THERMAL EQUILIBRIUM OF ELECTRONS IN METALS: CONTACT POTENTIALS AND THERMOELECTRIC FORCE

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The electrical behavior of metals is fundamental in any theory of electricity and until recently it has been a subject of much mystery and dispute. Thus the location of the e.m.f. in the galvanic cell has been a matter of controversy since the time of Volta and Faraday. Likewise in regard to the so-called "contact potentials," there were not only differences of opinion as to the interpretation but not even general agreement as to the experimental evidence. Recent experimental work of Millikan (1) and others (2) on the photoelectric effect and the brilliant theoretical papers of Schottky (3) and others (4) on the subject of electron emission have thrown much light on the problem. While we still know less about the structure of metals than about any other solid form of matter we can at least settle some of the mooted questions of the past and formulate the problem in the case of others.

THE PHOTOELECTRIC EFFECT AND THE THERMIONIC WORK FUNCTION

The electrical behavior of metals becomes more intelligible if we first get clearly in mind the experimental facts of the photoelectric effect. When light is allowed to impinge on the clean surface of a metal in a vacuum there is a limiting frequency ν_o below which electrons are not emitted by the metal even in the presence of an accelerating field. Light of higher frequency ν ejects electrons with a kinetic energy $\frac{1}{2}mv^2 = h\nu - h\nu_o$. In accord with the Einstein law the work of removing an electron from the metal is seen to be $h\nu_o$. ν_o the limiting frequency varies widely for different metals and is evidently one of the most fundamental characteristic properties of a metal.

Electrons may be emitted by a metal without the action of light. If the metal be heated to temperatures sufficiently high, electrons acquire kinetic energy in excess of the quantity $h\nu_o$ and escape. This process is analogous to the evaporation of atoms. It is beyond the scope of this paper to discuss the phenomena of the vaporization of electrons especially as the subject has been treated at great length by Richardson (5), Schottky (3), Dushman (6) and others (7). By making certain assumptions the vapor pressure of electrons from a hot metal may be treated by the laws of thermodynamics and the heat of vaporization may be calculated by familiar formulae. The value obtained in this way appears to be in good agreement with $h\nu_o$ as determined by photoelectric measurements (8). This heat of vaporization is usually expressed in volts and designated as ϕ, the "thermionic work function."

Schottky has analyzed the work of removal of an electron from a metal as being due to various effects such as the removal of the electron from the "structure" of the metal, the overcoming of fields due to a polarization layer at the surface and electrical image attraction after the electron is through the surface. While it is not possible to measure these effects separately we may suspect that variation in ϕ for different metals is largely due to the variation in the first effect.

According to the current theories of atomic structure the peculiar properties of a metal are due largely to the so-called free or conducting electrons which are presumably identical with the valence electrons. These electrons move in orbits which lie for the most part on the outside of the atom or if they do not move in orbits they occupy the outermost energy levels in the periphery of the atom. When the atom is in the metallic lattice these electrons pass from one atom to another without appreciable energy change. When the atom is isolated, as in the vapor state, the work of removing an electron to an infinite (practically a very short) distance from an atom can be measured by the determining the ionizing potential. Obviously in the theory of electricity in metals, the ionizing potential (22) of the atom is a still more fundamental quantity than the thermionic work function.

Presumably if we knew the configuration of the atom we could calculate the ionizing potential from Coulomb's law and simple mechanics. At any rate we may assume that the ionization potential varies directly as the effective nuclear charge on the atom and inversely as some power of the effective radius. Our knowledge of atomic structure confirms this generalization.

Of course when the atoms are packed into a lattice this work of removal of the electrons will be considerably changed in magnitude. Our knowledge of the mechanics of the lattice structure is not sufficient to make any predictions here although Born (9) has made progress along this line. It seems clear however, that with a better knowledge of atomic structure and the dynamics of crystal lattices we should be able to calculate the thermionic work function for any metal. In the accompanying table are given in volts the ionizing potential, photoelectric "work function" $h\nu_o$, and the standard electrode potential against hydrogen for the three metals for which satisfactory figures for all three quantities appear to be obtainable.

	IONIZING POTENTIAL	$h\nu_o$	E_o
Na	5.13	1.7	2.71
Li	5.36	2.36	2.96
Hg	10.2	4.52	−0.80

The correspondence of the values given is apparent. It is evident that the "affinity" of the atom for the "free" electron is fundamental in determining the electrical properties of the metal. A relative measure of this property is given by various quantities such as the ionizing potential of the vapor, the limiting frequency of the photoelectric effect or the thermionic work function. If the metals be arranged in a series according to the values of any of these quantities an order will be obtained which will be approximately that of the familiar electromotive series of the electrochemist.

Now if the conducting electrons lie on different energy levels in different metals it is clear that when two metals are brought in contact, the electrons will tend to pass from one metal to

the other the motion being in every case from the metal with the smaller value of $h\nu_o$ to the one with the larger value, and this process will continue until equilibrium is established. At low temperatures where the electrons do not have appreciable kinetic energy (10) the result is easily stated. It is a fundamental law of electrostatics that a system of electrical charges tends to take on a configuration of minimum potential energy. Electrons will pass from one metal to the other until the negative potential acquired by the metal having the higher value of ν_o balances the difference in the energy levels of the electrons in the two metals.

One very peculiar point needs to be noticed here. The transfer of electrons is entirely on the surface of the two metals. No transfer takes place within the body of the metal and it is impossible to produce or maintain a volume charge within a metal. For electrons free to move but without kinetic energy it can be demonstrated from Coulomb's law that the net charge on any volume in the body of a conductor will not differ appreciably from zero if the volume is taken large enough to contain a considerable number of atoms. Even if the electrons possess kinetic energy it has been shown by Lorentz (11) that the concentration of electrons in the interior of a metal remains constant and equal to the number of positive charges in the same area. It is only within a distance from the surface of the metal comparable to the atomic diameters that appreciable changes in electron concentration can be produced even by the application of the highest potentials available.

THE THERMAL EQUILIBRIUM OF ELECTRONS BETWEEN METALS

So long as the electrons do not possess an appreciable kinetic energy the ordinary laws of electrostatics would suffice to calculate the conditions for equilibrium between metals, provided of course that we were sufficiently well acquainted with the structure of the metals. At higher temperatures where the electrons begin to share in the kinetic energy of the metal the laws of electrostatics are no longer sufficient to determine equilibrium but we must make use of thermodynamics. Equilibrium will

be established between the electrons of two metals a and b when the escaping tendency of the electrons is the same from each metal (12).   The escaping tendency of any constituent from a phase is measured by the partial molal free energy of the constituent in that phase.   The partial molal free energy of the electrons in a metal is the ratio $\dfrac{\partial F}{\partial n}$ where ∂F is the increase in the total free energy of the metal on the addition of ∂n equivalents of electrons.   Other factors as temperature are constant.   Equilibrium between the two metals a and b then may be attained either by direct contact or through the vaporization and condensation of electrons and the condition for equilibrium is

$$\frac{\partial F_a}{\partial n} = \frac{\partial F_b}{\partial n} \tag{1}$$

So far, the condition for equilibrium appears the same as for the distribution of a solute between two immiscible solvents but certain important differences need to be considered.   The experimental measurement of the partial molal free energy of a constituent of a solution involves the change of concentration of that constituent and we do not know of any way to change the electron concentration inside a metal, as was pointed out above. This does not invalidate the thermodynamic formula however. A more serious complication arises because of the charge carried by the electron.   When we transfer electrons from one metal to another we leave a positive charge behind and carry the negative charge against the electrostatic attraction and do work so long as we increase the separation.   This action at a distance makes the case quite different from the separation of a neutral molecule of a solute from a solution when the forces cease to act as soon as the molecule is separated from the surface of the solution by a distance of the order of the molecular diameter.   In order to take account of the charge of the electron it is necessary to follow the method of Gibbs (13) and Schottky (3) and separate the partial molal free energy into two terms

$$\frac{\partial F}{\partial n} = \bar{F} - NeV \tag{2}$$

$\overline{F}$ is what Gibbs has called the intrinsic free energy corresponding to the free energy of a neutral molecule and V is the electrostatic potential. N is Avogadro's number, e the charge on the electron, while the minus sign takes care of the negative charge. This separation of the free energy into terms involving forces that act at molecular distances and forces acting at greater distances seems from one point of view quite arbitrary and meaningless, but it is justified by several considerations. V, the electrostatic potential, is the same for positive charges as for negative and so long as the distribution of charges does not change it is independent of temperature. $\overline{F}$ on the other hand depends upon the potential and kinetic energies of the electron in the lattice, is a function of the temperature, and the value for the electron is radically different from the value for a positive ion. Finally in some cases at least the value of V can be measured experimentally. The equation (1) for equilibrium of electrons between two metals at the same temperature then becomes

$$\overline{F}_a - NeV_a = \overline{F}_b - NeV_b \tag{3}$$

The metal with the larger value of the thermionic work function may be expected to have the lesser value of $\overline{F}$, lesser being used in the algebraic sense.

THE VOLTA DIFFERENCE OF POTENTIAL

The fact that electrons will pass from one metal to another on contact was observed by Volta near the beginning of the last century. The phenomenon was studied in detail by Lord Kelvin (14). In his method the two metals were made the plates of a condenser and an e.m.f. applied between of such magnitude and direction that no charge appears upon the condenser. By transforming equations (3) we have

$$V_b - V_a = \frac{\overline{F}_b - \overline{F}_a}{Ne} \tag{4}$$

It is obvious that the e.m.f. applied in the Kelvin experiment must be equal to $V_b - V_a$ in equation (4) and hence the latter term is the Volta difference of potential. Furthermore any tendency

to transfer electrons is from the surface of one metal to the surface of the other; hence the values of $\bar{F}_a$, $\bar{F}_b$ involved are the values for the metallic surfaces.

In the discussion of the photoelectric effect we assumed the existence of clean metallic surfaces but it is not certain that it is possible to obtain such a surface experimentally. Millikan in his work on the photoelectric effect of the alkali metals, shaved the surface of the metal in a high vacuum, but in the highest vacuum obtainable the surface of the metal would in all probability be quickly covered with a layer of gas molecules. Probably the cleanest surface that has been obtained is that of flowing mercury (15). It has already been emphasized that metals acquire charges only upon the surface and that in equation (4) the values of $\bar{F}_a$ and $\bar{F}_b$ are for the electrons in the surfaces. Impurities adsorbed on the surface of a metal affect profoundly the values obtained experimentally for ϕ_1 ν_0 and the Volta effect by the Kelvin method. Moreover, even if clean surfaces are obtained it is not likely that the value of $\bar{F}$ for electrons in the surface is the same as for the interior of the metal. Hence the Volta effect as measured by the Kelvin method is a superficial property of a metal and often without significance. It should be emphasized that the Volta effect is a difference of potential and not an e.m.f. The e.m.f. is applied by the experimenter. The case is analogous to the definition of osmotic pressure, where the pressure is one that is imagined to be applied rather than one that actually exists.

CONTACT POTENTIALS

If two metals are placed in contact without any e.m.f. applied between them, the electrons flow from one to the other in the direction of decreasing free energy until equilibrium is established according to equation (4), the difference in electrostatic potential being equal and opposite to the difference in intrinsic free energies. Between the surfaces of the metals which are not in contact there will exist a field due to the potential difference $V_b - V_a$ where $V_b - V_a$ is numerically equal to the Volta effect. This field it should be noted is external to the metals.

The difference of potential between the interior of one metal and the interior of another is given by equation (4) provided $\bar{F}_a$, and $\bar{F}_b$ are the values for the interior of the metals. Schottky has called this the "galvanic contact potential" and this is the true contact difference of potential encountered by a current flowing across the junction. It was the opinion of Volta that the e.m.f. of a galvanic cell was due to this difference of potential and resided at the junction and this opinion has persisted to the present (16). It must be obvious on consideration however that this difference of potential is exactly cancelled by the difference
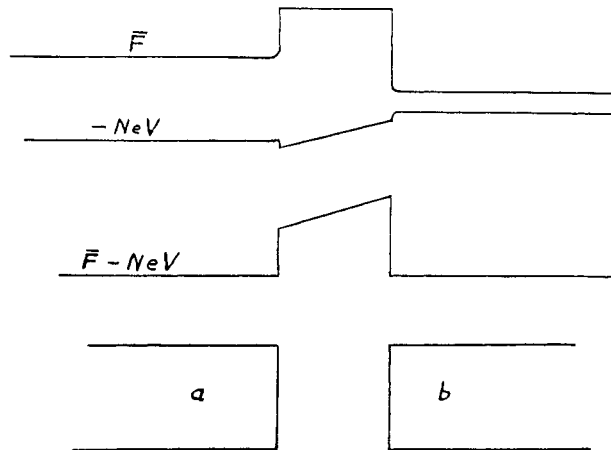

Fig. 1

in intrinsic free energies. There is no method known for measuring this true contact potential although we shall probably be able to calculate its value when we know more about the structure of metals.

The persistence of the idea that the e.m.f. of the galvanic cell is located at the metallic junction is probably due to the fact that the values of the Volta effect for pairs of metals seem to correspond in some cases at least to the differences in the standard electrode potentials of these metals. While there can be no direct relation between the "superficial" Volta effect and the

electrode potentials it would not be surprising if some parallelism were found since both depend upon the fundamental electrical properties of the metal.

In figure 1 are represented diagrammatically the course of the values of $\bar{F}$, $-NeV$, and the "total" free energy, $\bar{F}-NeV$, for the electrons of two metals a and b which are in thermal and electrical equilibrium. The value of F_b is less than F_a and the values of $\bar{F}_b$ and $\bar{F}_a$ are assumed to rise near the surface of the metals. The value of the total free energy is the same throughout the conducting regions of both metals as is required for equilibrium of "free" electrons. Hence there can be no e.m.f. at the junction of two metals so long as the metals are at uniform temperature throughout.

SINGLE ELECTRODE POTENTIALS

If a piece of metal is brought into contact and equilibrium with a solution containing its ions the chemical reaction may be written
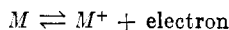
$$M \rightleftharpoons M^+ + \text{electron}$$

For equilibrium we have

$$F_M = \bar{F}_{M^+} + NeV_{sol} + \bar{F}_e - NeV_M \tag{5}$$

F_M is the molal free energy of the metal and $\bar{F}_{M^+}$ and V_{sol} are defined for the ions in solution in the same way that $\bar{F}_e$ and V were defined for the electrons in the metal. Transforming this equation

$$V_{sol} - V_M = \frac{F_M - \bar{F}_{M^+} - \bar{F}_e}{Ne} \tag{6}$$

It has been commonly assumed that the free energy term on the right of equation (6) is of profound significance and many attempts have been made to measure $V_{sol} - V_M$. On careful consideration the importance of this measurement is not so clear, supposing it could be made with accuracy. The process actually is the removal of an atom from the lattice, the transfer of an electron from the ion to the surface of the metal and the solvation of the ion resulting. This does not appear to be the exact equivalent

of one half the reaction in a cell where the electrons are transferred from one metal to the other instead of accumulating on the surface.

Granting that this somewhat complicated process is interesting it is certain that the accurate measurement of $V_{sol} - V_M$ presents enormous difficulties. We cannot measure the Volta difference of potential between two metals with certainty and the measurement must become still more difficult between a metal and a solution. In the former case only neutral molecules are adsorbed on the surface but in the latter ions may be adsorbed. Thus the hydrogen ion concentration may have a profound effect on the value of $V_{sol} - V_M$. At any rate we have a quantity here which will probably be calculated eventually more accurately than it can be measured.

THE TEMPERATURE COEFFICIENT OF CONTACT POTENTIAL

If we differentiate equation (4) with respect to temperature we obtain by well known relations of thermodynamics

$$\frac{\partial(V_b - V_a)}{\partial T} = \frac{1}{Ne}\left(\frac{\partial \overline{F}_b}{\partial T} - \frac{\partial \overline{F}_a}{\partial T}\right) = \frac{1}{Ne}(\overline{S}_a - \overline{S}_b) \qquad (7)$$

Here $\dfrac{\partial(V_b - V_a)}{\partial T}$ the temperature coefficient of the difference of electrostatic potential between the interior of two metals is seen to depend upon the respective partial molal entropies of the electrons in the interior of the metals.

THE THREE WAYS OF DEFINING THE HEAT CAPACITY OF THE ELECTRON

If we differentiate equation (7) a second time with respect to the temperature and introduce the relation $\dfrac{\partial S}{\partial T} = \dfrac{C_p}{T}$ we obtain

$$\frac{\partial^2 \overline{F}_b}{\partial T^2} - \frac{\partial^2 \overline{F}_a}{\partial T^2} = \frac{1}{NeT}\left(\frac{\partial C_{pa}}{\partial n} - \frac{\partial C_{pb}}{\partial n}\right) \qquad (8)$$

Here $\dfrac{C_p}{\partial n}$ is the partial molal heat capacity of electrons in the

metal, a quantity which cannot be measured experimentally because we cannot change the concentration of electrons in a metal except on the surface and there the change is too small to affect the heat capacity measurably.

Certain of the metals show values for the atomic heat capacity considerably above that predicted by the Debye equation. This is especially true of the metals with small ionizing potentials, such as potassium at ordinary temperatures and of many of the metals at higher temperatures. G. N. Lewis (17) has attributed this abnormally high heat capacity to the presence of electrons in an unusually free condition so that they share in the equipartition of energy. We may designate this excess heat capacity over the normal value as Ce, the "apparent heat capacity of the electrons in the metal."

Finally there is the Thomson effect. If a current flows along a wire in a thermal gradient, in addition to the joule heating there is a small heat effect that is proportional to the quantity of electricity which flows, and to the temperature change. If the current is reversed the heat effect is reversed. This is called the Thomson effect σ and may be defined as the heat absorbed per equivalent per degree rise in temperature when the electron current flows from a lower to higher temperature.[1]

Before we can discuss the possible relations of these heat capacities defined in different ways it is desirable to discuss the application of thermodynamics to the thermocouple.

THE THERMOCOUPLE AS A CARNOT CYCLE

If we neglect the irreversible flow of heat which always takes place in a thermal gradient because of the conductivity of matter, we may treat a thermocouple whose junctions are at different temperatures as a Carnot cycle. Whether we are justified in this procedure, in other words, whether the laws of thermodynamics apply strictly to thermocouple or not, is a question which has never been settled although most writers on the subject have inclined to the affirmative. The matter cannot be settled by

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[1] The Thomson effect has usually been defined for a positive current.

an experimental check because the heat quantities involved are too small to measure with accuracy. It may be pointed out that no Carnot cycle can be carried out without some irreversible flow of heat for we have no perfect insulators. In the ordinary Carnot cycle, however, the thermal gradient may be assumed to be external to the mechanism while in the thermocouple the electrons move through the thermal gradient. For purposes of discussion in the remainder of this paper we shall assume that the thermocouple may be treated as a Carnot cycle.

Let us consider a circuit of two metals a and b in a temperature gradient with one junction at the temperature T and the other junction at the temperature $T+dT$. Assuming the electrons to flow from a to b at the warmer junction then the net electromotive force of the circuit dE in the direction of the electron current is given by the First Law as

$$Ne\,dE = q_2 - q_1 + (\sigma_a - \sigma_b)dT \qquad (9)$$

Here q_2 and q_1 are the heats absorbed at the warmer and colder junctions respectively when one equivalent of electrons flows from a to b and σ_a, σ_b are the Thomson effects. By the Second Law:

$$Ne\,dE = \frac{q_2 dT}{T} \qquad (10)$$

T being the temperature of the warmer junction. The Thomson effects do not appear in the above equation since they would be of second order. Differentiating (10) with respect to T and combining with (9) we have

$$Ne\,\frac{\partial^2 E}{\partial T^2} = \frac{1}{T}\,(\sigma_b - \sigma_a) \qquad (11)$$

We shall use this equation in the next section.

It is important to note that in equation (10) there is no information as to the numerical value of an e.m.f., E, which many writers have assumed to exist at the junction. Here q is the reversible heat and it is well known that in the analogous case of a chemical reaction the reversible heat of a reaction bears no relation to the free energy. Nevertheless the list of writers who

have sought to set q equal to E contains some of the distinguished names of science.   Furthermore it should be noted that the existence of a reversible Thomson effect does not imply the existence of an e.m.f. along the gradient.   The laws of thermodynamics give only the total e.m.f. of the circuit without giving us any specific information as to the way this e.m.f. is distributed.

One inference however, may be drawn as to the relation between the Peltier heat, q, and the e.m.f. at the junction.   If we were to tabulate the reversible heats for a number of chemical reactions, while there would be no correlation we should expect that the reversible heats would be on the average of the same order of magnitude as the free energies.   It has been a source of con-
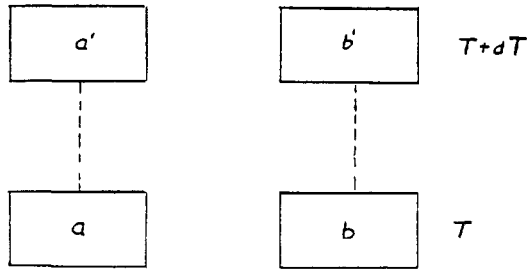

FIG. 2

cern to many writers that the values of q, as calculated from measurements of thermoelectric force, were so small compared with the Volta difference of potential.   This ceases to be a matter of concern when we recognize that the Volta effect has no relation to the e.m.f. at the junction of two metals.

A POSSIBLE CORRELATION OF THE THERMOELECTRIC POWER WITH THE "TRUE" CONTACT DIFFERENCE OF POTENTIAL

Let us consider two blocks each of metals a and b, designated as a, a' and b, b'; a and b are at the temperature T and a' and b' at the temperature $T + dT$.   Suppose each of the four pieces of metal to be electrically neutral and at the same electrostatic potential V.   The values of the intrinsic free energies will be

$\overline{F}_a, \overline{F}_b$ and $\overline{F}_a' = \overline{F}_a + \dfrac{\partial \overline{F}_a}{\partial T} dT$, $\overline{F}_b' = \overline{F}_b + \dfrac{\partial \overline{F}_b}{\partial T} dT$. Now suppose a, a' and b, b' to be joined by thin wires of the respective metals a and b. These wires will be in the temperature gradient. Let us assume that no transfer of electrons takes place along the wires. The plausibility of this assumption we will discuss later. If there be no tendency for electrons to move along the temperature gradient then we may suppose that no work will be required to move electrons along the wires. Let us imagine a transfer of N electrons to take place around the circuit a a' b' b. If the electrostatic potential is the same throughout the only work involved will be in the transfer of the electrons across the gaps a' b' and ba. The net work is seen to be

$$Ne\ dE = \left(\frac{\partial \overline{F}_a}{\partial T} - \frac{\partial \overline{F}_b}{\partial T} \right) dT \tag{12}$$

If we differentiate this equation with respect to T and combine with (8) and (11) we have

$$\frac{\partial C_{pb}}{\partial n} - \frac{\partial C_{pa}}{\partial n} = \sigma_b - \sigma_a \tag{13}$$

From this equation we may infer that[2]

$$\frac{\partial C_{pa}}{\partial n} = \sigma \tag{14}$$

Latimer (19) in an interesting paper has attempted to correlate the values of Ce the apparent heat capacity of the electrons with σ but the experimental data he considers do not give a very satisfactory correlation. His conclusion would also imply that Ce is equal to $\dfrac{\partial C_p}{\partial n}$ if equation (14) is true. If we consider the case of a solution as an analogy the partial molal heat and the apparent molal heat only have the same values in general in case the solution is thermodynamically "perfect."

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[2] Schottky (3) has demonstrated equation (14) by a different process of reasoning but making similar assumptions to those made here. It may be noted that the author (18) had previously called attention to the possibility that $\dfrac{\delta C_p}{\delta_n}$ and σ were identical.

None of the above conclusions are true of course unless our assumption that no variation of electrostatic potential exists along a wire in a temperature gradient is correct.[3] This assumption appears very improbable. We can prove nothing from thermodynamics since the relations of the free energies are without significance unless the system is at constant temperature and recent work on the Soret effect (21) throws no light on the laws of equilibrium in thermal gradients. No doubt the values of $\bar{F}_a$ and $\bar{F}_a{}'$ in the interior of the metal will be the same after a and a' are connected as before because the electron concentration will be the same but the movement of electrons along the wire will produce charges on a and a' which will alter the potentials V_a and $V_a{}'$ and similarly for V_b and $V_b{}'$. Assuming that equilibrium has been reached along the thermal gradients so that no e.m.f. need be considered except between metals as before we should have for the work of transfer of electrons around the circuit

$$Ne \, dE = \left(\frac{\partial \bar{F}_a}{\partial T} - \frac{\partial \bar{F}_b}{\partial T} + Ne \, \frac{\partial V_b}{\partial T} - Ne \, \frac{\partial V_a}{\partial T} \right) dT \qquad (16)$$

If $\dfrac{\partial V_b}{\partial t} - \dfrac{\partial V_a}{\partial t}$ is different from zero equation (12) does not hold. Furthermore it should be emphasized that no conclusions may be drawn as to the location of the e.m.f.'s in the thermocouple because of our lack of knowledge of the conditions for equilibrium along a gradient. The second law if it applies at all gives us information only as to the net e.m.f. of the whole circuit.

One more point needs to be emphasized. It has been commonly stated the thermoelectric power is the temperature coefficient of the contact difference of potential. If equation (12) is true then the thermoelectric power is the temperature coefficient of the "true" contact difference of potential which cannot be measured experimentally. If equation (12) is not true then there is no relation apparent between thermoelectric power and the contact potential.

[3] Compton (20) attempted to determine the relative charge at two ends of a wire in a thermal gradient and got a very large effect. It is likely that the adsorption of gas on the surface of the metal affected the results here as in most measurements of this kind.

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