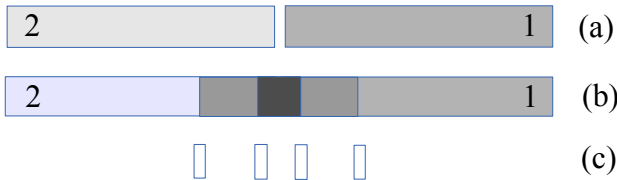


Fig. 4: Schematic of a butt weld of two different metals. The diagrams are: (a) A square butt joint before weld occurs; (b) Cross-section of the welded butt joint where the darkest gray center represents the fusion or weld zone, the lighter gray represents the heat-affected zone, and the outer light grays are the two thermocouple wires a.k.a. the base materials; (c) The locations of the electrical interface regions. Note: the size of the interface regions are greatly exaggerated in (c) and for two metals all interface regions are typically found to be much less than one atomic layer thick.

the TC physics is to understand the voltage drop across an interface when the interfacial region is defined by MOC; namely, the interface has a finite-thickness.

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 [4]. Clearly, in tribocharging some charges moved across the contacting interface during the time of contact. When any two materials are brought together in contact, there is no prior indication as to if the contact will be kept (to possibly make a thermocouple) or separated (to possibly produce tribocharging). As a result, just as in tribocharging [5], in TC physics theory there must be included a consideration of a current density \mathbf{J} that can occur across each interface when two dissimilar materials make contact as well as the usual consideration that a temperature gradient ∇T will have on the physics of the TC problem.

If the interfaces are to be treated as an important part of TC analysis, the question arises as to how to model these interfaces and especially the weld junction. The cross-section of a welded butt joint is shown in Fig. 4, with the darkest gray representing the weld or fusion zone, the medium gray the heat-affected zone, and the lightest gray the base materials.

The fusion zone in Fig. 4b is expected to be homogeneous based on the molecular mixing within the violent fusion process. However, the heat-affected zone in Fig. 4b may or may not be completely homogeneous (i.e., the same on both sides in the weld) as it depends on the conditions during the weld. In the present paper it is assumed homogeneous.

When modeling the weld it becomes convenient, in the first approximation, to model it as specific zones –each zone attached to the next via a *finite-thickness interface* as shown in Fig. 4c. Treated in this way the bead or weld has the same general form as any TC interface, so the equation giving the potential across a finite-thickness interface – which will be presented in Section VI– is applicable to each interface within the weld.

II. CHARGE FLUX, MOC AND TC ANALYSIS

As noted in Section I the concept of electricity being composed of charges which do not have mass –and, therefore, do not have size– led Maxwell to choose Maxwell's First Choice (MFC) in which charge on a surface can exist on a surface of zero-thickness. The later discovery that electricity was the result of the motion of electrons, and that the electrons had mass, requires the charge on a surface to exist on a surface of finite-thickness and is referred to in this paper as Maxwell's Other Choice (MOC). In thermocouple (TC) analysis there are three junctions or interfaces that must be analyzed, and these interfaces are shown within the constant temperature circles of Fig. 1. When free-electrons move through a TC in a closed circuit, a current i flows through each wire such that, if a plane is cut through either wire, there is a charge flux or current density \mathbf{J} – a current per unit area – flowing through each and every point in the plane of the wire. To obtain the current i flowing through the wire, it is a simple matter to sum up the current density at every point over the total area of the wire cut by the plane.

The charge flux can be written today in one of three ways as

$$\mathbf{J} = \sigma \mathbf{E} = -\sigma \nabla V \quad \text{(A) Ohm's Law}$$

$$\mathbf{J} = -\sigma \nabla V - G\rho \nabla T \quad \text{(B) Modified Ohm's Law} \quad (1)$$

$$\mathbf{J} = -\sigma \nabla V - D\nabla\rho - G\rho \nabla T \quad \text{(C) Full Charge Flux}$$

When written as (1A) the equation is known as the field form of Ohm's Law where \mathbf{E} is the electric field at some point of interest within either TC wire and σ is the electrical conductivity of the metal wire at the point. But, since $\mathbf{E} = -\nabla V$, Ohm's Law also relates the charge flux or current density \mathbf{J} to the potential difference ∇V along the wire. When combined with MFC Ohm's Law has an important significance to the TC analysis. Namely, if the thermocouple is held in an open circuit, then there can be no \mathbf{J} anywhere, so \mathbf{E} must be zero everywhere inside either of the metal conductors. Furthermore, with MFC there can be no potential difference across the zero-thickness interface.

Ohm's Law, when modified to account for the fact that the temperature is not constant at every point, is written as (1B) where G is defined as the thermophoresis coefficient and ρ is the free-electron charge density. Now, if the thermocouple is held in an open circuit, then there can be no \mathbf{J} and the *sum* of the two terms on the right hand side of (1B) must be zero everywhere inside either of the metal conductors. As a result, a temperature gradient along a TC wire gives rise to a potential gradient along the wire. This is the normal starting point in the analysis of a TC. Using (1B) in TC analysis reveals, if there is no thermal gradient, then there can be no potential gradient, and this is also found experimentally. However, using (1B) gives an equation to predict the potential along a wire; but the predicted potential is the same along any wire so it can't account for the TC voltage. It is this failure that has led to the emphasis on examining quantum physics to explain the voltage output of the TC [6]. However, even with quantum *adjustments* to give an electrical double layer, no theory has yet emerged that can predict the output voltage of a TC over a large temperature range.

In general within a volume element surrounding a point any number of scalar quantities can be defined; two examples would be number density and temperature. The charge flux equation (1C) can be developed based purely on the arguments of calculus when a gradient exists for any scalar quantity across the volume element [7]. However, – in the absence of magnetic affects – the charge flux equation has also been developed from a classical physics model of collisions [8]; when only electrons are free to move the charge flux equation (developed in [8]) reduces to (1C) where D is the diffusion coefficient of the free-electron and D and G are related by $D = GT$. However, the extra term of a gradient in charge density in (1C) is not compatible at an interface with MFC since a gradient needs to exist across a finite-thickness, even if that thickness is infinitesimally small. However, by applying MOC there exists a region of surface where the gradient can exist. It is this combination of (1C) and MOC that gives an interfacial potential across interfaces of two dissimilar materials when the free-electron charge density ρ of each material differs. The details of this problem have been worked out elsewhere including determining the thickness of the interfacial region [9] and the potential across the interface [10]. This interfacial potential and its application to TC analysis is discussed further in Section VI through Section IX.

III. VARIATION OF CHARGE DENSITY WITH TEMPERATURE

The free-electron charge density ρ at any point in the wire is defined as the charge per free electron times the number of these charges within a volume element at the point. If n is defined as the free-charge number density, then the free-electron charge density is

$$\rho = -q_0 n \quad (2)$$

where q_0 is the magnitude of the charge on an electron ($q_0 \approx +1.6 \times 10^{-19}$ C).

For a homogeneous metal cube of side L containing N free-electron charges the free-electron number density at any point is

$$n = n(L, N) = \frac{N}{L^3}. \quad (3)$$

But the total differential of n is ([11] see p. 689) $dn = \frac{\partial n}{\partial L} dL + \frac{\partial n}{\partial N} dN$, and based on

(3) it can be seen that

$$\frac{\partial n}{\partial L} = \frac{\partial}{\partial L} \left(\frac{N}{L^3} \right) = -3 \frac{N}{L^4} = -\frac{3}{L} \frac{N}{L^3} = -\frac{3}{L} n, \quad \text{and} \quad \frac{\partial n}{\partial N} = \frac{\partial}{\partial N} \left(\frac{N}{L^3} \right) = \frac{1}{L^3} = \frac{1}{N} \frac{N}{L^3} = \frac{1}{N} n,$$

so $dn = \frac{\partial n}{\partial L} dL + \frac{\partial n}{\partial N} dN = -3 \frac{n}{L} dL + \frac{n}{N} dN$, or $\frac{dn}{n} = -3 \frac{dL}{L} + \frac{dN}{N}$. Also note that, if

both $N = N(T)$ and $L = L(T)$, then $dN = \frac{dN}{dT} dT$ and $dL = \frac{dL}{dT} dT$ so

$$\frac{dn}{n} = -3 \frac{dL/dT}{L} dT + \frac{dN/dT}{N} dT = \left(-3 \frac{dL/dT}{L} + \frac{dN/dT}{N} \right) dT \quad \text{which can be written as}$$

$$\frac{dn}{n} = (-3\alpha_L + \alpha_N) dT = \alpha dT \quad (4)$$

where

$$\alpha = -3\alpha_L + \alpha_N \quad (5)$$

and where

$$\alpha_L = \frac{1}{L} \frac{dL}{dT} \quad (6)$$

is defined ([12], see Eq. 18, p. 358) as the instantaneous thermal coefficient of linear expansion (CLE) and is consistent with the starting equation in thermodynamic studies ([13], see Eq. 15, p. 14), and where

$$\alpha_N = \frac{1}{N} \frac{dN}{dT} \quad (7)$$

is defined (in this paper) as the coefficient of free-electron recombination/generation.

In general the CLE (α_L) for many metals has been found to increase with increasing temperature; the increase being most dramatic at very low temperature. The physical cause of the variation of the CLE with temperature has been shown to be related to the variation of the lattice constant with temperature [14]. However, in this paper it is assumed that $\alpha_L \neq \alpha_L(T)$ and $\alpha_N \neq \alpha_N(T)$ so that (6) when written as $\frac{dL}{L} = \alpha_L dT$ integrates to $L = L_0 e^{\alpha_L(T-T_0)}$ and if, $\alpha_L(T-T_0) \ll 1$ then $L \approx L_0 [1 + \alpha_L(T-T_0)]$ which is the equation for linear expansion found in physics textbooks ([15], see p 431 Eq. 19-9) and reference handbooks ([16], see p. F-117).

Likewise, (7) is written as $\frac{dN}{N} = \alpha_N dT$ which integrates to

$$N = N_0 e^{\alpha_N(T-T_0)} \quad (8)$$

and finally (4) integrates to

$$n = n_0 e^{\alpha(T-T_0)}. \quad (9)$$

Combining (2) and (9) gives

$$\rho = \rho(T) = -q_0 n_0 e^{\alpha(T-T_0)} = \rho_0 e^{\alpha(T-T_0)} \quad (10)$$

as the general equation giving the variation of charge density with temperature. Finally, measurements are often made at some reference temperature $T_0 \rightarrow T_{ref}$ and (10) becomes

$$\rho = -q_0 n_{ref} e^{\alpha(T-T_{ref})} = \rho_{ref} e^{\alpha(T-T_{ref})} \quad (11)$$

The free-electron charge density given by (11) is very important. Since the electrical conductivity is $\sigma = \rho b$ where b is the electron mobility, every term on the right hand side of (1C) contains ρ . Hence, solving problems using the full charge flux equation (1C) relies heavily on having specific knowledge of ρ .

IV. ESTIMATING THE FREE-ELECTRON DENSITY IN METALS AND ALLOYS

In (11) although it is not possible to look up the value of ρ_{ref} directly, for a metal it is possible to calculate its value based on a modification of the Drude model. If n_a is the mass number density of the atoms in a metal, then in the Drude model it is assumed that there is one free-electron per atom in the metal and, therefore, $n = f n_a$ where $f = 1$. A common practice is to assume the Drude model ($f = 1$) holds for all temperature, but experimental evidence at low temperature suggest that f is different than unity for most of the alkali [17] and alkaline [18] metals. Therefore, here the fraction f will be carried through the equations, and it will be shown later that experimental evidence for a thermocouple also suggests the fraction is not unity.

A. Pure Metals

If an elemental metal, has a molecular weight M , and a mass density δ_a at a temperature T , then it has a mass number density n_a given by $n_a[\text{atoms/volume}] = (N_A[\text{atoms/mole}]\delta_a[\text{g/volume}])/M[\text{g/mole}]$ where N_A is Avogadro's number; $N_A \approx 6.022 \times 10^{23}$ molecules per mole. So, if the metal has a mass density $\delta_{a,ref}$ measured at a reference temperature T_{ref} , it will have –as just noted– a number density $n_{a,ref}$ of atoms per unit volume based on this mass density $\delta_{a,ref}$. If there is, at this reference temperature, some fraction f_{ref} of these atoms that have a free-electron, then the number density of the free-electrons at this reference temperature is

$$n_{ref} = f_{ref} n_{a,ref} = f_{ref} \frac{N_A \delta_{a,ref}}{M} \quad (12)$$

As already mentioned, for the Drude model $f = 1$, but in this paper f will be included since, as already mentioned, experimental evidence suggest $f \neq 1$.

B. Metal Alloys

Thermocouple wires are often made of metal alloys. For example, constantan is a copper-nickel alloy nominally of 55 wt % copper and 45 wt % nickel but specific compositions can vary the copper between 50% and 65% (see [19], p. 158). For nominal constantan: $0.55 = m_{Cu}/(m_{Cu} + m_{Ni}) = \frac{m_{Cu}}{V_A} / \frac{(m_{Cu} + m_{Ni})}{V_A} = \frac{m_{Cu}}{V_A} / \delta_A$ where δ_A is the mass density of the alloy and V_A is the volume of the alloy. Hence, $m_{Cu}/V_A = 0.55 \delta_A$ and $m_{Ni}/V_A = 0.45 \delta_A$ so, the alloy number density –for the alloy constantan– is

$$\begin{aligned}
n_A &= n_{Cu} + n_{Ni} \\
&= \frac{N_A}{M_{Cu}} \frac{m_{Cu}}{V_A} + \frac{N_A}{M_{Ni}} \frac{m_{Ni}}{V_A} \\
&= \frac{N_A (0.55) \delta_A}{M_{Cu}} + \frac{N_A (0.45) \delta_A}{M_{Ni}} \\
&= N_A \delta_A \left(\frac{0.55}{M_{Cu}} + \frac{0.45}{M_{Ni}} \right) \\
&= \frac{N_A \delta_A}{M_A}
\end{aligned} \tag{13}$$

Where $\frac{1}{M_A} = \left(\frac{0.55}{M_{Cu}} + \frac{0.45}{M_{Ni}} \right)$ or upon rearranging the molecular weight of the alloy is

$$M_A = \frac{1}{\left(\frac{0.55}{M_{Cu}} + \frac{0.45}{M_{Ni}} \right)} \tag{14}$$

If at the reference temperature T_{ref} there is some fraction f_{ref} of these atoms in the alloy that have a free-electron, then the number density of the free-electrons at T_{ref} is

$$n_{ref} = f_{ref} n_{A,ref} = f_{ref} \frac{N_A \delta_{A,ref}}{M_A} \tag{15}$$

which is equivalent to (12) except (15) is for an alloy. Although (14) was developed here for nominal constantan, its conversion to any general alloy is simply to sum all the constituents in the denominator of (14) so the generalization will not be presented here.

C. Example: Type T Thermocouple – Copper and Constantan

For example, the density of the alloy constantan is $\delta_A = 8.86 \text{ g/cm}^3$ and, since $M_{Cu} = 63.546 \text{ g/mol}$ and $M_{Ni} = 58.6934 \text{ g/mol}$, then for constantan its molecular weight is

$$M_A = \frac{1}{\left(\frac{0.55}{63.546} + \frac{0.45}{58.6934} \right)} = 61.267 \text{ g/mol} \quad \text{and}$$

$$n_{A,ref} = \frac{N_A \delta_{A,ref}}{M_A} = \frac{(6.022 \times 10^{23})(8.86)}{61.267} = 8.71 \times 10^{22} \text{ atoms/cm}^3 = 8.71 \times 10^{28} \text{ atoms/m}^3.$$

From (2) and (15) the free-electron charge density of constantan, assuming the Drude model ($f = 1$), is $\rho_{ref} = -q_0 n_{A,ref} = (-1)(1.6 \times 10^{-19})(8.71 \times 10^{28}) = -1.39 \times 10^{10} \text{ C/m}^3$.

On the other hand, copper has a mass density of $\delta_{Cu} = 8.93 \text{ g/cm}^3$, so

$$n_{Cu,ref} = \frac{N_A \delta_{Cu,ref}}{M_{Cu}} = \frac{(6.022 \times 10^{23})(8.93)}{63.546} = 8.46 \times 10^{22} \text{ atoms/cm}^3 = 8.46 \times 10^{28} \text{ atoms/m}^3,$$

and from (2) and (12) the free-electron charge density of copper for the Drude model is $\rho_0 = \rho_{ref} = -q_0 n_{ref} = (-1)(1.6 \times 10^{-19})(8.46 \times 10^{28}) = -1.35 \times 10^{10} \text{ C/m}^3$. Thus, there is

just a marginally higher ($\approx 3\%$) free-electron charge density in constantan than in copper at the reference temperature T_{ref} when the Drude model ($f_{ref} = 1$) is assumed.

V. VOLTAGE ALONG A CONDUCTOR IN A THERMAL GRADIENT

A metal expands when heated. If a metal bar of any length has one end held at a cold temperature T_c and the other end held at a different temperature T , then, using (1C) it was shown in [20] that the voltage drop at the ends of the conductor due to the temperature gradient along the conductor is

$$V_T - V_c = \frac{k}{q_0} (T - T_c) \left[1 + \frac{\alpha}{2} (T + T_c) \right]. \quad (16)$$

where k is Boltzmann's constant ($k \approx 1.38 \times 10^{-23}$ J/K) and, since $q_0 \approx +1.6 \times 10^{-19}$ C, then $k/q_0 \approx 86.25$ μ V/K. A note in passing should be mentioned here where in [20] eq. 19 has $-k/(sq)$ and (16) here has $+k/q_0$ but there is no discrepancy; namely, $-k/(sq) = -k/(sZq_0)$ where s is the sign of the charge on the species and Z is the number of charges of the species; when electrons are the specie of interest, then $-k/(sq) = -k/(sZq_0) = -k/[(-1)(1)q_0] = k/q_0$. Also, in [20] no consideration was given to the fact that the number of free-electrons in the sample could change with temperature. In other words, it was tacitly assumed in (8) that $\alpha_N = 0$ so (16) had $\alpha = \alpha_L$ when derived in [20]. However, noting (16) contains both coefficients in (5) shows (16) is the more general equation for the voltage difference at the ends of the conductor. Based on convention the voltage difference $\Delta V = V_T - V_c$ is always defined as being taken from the reference end at T_c to the other end of the conductor held at $T = T_h$. If there are two *isolated (not connected)* conductors 1 and 2 with coefficients of linear expansion given by α_{L1} and α_{L2} , respectively, each held with one end at a general temperature T and the other at a referenced temperature T_c , then (16) allows the voltage drop –at the general T end with respect to the reference end– along each conductor to be written as

$$\Delta V_1 = \frac{k}{q_0} (T - T_c) \left[1 + \frac{1}{2} (T + T_c) \alpha_1 \right], \quad (17)$$

and

$$\Delta V_2 = \frac{k}{q_0} (T - T_c) \left[1 + \frac{1}{2} (T + T_c) \alpha_2 \right]. \quad (18)$$

If 1 and 2 are now connected as in the couple depicted in Fig. 1, then adding the voltage drop from the negative N(-) cold end of 1 (on the right in Fig. 1) to the hot end of 1 (as given by (17)) to the voltage drop from the hot end of 2 (on the left in Fig. 1) to the cold end of 2 (as given by the negative of (18)) give the total voltage across the couple as

$$\Delta V_{\Delta T} = \Delta V_1 - \Delta V_2 = \frac{1}{2} \frac{k}{q_0} (T - T_c) (T + T_c) (\alpha_1 - \alpha_2). \quad (19)$$

It was shown in [20] that (19), with $\alpha_N = 0$, when divided by $T - T_c$ gives the standard definition of the Seebeck coefficient of the couple but does not quantitatively predict the

correct value or necessarily the correct sign. It is interesting to note in passing that when both conductors are the same, then $\alpha_1 = \alpha_2$, and no voltage drop occurs at the ends of the couple no matter how large the temperature difference. On the other hand, when both conductors are the same except for the amount of impurities, then $N_1 \neq N_2$, and $\alpha_1 \neq \alpha_2$, so a very small voltage drop could occur at the ends of the couple its magnitude being dependent on how large of a temperature difference exists and the extent of the impurity concentration. Note that by the convention presented in this paper (19) is the voltage from the negative N(-) leg to the positive P(+) leg defining Conductor 1 as N(-).

VI. VOLTAGE ACROSS AN INTERFACE

The requirement of a finite-thickness interface and the extension of Ohm's Law to include the full charge flux (1C) brings an added consideration to the TC physics. In [20] it was noted –for a *finite thickness interface*– that there exists an *interfacial voltage drop* across an interface held at a temperature T as originally calculated in [10]. This interfacial voltage drop for two materials 1 and 2 in contact is

$$\Delta V_{12} = V_{02} - V_{01} = \frac{kT}{q_0} \ln \frac{\rho_{02}(T)}{\rho_{01}(T)} \quad (20)$$

where ρ_{01} and ρ_{02} are the free-electron charge densities of conductors 1 and 2, respectively, everywhere outside of the interfacial region. Specifically, for the TC physics under consideration here the free-electron charge density of each conductor contributes to the standard electrical conductivity of that conductor and is a single valued property of that conductor everywhere within the constant temperature region depicted by the circle in Fig. 1 –except inside the finite-thickness interface. The voltage drop across the interface ΔV_{12} is read as the “voltage at 2 with respect to 1” and measured from wire 1 to wire 2.

VII. THE AFFECT OF METER LEADS

The simplest method to measure a voltage difference across two terminals is to place a voltage sensing device –called a voltmeter– across the terminals. Both of the connecting wires of the voltmeter are made of the same conductor material (usually copper) but are not necessarily of the same material as either leg of the couple. As a result, when the voltmeter leads come in contact with the ends of a thermocouple, they create two extra interfaces that must be accounted for in the analysis.

Notice (20) indicates the sum of the voltages *just at the interfaces* in Fig. 1 is (starting from the right side and moving counter clockwise around the circuit)

$$\begin{aligned}
\Delta V_{IF} &= \Delta V_{wl}(T_c) + \Delta V_{12}(T) + \Delta V_{2w}(T_c) \\
&= \frac{kT_c}{q_0} \ln \frac{\rho_{01}(T_c)}{\rho_{0w}(T_c)} + \frac{kT}{q_0} \ln \frac{\rho_{02}(T)}{\rho_{01}(T)} + \frac{kT_c}{q_0} \ln \frac{\rho_{0w}(T_c)}{\rho_{02}(T_c)} \\
&= \frac{kT_c}{q_0} \ln \frac{\rho_{01}(T_c)}{\rho_{0w}(T_c)} + \frac{kT_c}{q_0} \ln \frac{\rho_{0w}(T_c)}{\rho_{02}(T_c)} + \frac{kT}{q_0} \ln \frac{\rho_{02}(T)}{\rho_{01}(T)} \\
&= \frac{kT_c}{q_0} \left(\ln \frac{\rho_{01}(T_c)}{\rho_{0w}(T_c)} + \ln \frac{\rho_{0w}(T_c)}{\rho_{02}(T_c)} \right) + \frac{kT}{q_0} \ln \frac{\rho_{02}(T)}{\rho_{01}(T)} \\
&= \frac{kT_c}{q_0} \ln \frac{\rho_{01}(T_c)}{\rho_{02}(T_c)} + \frac{kT}{q_0} \ln \frac{\rho_{02}(T)}{\rho_{01}(T)} \\
&= \frac{kT}{q_0} \ln \frac{\rho_{02}(T)}{\rho_{01}(T)} - \frac{kT_c}{q_0} \ln \frac{\rho_{02}(T_c)}{\rho_{01}(T_c)}
\end{aligned} \tag{21}$$

where $\ln \frac{\beta_{01}}{\beta_{0w}} = \ln \beta_{01} - \ln \beta_{0w}$ was used in line 4 of (21) to obtain line 5 of (21). As can be seen in (21) the affect of adding the lead-wires of the meter does not add any extra potentials because both lead-wires are at the same temperature T_c . Furthermore, in line 6 of (21), if $T = T_c$, then the \ln terms cancel resulting in $\Delta V_{IF} = 0$. By the same procedure it can be shown that adding any number of wires together – all at the same temperature – will always result in $\Delta V_{IF} = 0$. It is only when one junction is at a different temperature that the result $\Delta V_{IF} \neq 0$ will occur. In Fig. 4c application of (21) shows that the bead interfaces also cancel leaving only the interface between conductor 1 and 2 of interest.

In [20] it was found that when the interface potential drop given by (21) –which was found at the three constant temperature junctions of the couple, i.e., within the circles in Fig. 1– is added to the potential given by (19) –which was found as the sum of the potential drops across the ends of each wire in the thermal gradient– that this total potential V_i across the couple comes closer to experimentally measured values. However, in [20] no attempt was made to correct the value of ρ for its value at the junction temperature T . In this paper that correction will now be made explicitly in the next section.

VIII. INTERFACIAL POTENTIAL – CORRECTIONS FOR TEMPERATURE

In (21) there is no way to determine the value of ρ at the temperatures of interest. However, (11) and (12) show it is possible to estimate the free-electron charge density at some reference temperature T_{ref} if the density of the material is known at that temperature. Hence, it is useful to write (21) as

$$\begin{aligned}
\Delta V_{IF} &= \frac{kT}{q_0} \ln \frac{\rho_{02}(T)}{\rho_{01}(T)} - \frac{kT_c}{q_0} \ln \frac{\rho_{02}(T_c)}{\rho_{01}(T_c)} \\
&= \frac{kT}{q_0} \ln \frac{\rho_{02\text{ref}} e^{-3\alpha_2(T-T_{\text{ref}})}}{\rho_{01\text{ref}} e^{-3\alpha_1(T-T_{\text{ref}})}} - \frac{kT_c}{q_0} \ln \frac{\rho_{02\text{ref}} e^{-3\alpha_2(T_c-T_{\text{ref}})}}{\rho_{01\text{ref}} e^{-3\alpha_1(T_c-T_{\text{ref}})}} \\
&= \frac{k(T-T_c)}{q_0} \ln \frac{\rho_{02\text{ref}}}{\rho_{01\text{ref}}} + 3 \frac{kT}{q_0} [(\alpha_1 - \alpha_2)(T - T_{\text{ref}})] \\
&\quad - 3 \frac{kT_c}{q_0} [(\alpha_1 - \alpha_2)(T_c - T_{\text{ref}})]
\end{aligned} \tag{22}$$

Since, from (2) $\rho_{\text{ref}} = -q_0 n_{\text{ref}}$, then (22) with the aid of (12) can be rewritten as

$$\begin{aligned}
\Delta V_{IF} &= \frac{k(T-T_c)}{q_0} \ln \frac{f_{2,\text{ref}} \delta_{2,\text{ref}} M_1}{f_{1,\text{ref}} \delta_{1,\text{ref}} M_2} \\
&\quad + 3 \frac{kT}{q_0} [(\alpha_1 - \alpha_2)(T - T_{\text{ref}})] \\
&\quad - 3 \frac{kT_c}{q_0} [(\alpha_1 - \alpha_2)(T_c - T_{\text{ref}})]
\end{aligned} \tag{23}$$

where in (23) only f_1, f_2 and $(\alpha_1 - \alpha_2)$ are unknown.

In the past in any TC model two assumptions are usually made. First, it is assumed that the total number of free-electrons does not change with temperature, for which case, $\alpha_N = 0$, and as a result $(\alpha_1 - \alpha_2) \rightarrow (3\alpha_{L2} - 3\alpha_{L1})$. Second, the Drude model is assumed, i.e., $f_1 = f_2 = 1$, and then everything in (23) is known. However, to keep the study more general, these assumptions will not be made in this paper.

IX. THE COMPLETE PICTURE

In Section V the voltage dropped along the full length of a conductor whose ends are held at two different temperatures T and T_c was given by (16) so that for the thermocouple shown in Fig. 1 there is a voltage drop along conductor 1 –given by (17)– that must be added to the (negative of the) voltage drop coming back down conductor 2 –given by (18)– which gives (19) as the full voltage drop $\Delta V_{\Delta T}$ of the thermocouple due to the temperature gradient *along* the conductors.

However, this is not the complete picture because each interface also has a potential that develops due to the difference in the free-electron charge density of the two materials. As was shown in Section VII the leads, which are held at the same temperature, have no net affect. However, because one junction is held at a higher temperature (21) shows an extra potential is developed across the terminals of Fig. 1. When corrected for quantities measured at a reference temperature (21) becomes (23) as the final interfacial potential ΔV_{IF} developed across the couple.

Thus, the total output voltage of a thermocouple having the temperatures and conductors at the locations shown in Fig. 1 is

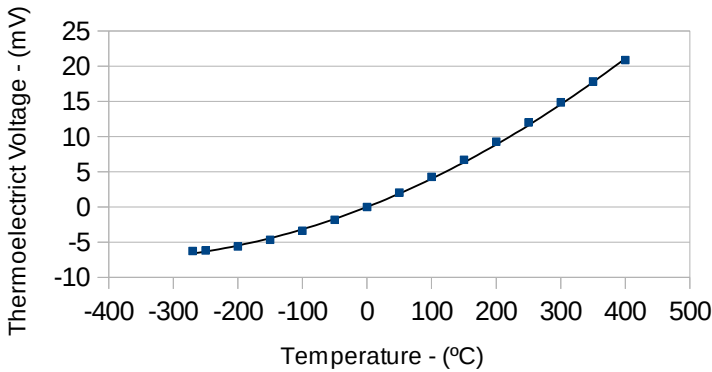


Fig. 5: TC Output Voltage vs Temperature for a Type T thermocouple. The square symbols represent measured data points from [22] and the solid line is given by (24) using (19) and (23) with $f_{2,ref}/f_{1,ref} = 1.35$ and $(\alpha_1 - \alpha_2) = 1.4 \times 10^{-4}/^{\circ}\text{C}$, where α_1 and α_2 are assumed independent of temperature.

$$\Delta V_i = \Delta V_{\Delta T} + \Delta V_{IF} \tag{24}$$

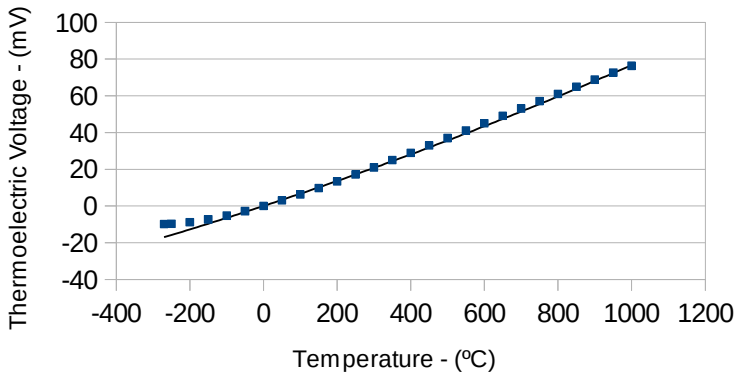


Fig. 6: TC Output Voltage vs Temperature for a Type E Thermocouple. The square symbols represent measured data points from [22] and the solid line is given by (24) using (19) and (23) with $f_{2,ref}/f_{1,ref} = 1.9$ and $(\alpha_1 - \alpha_2) = 3.6 \times 10^{-5}/^{\circ}\text{C}$, where α_1 and α_2 are assumed independent of temperature. As seen from the solid line for temperatures very much below 0°C , the assumption that α_1 and α_2 are constants independent of temperature does not fit the data. To conform to the data very much below 0°C , either α_1 or α_2 or both must be temperature dependent.

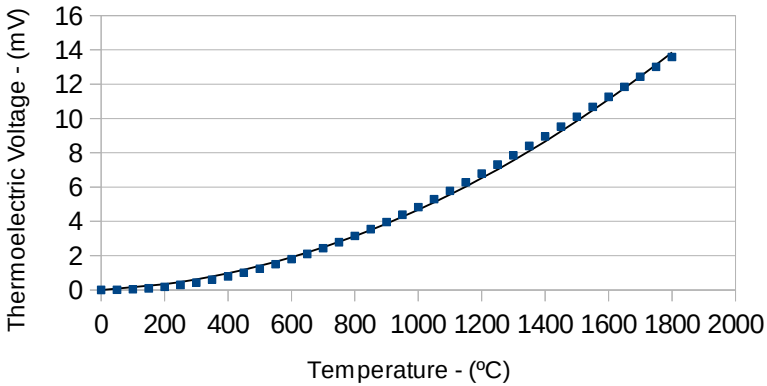


Fig. 7: TC Output Voltage vs Temperature for a Type B Thermocouple. The square symbols represent measured data points from [22] and the solid line is given by (24) using (19) and (23) with $f_{2,ref}/f_{1,ref} = 0.97$ and $(\alpha_1 - \alpha_2) = 1.25 \times 10^{-5}/^{\circ}\text{C}$ where α_1 and α_2 are assumed to be constants independent of temperature.

where ΔV_i is the voltage drop from the lead connected to conductor 1 (referred to as the negative leg) to the lead connected to conductor 2 (the positive leg) [21]. In (24) the $\Delta V_{\Delta T}$ term is given by (19) and the ΔV_{IF} term is given by (23).

X. APPLICATION TO TYPE E, T AND B THERMOCOUPLES

There are several thermocouples in use today with each listed by a letter. Listed from the highest to the lowest μV output per degree temperature change they are Type E, J, T, K, N, R, S and B. Type K, N and T are the most commonly used. Specific data for Type E, T and B thermocouples are shown in Table 1.

| Type | Pos(+) Material | Neg(-) Material | Pos(+) vs. Neg(-) Alloy Wt - g/mol | Pos(+) vs. Neg(-) Density - g/cc |
|------|--------------------|--------------------|---------------------------------------|-------------------------------------|
| B | Pt, 30%Rh | Pt, 6%Rh | 153.76 vs. 185.13 | 17.52 vs. 20.51 |
| E | Ni, 10%Cr | Cu, 45%Ni | 57.947 vs. 61.267 | 8.73 vs. 8.86 |
| T | Cu | Cu, 45%Ni | 63.546 vs. 61.267 | 8.93 vs. 8.86 |

Table 1: Some Material Properties of Type B, E and T Thermocouples. Composition percentages and densities are from [21]. Alloy weight calculated using (14).

The voltage-temperature data for the various metal TCs listed in Table 1 can be found in reference tables [22]. The TC output voltage vs temperature data for a Type T thermocouple are shown in Fig. 5 as data points. Using the information in Table 1 and in-

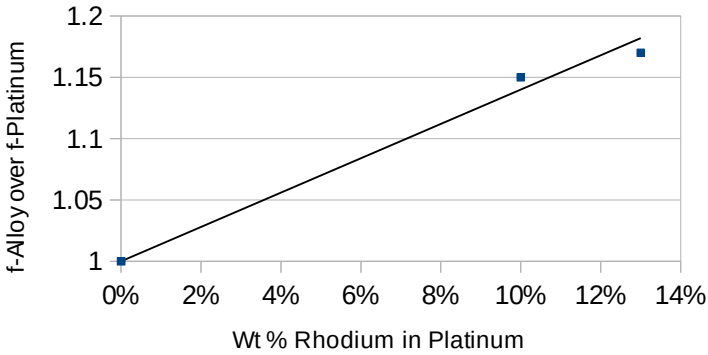


Fig. 8: Affect of % Rhodium on the Drude Fraction Ratio When Using a Platinum Reference Wire.

serting (19) and (23) into (24) and then plotting (24) gives the solid line in Fig. 5 when $f_{2_{ref}}/f_{1_{ref}} = 1.35$ and $(\alpha_1 - \alpha_2) = 1.4 \times 10^{-4}/^{\circ}\text{C}$ and where α_1 and α_2 are held constant and independent of temperature. Since the coefficients of thermal expansion are typically in the range of $5 - 30 \times 10^{-6}/\text{K}$ near room temperature (see [23] Section 2.3.5), the large value for $(\alpha_1 - \alpha_2)$ suggests that $(\alpha_1 - \alpha_2) \approx (\alpha_{N1} - \alpha_{N2})$. Likewise, since $f_{2_{ref}}/f_{1_{ref}} = 1.35$, it is clear that the Drude model ($f = 1$) is not applicable to this TC any more than it is applicable to a quantum-mechanical description that describes the resistivity of pure metals at low temperature for the alkali [17] and alkaline [18] metals.

The TC output voltage vs temperature data for a Type E thermocouple are shown in Fig. 6 as data points. Using the information in Table 1 for the Type E thermocouple and plotting (24) gives the solid line in Fig. 6 when $f_{2_{ref}}/f_{1_{ref}} = 1.9$ and $(\alpha_1 - \alpha_2) = 3.6 \times 10^{-5}/^{\circ}\text{C}$, and where α_1 and α_2 are kept independent of temperature. Again, since $(\alpha_1 - \alpha_2)$

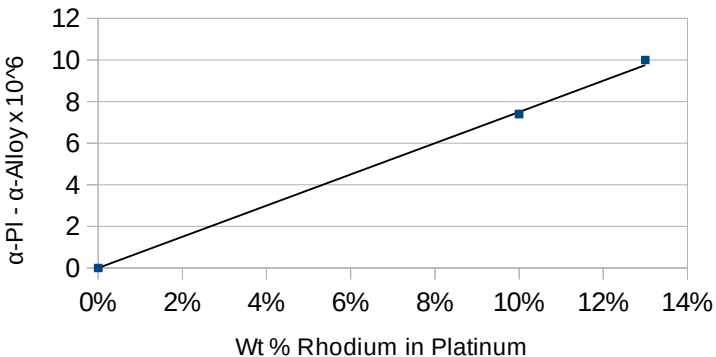


Fig. 9: Affect of % Rhodium on the α Coefficient Difference When Using a Platinum Reference Wire.

is large compared to the values of the CLEs, it may suggest that $(\alpha_1 - \alpha_2) \approx (\alpha_{N1} - \alpha_{N2})$. Likewise, since $f_{2_{ref}}/f_{1_{ref}} = 1.9$ it is clear that the Drude model ($f = 1$) is not applicable to a Type E thermocouple. In Fig. 6 a poor fit of (24) to the data exists at very cold temperatures which suggests that either α_1 or α_2 or both are temperature dependent.

The TC output voltage vs temperature data for a Type B thermocouple are shown in Fig. 7 as data points. The solid line in Fig. 7 results with $f_{2_{ref}}/f_{1_{ref}} = 0.97$ and $(\alpha_1 - \alpha_2) = 1.25 \times 10^{-5}/^\circ\text{C}$. Here again the large value for $(\alpha_1 - \alpha_2)$ opens up the possibility that $(\alpha_1 - \alpha_2) \approx (\alpha_{N1} - \alpha_{N2})$. Since $f_{2_{ref}}/f_{1_{ref}} = 0.97$ the Drude model ($f = 1$) might be applicable for a Type B thermocouple, but other values of f are possible since it is only a ratio of $f_{2_{ref}}/f_{1_{ref}}$ that is important in (23).

| TC Type | Ratio of f | $(\alpha_1 - \alpha_2)$ ($^\circ\text{C}$) | Comment |
|---------|--------------|--|-----------------|
| B | 0.965 | 1.33×10^{-5} | Good full range |
| E | 1.9 | 3.6×10^{-5} | Poor sub zero |
| J | 1.79 | 2.3×10^{-5} | Fair sub zero |
| K | 1.6 | 2×10^{-7} | Poor sub zero |
| N | 1.4 | 1.8×10^{-5} | Poor sub zero |
| R | 1.17 | 1×10^{-5} | Good full range |
| S | 1.15 | 7.4×10^{-6} | Good full range |
| T | 1.35 | 1.4×10^{-4} | Good full range |

Table 2: Constants used in (24) for the various metal TC Types.

In this paper, using only classical physics, it has been shown that each voltage-temperature graph of a TC is defined by a set of properties of $f_{2_{ref}}/f_{1_{ref}} = c_1$ and $\alpha_1 - \alpha_2 = c_2$ where c_1 and c_2 are constants of the couple and these constants for the most common metal TCs are given in Table 2. Unfortunately, the specific values of f_1, f_2, α_1 and α_2 cannot be determined from a succession of voltage-temperature graphs. However, it may be possible to determine the value of α from the measured potential across an isolated metal bar in a thermal gradient using (16) provided care were taken to somehow insure that any interfacial potentials cancel in the measurement.

Although the specific values of f_1, f_2, α_1 and α_2 have yet to be determined for any of the metals used in a TC, it is possible to extract some information from further examining the Type R and S couples. The negative wire for both couples is pure platinum. The positive wire of a Type S couple is platinum with 10% rhodium while the positive wire of a Type R couple is platinum with 13% rhodium. Furthermore, if a third (useless) couple were made with the positive wire consisting of platinum with 0% rhodium, then for this couple $f_1 = f_2$, and $\alpha_1 = \alpha_2$. Using the information in Table 2 the values of $f_2/f_1 = c_1$ and $\alpha_1 - \alpha_2 = c_2$ are plotted as a function of the % rhodium in the positive wire in Fig. 8

and Fig. 9. The results in Fig. 8 show the addition of rhodium increases the Drude fraction above that found for a pure platinum wire. Likewise, Fig. 9 shows that the addition of rhodium in platinum increases the value of α in the alloy relative to that in pure platinum if α is required to be negative to help account for the experimentally observed decrease in electrical conductivity with temperature found in metals. These results can only be consistent if in (5) $\alpha_N \gg -3\alpha_L$ so that $\alpha = -3\alpha_L + \alpha_N \approx \alpha_N$ and requiring α_N be negative requires $\alpha_{NPt} < \alpha_{Naly}$ and therefore in (11) the charge density decreases with temperature faster in the platinum-rhodium alloy than in platinum. This is added to the other finding that creating the alloy gives a higher Drude fraction.

XI. CONCLUSIONS

Using classical physics it has been shown in this paper that in a thermocouple (TC) the output potential consists of two terms as given by (24). The first term given by (19) accounts for the change in the free-electron charge density along each conductor when one end is at a temperature T different from the other end which is at some known temperature T_c . The second term given by (23) is a logarithmic term which accounts for the potential that exists across any interface of two materials having different free-electron charge densities. This potential is not measurable unless at least one interface is at a different temperature from the others as can be seen from the top line in (22). From (23) it can be seen that, if $T = T_h = T_c$, then the first term is zero and the second and third terms in (23) cancel; so there is never a total potential difference unless one of the junctions is held at a different temperature than the other junctions.

Except for some below freezing temperatures as listed under Comments in Table 2, when the constants shown in Table 2 are used in (24) a reasonable fit to the experimental data is found for all the popular (i.e., Type B, E, J, K, N, R, S and T) thermocouples.

In the study of metals using either classical physics or quantum physics a standard assumption made in all calculations is that the number density n of the free-electrons is a constant and does not vary with temperature. There are two problems with this assumption. One occurs due to linear expansion of the metal, which – for the same number of free-electrons – causes these electrons to occupy a larger volume as the temperature increases. Hence, logic suggests that the free-electron number density should go down with increasing temperature. The second affect occurs when the temperature causes an increase in the vibration of the atoms (ions). The movement of a positive ion closer to a free-electron might result in a recapture of the electron which reduces the number of free-electrons. This recapture is found in (8) when α_N is negative. An example is found in metals where the electrical conductivity decreases with increasing temperature. Likewise, the increased energy due to increasing temperature could produce more free electrons when α_N is positive. An example is found in semiconductors where the electrical conductivity increases with increasing temperature. Both effects are accounted for in (5) which gives a temperature dependent free-electron number density n given by (9). However, the physics behind the sign and magnitude of α_N has not been explained in this paper and more work on the subject is needed.

Equation (24) which consists of (19) and (23) describes reasonably well the output voltage vs. temperature for various metal thermocouples as shown in Fig. 5, Fig. 6 and

Fig. 7. The poor fit to data in Fig. 6 at very low temperature suggests either α_1 or α_2 or both must be temperature dependent at these low temperatures. However, (23) requires a knowledge of a metal's deviation from the ideal Drude model ($f = 1$) as well as its thermal coefficient of free-electron recombination/generation α_N both of which are hidden within the analysis of the theory as presented here. The reasonable fit to the experimental data over most of the useful ranges for all the common metal TCs suggests that further pursuit of this classical physics model should offer greater insight into the basic physics of the thermocouple and the Seebeck effect.

Finally, the fit between the classical theory given here by (24) and the experimental data is only within about 5% over any extended temperature range. As a result, there is room for improvement, suggesting there might still be some quantum-mechanical considerations that will be required to obtain a more accurate prediction of the voltage-temperature curve of a thermocouple. Furthermore, it is well known that a quantum-mechanical description is presently needed to predict the linear temperature increase of electrical resistivity with temperature ([24] pp. 449–463). This experimental result has so far alluded prediction using classical physics. However, it might be worth reexamining the affect of temperature on metal resistivity using classical physics with the new implication of a temperature dependent free-electron charge density as given by (10). Likewise, only the ratio $f_{2_{ref}}/f_{1_{ref}}$ can be obtained from voltage-temperature measurements on a TC because a TC is a two metal system. This suggests f for a specific metal must be determined from measurements pertaining to that specific metal. Here again this suggests the need to apply the temperature dependent free-electron charge density as given by (10) and the modified Drude model ($f \neq 1$) to classical theory in an effort to predict the resistivity-temperature curve of a metal.

XII. NOMENCLATURE

| Description | Symbol | Units or Value |
|--|--------------|--|
| Electron diffusion coefficient | D | m^2s^{-1} ; m^2/s |
| Electric field at a point inside TC | \mathbf{E} | Vm^{-1} ; V/m ; $\mathbf{E} = -\nabla V$ |
| Drude fraction | f | $f = n/n_a$ (or $f = n/n_A$ for an alloy) |
| Thermophoresis coefficient | G | $\text{m}^2\text{s}^{-1}\text{K}^{-1}$; $\text{m}^2/(\text{s K})$ |
| Current density (charge flux) at a point inside the TC | \mathbf{J} | $\text{Cs}^{-1}\text{m}^{-2}$; (or Amp/m^2) |
| Boltzmann's Constant | k | $k \approx 1.38 \times 10^{-23} \text{ J/K}$ |

| Description | Symbol | Units or Value |
|--|------------|---|
| Length of a cube of material | L | m |
| Length at temperature T_0 | L_0 | m |
| Atomic weight of metal | M | $\frac{\text{kg}}{\text{mol}} : M \left(\frac{\text{kg}}{\text{mol}} \right) = 10^{-3} M \left(\frac{\text{g}}{\text{mol}} \right)$ |
| Atomic weight of alloy | M_A | $\frac{\text{kg}}{\text{mol}} : M_A \left(\frac{\text{kg}}{\text{mol}} \right) = 10^{-3} M_A \left(\frac{\text{g}}{\text{mol}} \right)$ |
| Free-electron number density | n | $\text{m}^{-3} : n[\text{m}^{-3}] = 10^6 n[\text{cm}^{-3}]$ |
| Electron number density at T_0 | n_0 | $\text{m}^{-3} : n_0[\text{m}^{-3}] = 10^6 n_0[\text{cm}^{-3}]$ |
| Electron number density at T_{ref} | n_{ref} | $\text{m}^{-3} : n_{ref}[\text{m}^{-3}] = 10^6 n_{ref}[\text{cm}^{-3}]$ |
| Number density of atoms | n_a | $\text{m}^{-3} : n_a[\text{m}^{-3}] = 10^6 n_a[\text{cm}^{-3}]$ |
| Number density of alloy | n_A | $\text{m}^{-3} : n_A[\text{m}^{-3}] = 10^6 n_A[\text{cm}^{-3}]$ |
| Number of free-electron charges | N | dimensionless |
| Number FE at temperature T_0 | N_0 | dimensionless |
| Avogadro's Number | N_A | $N_A \approx 6.022 \times 10^{23}$ molecules/mol |
| Seebeck coefficient | S | VK^{-1} : (or $\text{V}/^\circ\text{C}$); $\Delta V_i = S \Delta T$ |
| Temperature | T | K |
| Cold junction temperature of TC | T_c | K |
| Hot junction temperature of TC | T_h | K |
| Electron charge | $-q_0$ | $q_0 \approx +1.6 \times 10^{-19}$ C |
| Coefficient of charge variation | α | K^{-1} |
| Coefficient of linear expansion | α_L | K^{-1} |
| Coefficient of electron recombination/generation | α_N | K^{-1} |

| Description | Symbol | Units or Value |
|---------------------------------------|-----------------------|---|
| Mass density of elemental metal | δ_a | $\frac{\text{kg}}{\text{m}^3}$: $\delta_a \left(\frac{\text{kg}}{\text{m}^3} \right) = 10^3 \delta_a \left(\frac{\text{g}}{\text{cm}^3} \right)$ |
| Mass density of metal at T_{ref} | $\delta_{a_{ref}}$ | $\frac{\text{kg}}{\text{m}^3}$: $\delta_a \left(\frac{\text{kg}}{\text{m}^3} \right) = 10^3 \delta_a \left(\frac{\text{g}}{\text{cm}^3} \right)$ |
| Mass density of an alloy | δ_A | $\frac{\text{kg}}{\text{m}^3}$: $\delta_A \left(\frac{\text{kg}}{\text{m}^3} \right) = 10^3 \delta_A \left(\frac{\text{g}}{\text{cm}^3} \right)$ |
| Mass density of an alloy at T_{ref} | $\delta_{A_{ref}}$ | $\frac{\text{kg}}{\text{m}^3}$: $\delta_{A_{ref}} \left(\frac{\text{kg}}{\text{m}^3} \right) = 10^3 \delta_{A_{ref}} \left(\frac{\text{g}}{\text{cm}^3} \right)$ |
| TC Temperature difference | ΔT | K: (or °C); $\Delta T = T_h - T_c$ |
| Voltage across the TC terminals | ΔV_i | V: volts |
| Voltage along the TC wires | $\Delta V_{\Delta T}$ | V: volts |
| Voltage across the TC interfaces | ΔV_{IF} | V: volts |
| Free-electron charge density | ρ | Cm^{-3} : C/m^3 ; ($\rho = -q_0 n$) |
| Electrical conductivity | σ | Sm^{-1} : S/m; siemens/m |
| Gradient in charge density | $\nabla \rho$ | Cm^{-4} : C/m^4 |
| Gradient in temperature | ∇T | Km^{-1} : K/m; (or °C/m) |
| Gradient in potential | ∇V | Vm^{-1} : V/m; volts/m |
| Thermocouple | TC | |
| Maxwell's First Choice | MFC | Charge has no size; zero-thickness interface is allowed |
| Maxwell's Other Choice | MOC | Charge has a mass and size; zero-thickness interface not allowed. |

REFERENCES

- [1] Enn Velmre, "Thomas Johann Seebeck (1770–1831) ," *Estonian Journal of Engineering*, Vol. 13, No. 4, 2007, pp. 276–282.
- [2] J. C. Maxwell, *A Treatise on Electricity and Magnetism*, Dover: Vol. 1 and Vol. 2, New York, 1954.
- [3] Lasance, C. J. M., *The Seebeck Coefficient*, 2006, Available: <http://www.electronics-cooling.com/2006/11/the-seebeck-coefficient/>
- [4] J. A. Cross, *Electrostatics: Principles, Problems and Applications*, Adam Hilger: Bristol, 1987.
- [5] Seaver, A. E., "Tribocharging and the finite thickness interface," Proceedings of the 2012 Electrostatics Joint Conference, Cambridge, ON, Canada, June 12-14, 2012, ESA2012 e-Proceedings, : , 2012, pp. 1-12.
- [6] 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.
- [7] 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.
- [8] A. E. Seaver, "Development of the charge flux equation using the contiguous collision averaging method," *J. Electrostat*, Vol. 46, No. , 1999, pp. 177-192.
- [9] 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.
- [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] Thomas, G. B., *Calculus and Analytic Geometry*, Addison-Wesley Publishing: Reading, MA, 1960.
- [12] Paquin, R. A., "Properties of metals," in *Handbook of Optics, Volume II, Devices, Measurements and Properties*, McGraw-Hill Professional Publishing, New York, NY, 1994, pp. 35.1-35.78.
- [13] Lu, X-G., *Theoretical modeling of molar volume and thermal expansion*, Doctoral Dissertation, Royal Institute of Technology, Stockholm, Sweden, 2005.
- [14] Quong, A. A. and Liu, A. Y., "First-principles calculations of the thermal expansion of metals," *PHYSICAL REVIEW B*, Vol. 56, No. 13, 1997, pp. 7767-7770.
- [15] D. Halliday, R. Resnick and J. Walker, *Fundamentals of Physics*, Wiley: New Jersey, 2001.
- [16] R. C. Weast, *CRC Handbook of Chemistry and Physics*, CRC Press: Boca Raton, Florida, 1981-82.
- [17] D. K. C. MacDonald and K. Mendelssohn, "Resistivity of pure metals at low temperatures. I. The alkali metals," *Proceedings of the Royal Society of London. Series A, Mathematical and Physical Sciences*, Vol. 202, No. 1068, 1950, pp. 103-126.
- [18] D. K. C. MacDonald and K. Mendelssohn, "Resistivity of pure metals at low temperatures. II. The alkaline metals," *Proceedings of the Royal Society of London. Series A, Mathematical and Physical Sciences*, Vol. 202, No. 1071, 1950, pp. 523-533.

- [19] Davis, J. R., *ASM Specialty Handbook: Copper and Copper Alloys*, ASM International: Materials Park, OH, 2001.
- [20] Seaver, A. E. and Seaver, B. P., "Voltage induced across a conductor in a thermal gradient," Proceedings of the 2013 ESA Annual Meeting on Electrostatics, June 11-13, 2013, Cocoa Beach, FL, : , 2013, pp. 1 - 12.
- [21] Omega Engineering, *Thermoelectric Alloy Property Data*, , Available: <http://www.omega.com/temperature/Z/pdf/z049-050.pdf>
- [22] N.I.S.T. , *Monograph 175 Revised to ITS-90: Revised Thermocouple Reference Tables*, , Available: <http://srdata.nist.gov/its90/main/>
- [23] 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
- [24] P. A. Tipler and Ralph A. Llewellyn, *Modern Physics*, W. H. Freeman: New York, 2002.