A CRITICAL THERMODYNAMIC DISCUSSION OF THE VOLTA, THERMO-ELECTRIC AND THERMIONIC EFFECTS.

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SYNOPSIS.

In this paper the various relations between the Volta effect, thermo-electric effects, and thermionic effects are critically discussed from the general view point of thermodynamics, avoiding assumptions involving special mechanisms. The ordinary concept of an impressed E.M.F. is found inadequate, and a general definition is proposed, competent to include systems in which the force driving electricity has not the character of a spatially distributed field of force. A thermodynamic proof, dispensing with all special assumptions, is given for a formula for the temperature coefficient of the Volta effect originally given by Lorentz and Kelvin. This temperature coefficient involves a surface heat, the existence of which has not yet been established experimentally, and the possibility of which is usually overlooked. It is shown that Richardson has neglected this surface heat, and that the formula of Lorentz and Kelvin may be deduced also from the phenomena of thermionic emission when the surface heat is taken into account. Formulas are deduced connecting the latent heat of vaporization of electrons, surface heat, surface E.M.F., surface potential jump, Thomson heat, E.M.F. and potential gradient. It is shown that in general local heat, potential difference, and E.M.F. cannot be equal to each other. An expression is found from thermionic considerations for the Volta difference of potential between two parts of the same unequally heated metal, and the possibility suggested of using this effect in determining the hypothetical surface heat. It is shown that it is almost certain that in an unequally heated metal there are currents continuously flowing in closed circuits through the metal and the surrounding electron gas. It is shown that the Volta law of tensions must be capable of extension to include the local potential jumps and E.M.F.'s, although these are not susceptible of direct measurement. Finally, expressions are deduced for the effects of pressure and change of state on the Volta contact difference of potential. These involve the change of volume with surface charge and the effect of surface charge on melting pressure; effects for which no search has been made yet experimentally.

INTRODUCTION.

IN a recent paper I have described the effect of pressure on the thermo-electric properties of metals. In an effort to obtain as much information as possible from the results I later undertook to discuss the relations of thermo-electric phenomena to the Volta effect and the phenomena of thermionic emission. This discussion proved to be difficult because of the great differences of opinion prevalent with respect to fundamental ideas. The old controversies as to the location of the E.M.F. of a cell, the nature of the Volta potential difference, and a locally absorbed heat are all involved and discouragingly confuse the issues. Nearly all previous discussions of these matters have involved special assumptions as to the relations of these phenomena. It is a question to what extent the correctness of the previous results depends on the special assumptions. In order that the discussion of the effects of high pressures might be free from such elements of uncertainty, I have started at the beginning and examined the whole field from a single point of view. In this examination I have tried to avoid every special assumption, for instance assuming neither that the jump of potential at two metals in contact is equal to the Volta contact difference, as does Kelvin, nor that it is equal to the Peltier heat, as do Heaviside and Richardson. The methods employed in this examination are largely the general methods of thermodynamics; in this way the assumption of special mechanisms is avoided. The results of this critical examination constitute this paper.

It turns out that a number of the previous results are unaffected by the special assumptions under which they were developed. In Richardson's work, however, I believe that I have discovered an effect which he has neglected, and which will bring his formula for the temperature coefficient of Volta contact difference of potential into agreement with a formula previously given by Lorentz and later by Kelvin. The effect neglected is a hypothetical surface heat, whose existence has not yet been searched for experimentally and whose magnitude may well be, for any information we have at present, large enough to essentially modify many of the thermionic formulas. In the following a number of thermionic formulas are given as modified by this effect. In addition, the specific relations are developed between the local E.M.F.'s, local potential jumps, and local heats which express the necessary relations when these quantities are not assumed respectively equal, as has frequently been done previously. A connection is found between the surface heat and the Volta difference of potential between two parts of the same unequally heated metal. Finally the effects of pressure and change of state on the various effects are discussed from the point of view of thermodynamics.

The Concept of Impressed E.M.F.

It is in the first place necessary to examine the concept of an impressed E.M.F., because with the discovery of new facts, such as those of electron emission, the old concepts have become inadequate. As commonly understood, a part of the E.M.F. between two points in a stationary medium is due to forces of electro-magnetic origin, and is given by the line integral of the "electric" force. The electric force is to be computed in the classical way from the field equations. In addition to forces of electro-magnetic origin, however, it is necessary to recognize the presence of non-electro-magnetic forces acting on electricity. For instance, in an electron gas in which there is a pressure gradient, the pressure gradient gives rise to a non-electro-magnetic forec acting on electricity. Such forces may be specifically introduced into our equations and are called "impressed forces," in the same way that impressed forces are introduced into mechanics. In an electrical system in which there are impressed forces it is usual to recognize the presence of an impressed E.M.F.; it is this concept of impressed E.M.F. and its relation to that of impressed force which requires examination.

It is usual to connect in a simple way the impressed forces with the impressed E.M.F. A careful exposition of this point of view will be found in Abraham (2), for example. Consider a conductor in which the electricity is in equilibrium under the action of the electric and the impressed forces. We may denote the electric force by E^s and the impressed force by E^e. Then since there is equilibrium, $E^s+E^e=0$. The impressed E.M.F. between two points in such a system is usually defined as $\int E^e ds$. This analysis of the situation is inadequate, however, as the following considerations will show.

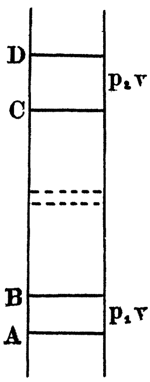

Fig. 1.

Consider the behavior of a gas in a field of force, such as an ordinary gas in a gravitational field or an electron gas in a potential field. Let a portion of the gas originally at *AB* (Fig. 1) rise isothermally under equilibrium conditions to *CD*. The work done by the pressures acting across the boundaries in this displacement is zero. This may be proved by a direct integration, or may be simply seen as follows: Consider the work done across the surfaces during a displacement shown by the dotted lines. The work done by the top surface in moving through this displacement will be exactly neutralized at some later instant by the work received by the bottom surface in moving through the same displacement. Hence no net work will be done by the top and bottom surfaces together in the region *CB*. The total work of the operation will be that received by the bottom surface in moving from *A* to *B* minus that done by the top surface in moving from *C* to *D*. The first is p_1v_1, and the second is p_2v_2. But $p_1v_1 = p_2v_2$ (isothermal). Hence no net work is done by the pressures acting across the boundaries in a displacement under equilibrium conditions. Work, however, is done against the gravitational or electrical forces during the displacement considered.

We are here confronted with a paradox, the gravitational force being always equilibrated by other forces, but the gravitational force doing work during a given displacement while the others do none. (There is here no contradiction of the first law of thermodynamics, the energy required to increase the potential energy of position being provided by heat inflow as the gas expands isothermally.) The solution of the paradox lies in the observation that the two forces concerned, the gravitational force and the equilibrating forces, are entirely different in nature. One is a body force, and the other a differential pressure, of the nature of the stresses in an elastic solid. One would never think of saying that a gravitational force and the stresses called into play by it in an elastic solid were equal to each other. Still less can one speak of the line integral of the equilibrating forces; such an expression can have only a formal meaning and cannot be equal to the work done by such forces during the given displacement.

It follows that the concept of an impressed E.M.F. as the line integral of a non-electric force has a chance of being correct only in those cases in which the non-electric force is in its nature a body force, like the forces of the electrostatic field.

Before defining precisely what we shall mean by an impressed E.M.F. it is to be noticed that the idea is a relative one, as in all cases of energy transformation. Consider a closed circuit, for example, in which every one is pretty well agreed in calling the impressed E.M.F. the work done when unit quantity of electricity flows around the circuit. But work done on what? If the circuit consists of a dynamo and a motor, shall we mean the total work done by the motor, or the net work of dynamo and motor together? It must be obvious that to give impressed E.M.F. a precise meaning we must divide our universe into two parts; one is the part in which the action takes place which we specify as E.M.F., and the other we shall call the "outside" part, on which the action of the impressed E.M.F. is expended. We could therefore say that the impressed E.M.F. of a closed circuit is the energy, including heat, delivered to "outside" agencies when unit quantity of electricity flows around the circuit. In the example above, the motor may be taken as the outside agency to which energy is delivered by the E.M.F. of the dynamo when unit quantity flows.

With this recognition that impressed E.M.F. involves the specification of some outside agency to receive energy, and that the magnitude of the E.M.F. will depend on the choice of the outside agency, we define as follows the impressed E.M.F. operative between any two points of a stationary system. "The impressed E.M.F. between two points A, B

in the direction B to A is the energy delivered to outside agencies per unit quantity when positive electricity passes from B to A, plus the increase of energy of the electricity, including in this both increase of energy in the electro-magnetic field and intrinsic energy (as for example in an electron gas)." This reduces to the ordinary definition for a closed circuit, and for a battery on open circuit with terminals of the same metal reduces to the electrostatic potential difference of the terminals, as it should. By "energy per unit quantity" as used in the definition is to be understood the limit of the ratio of energy to quantity for quantities sufficiently large. That is, the distinction emphasized by Lorentz between "mathematical" and "physical" infinitesimals is to be kept in mind, and in the limiting process contemplated in this definition the "physical" infinitesimal quantity of electricity is large enough to include many electrons.

The discussion of this paper will be largely concerned with thermoelectric processes, in which heat energy is converted into electrical energy. This point of view demands that all the heat processes connected with this conversion, except the irreversible Joulean heat, be ascribed to the internal part of the system whose E.M.F. is discussed, as opposed to the outside agencies which receive the converted energy. In particular, the reversible Peltier heat in a thermo-electric circuit is not to be treated as energy delivered to an "outside" source.

These views of impressed E.M.F. are not in agreement with those commonly held. Consider, for instance, the example of the electric double layers which may exist on the surface of separation of metal and ether. The existence of such layers demands a jump in the electrostatic potential. It is common to say that in this double layer there is an equal and opposite impressed E.M.F.[1] The argument is that otherwise the electricity in the double layers could not be in equilibrium. But the argument is not valid if the non-electrical forces are different in nature from the electrostatic forces. We have seen in one special case that the non-electrostatic forces may be like the stresses of an elastic body, instead of like body forces. In the case of double surface layers, we have the further possibility that there may be forces of the nature of kinetic reactions due to bombardment by flying electrons. Such forces are certainly not like body forces in nature. Furthermore, the equilibrium argument demands an inexhaustible supply of freely movable electricity in the surface layer; we have no assurance that this electricity is present. In this paper my position is that it is not justifiable to put local impressed E.M.F.'s equal to local potential jumps. I shall use separate letters for these quantities and keep them distinct.

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[1] See, for example, Heaviside, Electrical Papers, Vol. I, p. 343.

The Volta Effect.

The Volta effect next concerns us. There has been continuous discussion over this without yet any final agreement. There is, however, no question regarding the fundamental experimental facts. If two pieces of metal, say Cu and Zn, are brought into metallic contact, it is found that points in the surrounding medium, gas or vacuum, immediately outside the surfaces of the two metals, are at a difference of potential characteristic of the metals and the medium. When the medium is a perfect vacuum we define the potential as the true Volta potential difference. This difference may be measured in the regular way as the limit of the ratio of the work done on an electrostatic charge to the charge as the charge is made smaller.

The existence of a Volta potential difference follows as a matter of necessity if we suppose jumps of potential between the interior of Zn and ether, interior of Cu and ether, and between interior of Zn and Cu. The Volta jump Zn-Cu is the sum of the jumps ether-Zn, Zn-Cu, and Cu-ether. These jumps of potential demand the existence of corresponding double layers at the corresponding surfaces of separation. The precise strength of each double layer must remain conjectural as long as we have no method of determining the potential of points inside the metal. On the surfaces of Zn and Cu there is, in addition to the double layers, such a distribution of true electricity that under its action and that of the double layers, as computed by the law of the inverse first power, the space immediately outside the surface of each conductor is at constant potential, the potentials outside each conductor differing by the characteristic difference. If the geometrical configuration of Zn and Cu is changed, the single charges redistribute themselves on the surface so as to continue to satisfy the conditions. In particular, if Zn and Cu are made in the shape of plates, we may get the well known condenser action as their distance apart is varied.

The Volta potential difference is maintained automatically by some mechanism in the metal. A consequence of this is that if two pieces of Zn and Cu are charged out of contact with each other to a potential difference V (as measured between points in the surrounding ether immediately outside each metal), and are then brought into contact with a drop of potential difference to V_{zc} (where V_{zc} is the Volta difference), and passage of an amount of electricity E, the amount of electrical energy yielded by the system available to outside agencies is $E[(V - V_{zc})/2]$.

It may be shown by detailed analysis of any cyclic process involving the Volta effect that such a mechanism, automatically maintaining a constant difference between the metals, does not involve a violation of the first law of thermodynamics.

Up to the present no way has been discovered of isolating the jumps of potential involved in the Volta effect. There have, however, been two principal points of view. One is that between points in different metals on opposite sides of a surface of separation there is only a very small potential jump, numerically equal to the Peltier heat, and that the characteristic jumps are located between the metal and the ether; while the other point of view is that there is no jump between metal and ether, but that the entire Volta jump takes place between points within the metals, on opposite sides of their surface of separation. In the following I shall assume neither of these extreme positions, but shall assume potential jumps and the corresponding double layers both between metal and ether and between metal and metal, subject to the single restriction that the sum of the jumps gives the observed Volta jump.

As already mentioned I shall not assume that there are impressed E.M.F.'s at the surfaces equal and opposite to the potential jumps. Neither shall I make the assumption, to me entirely unjustifiable, that at the surface of separation of two metals here is an impressed E.M.F. equal to the Peltier heat. Electricity must now be recognized as a substance capable of possessing kinetic and potential energy. Under these conditions there is no necessary connection between merely the heat and work absorbed when electricity passes from one locality to another.

THE THERMO-ELECTRIC CIRCUIT.

We are now in a position to discuss the ordinary thermo-electric circuit. In order to have the entire situation immediately before us it will pay to reproduce the usual analysis. Consider a circuit of two metals A and B with junctions at t and $t + \Delta t$. The thermo-electric action shall be in such a direction that current flows from A to B at the hot junction. In practise the current usually attains such a value that the energy input is all used in overcoming Ohmic resistance, but we might, if we pleased, insert an electromagnetic engine in the circuit and obtain useful mechanical work. For the present we disregard the irreversible aspects of this process, and assume that the circuit may be treated like a perfect thermodynamic engine. The first law of thermodynamics states that in any closed cycle the energy input equals the energy output. We will take the closed cycle to be constituted by the flow around the circuit of unit quantity of electricity; this extension of the idea of cycle is justified by the fact that after completion of the process every part of the system has returned to its original condition, and so there has been no change of internal energy. The energy output of the cycle is that which might be obtained from the current by an electro-magnetic engine, and for unit quantity of electricity is simply equal the E.M.F. of the circuit measured in appropriate units. We denote this E.M.F. by ΔE_0, where E_0 is the E.M.F. of the cycle between the fixed lower temperature t_0 and a variable upper temperature. The energy input of the cycle is heat input and occurs in four places: at the two junctions and in the two metals A and B. At the junction the reversible heat generated is called the Peltier heat. We denote by P_{AB} the heat absorbed by unit quantity of positive electricity in flowing from A to B. In a steady state, heat absorbed by the current is provided by an inflow of heat from the surroundings. In virtue of reversibility, $P_{AB} = - P_{BA}$. In the wires themselves there is also the reversible Thomson heat. We denote by σ_A the heat absorbed by unit quantity of positive electricity in flowing in the metal A from a lower temperature to a temperature 1 degree higher. σ corresponds to the "specific heat" of electricity. P_{AB}, σ_A, and σ_B are all functions of the temperature. It is a matter of experiment that σ does not depend on the temperature gradient.

There have been in the past numerous attempts to show that σ does depend on the temperature gradient, but the overwhelming concensus of opinion has been that all such supposed effects are to be explained by local inhomogeneities in the metal. Recently, however, Benedicks (3) has reopened the question, claiming to have established the existence of a legitimate effect. As far as his work on solids goes, a paper by Foote and Harrison (4) seems to me to fully meet the situation. With regard to liquid mercury I had, before knowing of Benedick's work, found negative results (5). I had shown that positive results will be obtained unless the apparatus is symmetrically located in the gravitational field. Benedicks does not mention any precaution of this nature, and I believe that his positive results are to be explained in this way. I shall assume in this paper that the effect does not exist.

The first law applied to the cycle now gives at once

$$\Delta E_0 = P_{AB}(t + \Delta t) - \sigma_B \Delta t - P_{AB} + \sigma_A \Delta t,$$

or

$$\frac{dE_0}{dt} = \sigma_A - \sigma_B + \frac{dP_{AB}}{dt}. \tag{1}$$

In virtue of the experimental fact that the E.M.F. of a circuit from t_1 to t_2 plus that of one from t_2 to t_3 is equal that of a single one from t_1 to t_3, dE_0/dt is independent of t_0, and we write simply dE/dt, where the t_0 from which E is measured need not be specified, and in particular has no relation to the temperature at which the σ_A, σ_B, and dP_{AB}/dt of the equation are taken.

The second law may also be applied, giving

$$\frac{P_{AB}(t+\Delta t)}{t+\Delta t} - \frac{\sigma_B \Delta t}{t+\Delta t/2} - \frac{P_{AB}}{t} + \frac{\sigma_A \Delta t}{t+\Delta t/2} = 0.$$

This may at once be rewritten in the form

$$\Delta\left(\frac{P_{AB}}{t}\right) + \frac{\sigma_A - \sigma_B}{t+\Delta t/2}\Delta t = 0,$$

and gives in the limit

$$\frac{d}{dt}\left(\frac{P_{AB}}{t}\right) + \frac{1}{t}(\sigma_A - \sigma_B) = 0. \tag{2}$$

We may now eliminate $\sigma_A - \sigma_B$ or P_{AB} between 1 and 2, obtaining

$$P_{AB} = t\frac{dE_{AB}}{dt} \tag{3}$$

$$\sigma_B - \sigma_A = t\frac{d^2E_{AB}}{dt^2}. \tag{4}$$

In order to show that the E.M.F. is in such a direction that the current flows from A to B at the hot junction, we write E with the subscripts A and B.

Two aspects of these equations require discussion; first the irreversible aspects of the process, and second the location of the E.M.F.

There are two irreversible processes always involved in any thermo-electric circuit; generation of Joulean heat by the current in overcoming the resistance of the wire, and conduction of heat from the hotter to the colder end of the wire. In the early days of the subject it did not seem very objectionable to entirely disregard these effects, because of the probability that they were due to entirely unrelated parts of the mechanism, so that it would be conceivable that a metal might exist with the same thermo-electric properties as any actual metal, but with negligible thermal conduction and Joulean heat loss. But with the rise of electron theories of metals it became exceedingly probable that all these effects, reversible and irreversible, are tied together by the same mechanism, so that we cannot, at least without justification, assert that any aspect is unimportant. It was this feeling which inspired Lorentz's article in the Wolfskehl conference collection. (6) Thomson also always regarded the thermodynamic argument as by itself unsatisfactory, and looked on the equations obtained by the method above merely as suggestive relations to be tested by experiment.

It is not unusual in elementary text books to find the statement that by properly choosing the dimensions of the circuit the irreversible aspects may be made vanishingly small. An argument by Boltzmann (7) in a much neglected paper shows, however, that this is not true, but that the ratio of irreversible to reversible heat can be reduced only to a minimum, not zero, by a proper choice of the constants of the circuit. Work is extracted from the circuit reversibly by an electro-magnetic engine of properly chosen back E.M.F. The dimensions of the parts of the circuit and the magnitude of the back E.M.F. are the only variables under our control. Suppose now that the best construction possible has been given to the circuit by a proper choice of all the independent variables. We may write down the thermodynamic inequalities that hold for an irreversible process, and obtain a necessary condition between the electrical and thermal conductivities and the thermo-electric constants. This condition is given by Boltzmann and is

$$t\frac{dE}{dt} - P \leqq 2A\sqrt{t}, \tag{5}$$

where

$$A = R_A{}^{1/2}K_A{}^{1/2} + R_B{}^{1/2}K_B{}^{1/2}$$

and R_A = specific electrical resistance of A,
K_A = specific thermal conductivity of A,

with corresponding letters with subscripts B for the corresponding properties of B.

The necessary condition written down above on the assumption that the reversible and irreversible aspects of the thermo-electric circuit are inextricably tied together to form one essentially irreversible process is not one which in practice imposes any useful restriction on the constants. $2A\sqrt{t}$ is in nearly every known case greater than $t \cdot dE/dt$ alone, which may always be made positive by a proper arrangement of the metals, and is thus necessarily greater than $t \cdot dE/dt - P$, because in every known case P is also positive when $t \cdot dE/dt$ is made positive. Experimentally, $t \cdot dE/dt$ is fairly easy to determine accurately, the difficulty being with P. So long, therefore, as $t \cdot dE/dt$ alone is less than $2A\sqrt{t}$, no amount of experimental inaccuracy would vitiate the inequality, which thereby loses all interest.

Many direct experimental attacks have been made on the question of the equality of $t \cdot dE/dt$ and P, but the experimental difficulties are great, and the experimental verification is still far from complete. Thus it was not until 1906 (8) that the reversibility of the Peltier heat was shown with any accuracy, the reversibility usually being assumed in experimental work and used as a means of eliminating the Joulean heat.

So far as I know, there is no evidence that $t \cdot dE/dt$ and P are not equal, and with increasing accuracy of experimentation the verification becomes closer. Gottstein (9) has published data on silicon, molybdenite and graphite, in which the effects are large, and which other considerations suggest as the most likely field for discrepancies, and has obtained verification within the limits of accuracy of P, which are about 8 per cent. Caswell (10) has also recently published data on several Bi-Sn alloys, in which the effects are also large, and obtained verification within 6 per cent. He states that the accuracy of the Peltier heat measurements is 2 per cent., but also explicitly emphasizes that his measurements have proved the thermodynamic relation.

Mention should be made in this connection of a theorem of Baedeker (11) to the effect that if the relation

$$\frac{dE_{AB}}{dt} = \frac{1}{t} P_{AB}$$

is true for a single pair of substances it is true for every pair. The proof given by Baedeker does not justify so general a statement as this, however, and presumably the theorem itself does not hold. Baedeker's proof is as follows. The relation (2) above becomes, if extended to include irreversibility,

$$\frac{d}{dt}\left(\frac{P_{AB}}{t}\right) + \frac{1}{t}(\sigma_A - \sigma_B) \geqq 0.$$

Combining this with equation 1 gives

$$\frac{dE_{AB}}{dt} \geqq \frac{1}{t} P_{AB}.$$

The equality sign holds for perfect reversibility. Suppose now that the equality sign holds for a special pair of metals, so that

$$\frac{dE_{AB}}{dt} = \frac{1}{t} P_{AB}.$$

Consider now the couples AC and CB, where C is any third metal. Because of the addition theorem we have

$$\frac{dE_{AC}}{dt} + \frac{dE_{CB}}{dt} = \frac{1}{t}(P_{AC} + P_{CB}).$$

Now if

$$\frac{dE_{AC}}{dt} > \frac{P_{AC}}{t},$$

we must evidently have

$$\frac{dE_{CB}}{dt} < \frac{P_{CB}}{t},$$

which, Baedeker says violates the second law, and hence the theorem. Baedeker failed to notice, however, that in the above inequality the metals must be arranged in such an order that dE_{AB}/dt is positive. His proof therefore holds only when dE_{AC}/dt and dE_{CB}/dt are both positive. The correct theorem is that if the relation of perfect reversibility holds for any pair of metals A and B (dE_{AB}/dt being positive), it also holds for all pairs of metals between A and B that may be chosen from the series of metals arranged in ascending order of dE_{Ax}/dt.

In practise, however, an equation can only be shown to hold within limits. So that instead of a perfect equality we should only have

$$\frac{dE_{AB}}{dt} = \frac{1}{t} P_{AB} + \epsilon,$$

where ϵ is some positive quantity. The argument above now shows that if C is any third metal intermediate between A and B, dE_{AC}/dt cannot exceed P_{AC}/t by more than ϵ. But dE_{AC}/dt is numerically less than dE_{AB}/dt, so that the percentage verification of the formula for the pair AC is not so good as for the pair AB.

If therefore a method is available in which the limits of accuracy are percentage limits, this theorem, contrary to what Baedeker supposed, does not allow us to dispense with an experimental verification of the formula for every pair of metals.

There is no inequality corresponding to

$$\frac{dE_{AB}}{dt} \geqq \frac{P_{AB}}{t}$$

connecting the Thomson heats with the electromotive force of the circuit. The analytical reason is that the two sides of an inequality may not be differentiated. The experimental verification of the formula for the Thomson heats is not yet as complete as that for the Peltier heat.

I shall assume in the following, as most probable from the present data, that the thermodynamic relations obtained by neglecting irreversibility are strictly true, but in my opinion the question cannot yet be regarded as closed.

Consider next the location of the E.M.F. A glance at the thermodynamic arguments shows that we have said nothing about the intensity of the forces at any locality; we have merely equated the total work done in the circuit by the E.M.F. to the total energy inflow in the form of heat, and our justification is the experimental fact that in the complete cycle no other forms of energy have any net effect. The thermodynamic results are entirely unaffected by adding to any possible physical distribution of E.M.F. any other distribution which integrates to zero around the complete circuit. Any argument for a localized E.M.F. must use other kinds of experimental fact than those which we have up to the present used. There has, nevertheless, been an attempt by many physicists to identify the reversible heats with exactly equal E.M.F.'s at the same localities, and conversely. Maxwell does this, as did also Heaviside (12), who speaks with impassioned irritation of those who would "make a force do work where it is not." All the objections of Heaviside as to energy manifestations at the junctions seem to me to be fully answered by a careful consideration of the nature of the Poynting vector, together with a recognition of the fact that within the metal electricity may possess kinetic and potential energies characteristic of the metal. Whatever assumption one cares to make about the location of the E.M.F. will be found to involve such a distribution of the Poynting vector as to automatically take care of any unusual energy transformations introduced by the assumptions. However, in accordance with the mode of thought of Maxwell and Heaviside it is usual to speak of a Peltier E.M.F. and a Thomson E.M.F. (*e.g.*, Caswell (10), 1916) which are precisely equal to the corresponding reversible heats, and to assume that these are the total E.M.F.'s at the junction or in the unequally heated metal. This, it seems to me, is entirely unjustified, and my position in this paper is that we know nothing about these localized E.M.F.'s from experiments such as these on closed circuits. When in the following I speak of a Peltier E.M.F., I mean whatever E.M.F., if any, there may be at the junction, but shall assume no relation with the heat at the junction. Similarly by the Thomson E.M.F. I mean the E.M.F. distributed throughout the metal in virtue of the temperature gradient, but again shall assume no relation with the Thomson heat.

A second point of view, that other specifiable E.M.F.'s than those corresponding to the local heats are involved has been maintained by many. Among the prominent early holders of this view was Lord Kelvin, who believed that at the junction of two metals there is an E.M.F. equal to the ordinary Volta contact potential difference. Adopting this point of view, Kelvin in one of his later papers (13) deduced a relation between Volta potential difference and a quantity analogous to the Peltier heat by a purely isothermal process, thus avoiding the difficulties of irreversibility. The same relation had also been given nine years previously by Lorentz (14) in a paper corrected by him to meet the criticisms of Budde (15). Both the papers of Kelvin and Lorentz seem to have been entirely overlooked by subsequent writers. It is now becoming evident, however, from such work as that of Richardson (16) on thermionic emission, that Kelvin's view is probably no more correct than the other, and that there may be a potential jump between the surface of the metal and the surrounding ether. I shall show from an examination of the phenomena of thermionic emission that there are certain relations between the E.M.F. of a circuit, Peltier heat, Volta potential difference, etc., irrespective of what hypothesis one adopts about the location of the potential jumps. Richardson himself makes the assumption that the local E.M.F. is equal the local heat, and with this assumption obtains a relation similar to Kelvin's.

Temperature Coefficient of Volta Effect.

The following deduction of a relation involving Peltier heat and Volta difference is considerably simpler than that of either Lorentz or Kelvin, and furthermore makes no assumptions as to the location and magnitude of the surface potential jumps accompanying the Volta potential difference. The method also permits somewhat more general conclusions.

Imagine an infinite plate condenser composed of two different metals A and B, all parts of which are maintained at the same temperature, and the distance apart of which is variable. The two plates may be connected by a wire. We imagine this wire to be half of A and half of B, so that when charge is transferred from one plate to the other through the wire the ordinary Peltier heat is developed at the junction.

As the independent variables fixing the state of the system we choose:

t = absolute temperature,
ρ = positive charge per unit area on A (there is of course an equal negative charge on B),
c = capacity per unit area (this depends only on the distance apart of the plates).

The following dependent variables are to be considered:

V_{BA} = Volta contact difference of potential,
u = internal energy per unit area,
dW = work done by the system in any infinitesimal change,
dQ = heat absorbed in any infinitesimal change.

Now the second law states that $(du+dW)/t$ is an exact differential for any reversible change. We accordingly have to find dW and du. For dW we have the equation

$$dW = \left(\frac{\partial W}{\partial T}\right)_{\rho c} dt + \left(\frac{\partial W}{\partial \rho}\right)_{tc} d\rho + \left(\frac{\partial W}{\partial c}\right)_{t\rho} dc.$$

The partial derivatives may be evaluated as follows. Obviously no work is done if the temperature of the system is changed, keeping the distance of separation of the plates constant, if at the same time no charge is transferred from plate to plate. The analytic statement of this is

$$\left(\frac{\partial W}{\partial t}\right)_{\rho c} = 0.$$

Again, if work is obtained by letting current flow from plate to plate the effective driving force is the difference of potential minus the Volta difference. The work done during this passage of current may be extracted by a reversible electro-magnetic engine in the wire between the plates. This gives

$$\left(\frac{\partial W}{\partial \rho}\right)_{tc} = -\left(\frac{\rho}{c} - V_{BA}\right) d\rho.$$

This is independent of assumption as to the location of the Volta jump, whether it is a surface affair between the metal and the surrounding electron gas, or between the two metals, or both. The conclusions are therefore independent of special hypothesis. Finally, if the distance apart of the plates is changed, thus changing the capacity, but keeping temperature and charge constant, we have the mechanical work

$$\left(\frac{\partial W}{\partial c}\right)_{T\rho} dc = \frac{1}{2}\frac{\rho^2}{c^2} dc.$$

This is an immediate consequence of the familiar expression for the work of collecting an electrical distribution from infinite subdivision, $\frac{1}{2}\rho \times$ pot. diff. ($= \frac{1}{2}(\rho^2/c)$ in this case).

We may also treat du as we have dW, writing

$$du = \left(\frac{\partial u}{\partial t}\right)_{\rho c} dt + \left(\frac{\partial u}{\partial \rho}\right)_{tc} d\rho + \left(\frac{\partial u}{\partial c}\right)_{t\rho} dc.$$

Substituting now above, we have

$$\frac{1}{t}\left\{\left(\frac{\partial u}{\partial t}\right)_{\rho c} dt + \left[-\frac{\rho}{c} + V_{BA} + \left(\frac{\partial u}{\partial \rho}\right)_{tk}\right] d\rho + \left[\frac{1}{2}\frac{\rho^2}{c^2} + \left(\frac{\partial u}{\partial c}\right)_{t\rho}\right] dc\right\}$$

is a perfect differential. This statement will give us three equations, because of the three independent variables, instead of only one equation, as in the examples of elementary thermodynamics, where we are concerned with only two independent variables.

In the first place, from the coefficients of dt and dc, we obtain

$$\frac{\partial}{\partial c}\left\{\frac{1}{t}\left(\frac{\partial u}{\partial t}\right)_{\rho c}\right\}_{t\rho} = \frac{\partial}{\partial t}\left\{\frac{1}{t}\left[\frac{1}{2}\frac{\rho^2}{c^2} + \left(\frac{\partial u}{\partial c}\right)_{t\rho}\right]\right\}_{c\rho},$$

whence

$$-\frac{1}{2}\frac{1}{t^2}\frac{\rho^2}{c^2} - \frac{1}{t^2}\left(\frac{\partial u}{\partial c}\right)_{t\rho} + \frac{1}{t}\left(\frac{\partial^2 u}{\partial c \partial t}\right)_{\rho} = \frac{1}{t}\left(\frac{\partial^2 u}{\partial c \partial t}\right)_{\rho}$$

giving

$$\left(\frac{\partial u}{\partial c}\right)_{t\rho} = -\frac{1}{2}\frac{\rho^2}{c^2}.$$

But we have already seen that

$$\left(\frac{\partial W}{\partial c}\right)_{t\rho} = \frac{1}{2}\frac{\rho^2}{c^2},$$

so that

$$\left(\frac{\partial Q}{\partial c}\right)_{t\rho} = 0. \tag{6}$$

Therefore no heat is absorbed when the plates are moved with respect to each other at constant temperature and charge. This states a fundamental assumption of electrostatics to the effect that charged bodies may be moved relatively to each other with no thermal effects.

Secondly, from the coefficients of $d\rho$ and dc we get

$$\frac{\partial}{\partial c}\left\{\frac{1}{t}\left[-\frac{\rho}{c} + V_{BA} + \left(\frac{\partial u}{\partial \rho}\right)_{tc}\right]\right\}_{t\rho} = \frac{\partial}{\partial \rho}\left\{\frac{1}{t}\left[\frac{1}{2}\frac{\rho^2}{c^2} + \left(\frac{\partial u}{\partial c}\right)_{t\rho}\right]\right\}_{ct},$$

which expands to

$$\frac{\rho}{c^2} + \left(\frac{\partial V_{BA}}{\partial c}\right)_{t\rho} + \left(\frac{\partial^2 u}{\partial \rho \partial c}\right)_t = \frac{\rho}{c^2} + \left(\frac{\partial^2 u}{\partial \rho \partial c}\right)_t,$$

or

$$\left(\frac{\partial V_{BA}}{\partial c}\right)_{t\rho} = 0, \tag{7}$$

which states that merely changing the distance between the plates does not change the Volta difference. We have not thereby proved that the Volta difference cannot depend on the distance apart of the plates; we have merely proved that such independence is a logical consequence of the statements that we made about the nature of the Volta effect.

Formulas 6 and 7 are not given by Kelvin or Lorentz.

Finally, we obtain from the coefficients of dt and $d\rho$,

$$\frac{\partial}{\partial \rho}\left\{\frac{1}{t}\left(\frac{\partial u}{\partial t}\right)_{\rho c}\right\}_{tc} = \frac{\partial}{\partial t}\left\{\frac{1}{t}\left[-\frac{\rho}{c} + V_{BA} + \left(\frac{\partial u}{\partial \rho}\right)_{tc}\right]\right\}_{\rho c}.$$

Expanding,

$$\frac{1}{t}\left(\frac{\partial^2 u}{\partial \rho \partial t}\right)_c = -\frac{1}{t^2}\left[-\frac{\rho}{c} + V_{BA} + \left(\frac{\partial u}{\partial \rho}\right)_{tc}\right] + \frac{1}{t}\left[\left(\frac{\partial V_{BA}}{\partial t}\right)_{\rho c} + \left(\frac{\partial^2 u}{\partial t \partial \rho}\right)_c\right].$$

$(\partial^2 u/\partial \rho \partial t)_c$ cancels. $(\partial V_{BA}/\partial t)_{\rho c}$ we may take as the ordinary temperature derivative of the Volta contact difference of potential. Experimentally there is yet no evidence for a variation of V with ρ, and we have shown that it does not depend on c, so that we might write simply

dV_{BA}/dt, but the thermodynamic distinction between the derivatives should not be forgotten. It might be proved experimentally at some later time that V_{BA} does depend on ρ, and in fact there are some plausible reasons for expecting an effect of this nature. I am not aware that any very careful search has been made for a variation of V with ρ.

The only unknown now remaining in the above equation is $(\partial u/\partial\rho)_{tc}$. Under all conditions we have $du = dQ - dW$. Now if the temperature is constant, and the distance apart of the plates is constant (c = constant), the only mechanical work is that which might be got out of the electrical current when ρ changes, and the heat absorbed is the heat involved in the transfer of electricity from one plate to the other. Write this for the moment as P_{BA}', this being the heat absorbed when unit quantity of electricity passes from B to A. Then

$$\left(\frac{\partial u}{\partial \rho}\right)_{tc} d\rho = P_{BA}'d\rho + \left(\frac{\rho}{c} - V_{BA}\right)d\rho.$$

Substitute this above and we get

$$O = -\frac{P_{BA}'}{t} + \frac{dV_{BA}}{dt},$$

or

$$\frac{dV_{AB}}{dt} = \frac{P_{AB}'}{t}. \tag{8}$$

This is the equation deduced by Lorentz (14) and Kelvin (13). It is to be noticed that all parts of the system have been at the same temperature, so that during the cycle there have been no irreversible heat transfers, and therefore there is no question of the validity of the conclusions, as there was in the case of the ordinary thermoelectric circuit. Kelvin hoped that an experimental confirmation of this formula would make more probable the correctness of the ordinary formulas for the thermo-electric circuit. In attempting the confirmation he at first identified, as one naturally would, the heat P_{BA}' with the ordinary Peltier heat P_{BA}. This amounts to assuming that all the thermal effects involved in the transfer of charge from B to A are to be found at the surface of separation of A and B. Making this identification of P' with P, the experimental verification failed by a thousand fold. Now the ordinary thermodynamic formulas hold within much narrower limits. So that not only did this attempt of Kelvin's to place the ordinary thermodynamic reasoning on a firmer basis fail, but in order to explain the discrepancies between the new formula and experiment, he was driven to postulate the existence of another surface thermal effect, in much the same way that he had previously postulated the existence of the Thomson heat. The possibility of such a surface heat was also explicitly recognized by Lorentz (14), after it was suggested to him by Budde (15).

The new surface heat that Kelvin had to postulate was a reversible generation or absorption of heat at the surface of a conductor when the surface charge changes. So far as I am aware the existence of the effect has never been demonstrated; in fact the papers of Lorentz and Kelvin seem not to be generally known, and apparently no serious attempt has been made to discover the effect. I shall return to this matter later in connection with a deduction of the same formula by a method similar to that of Richardson.

THERMIONIC EFFECTS.

This is probably as far as we can get by an application of the two laws of thermodynamics to these two phenomena. Further progress demands different types of experiments from those contemplated in the applications above. Now this new order of experimental fact has been supplied in the last few years, in principal part by the work of Richardson (16) on thermionic emission. In this work the energy relations and transformations are discussed when electricity is taken directly through the surface of the metal from metal to ether. In the previous work of this paper we have been restricted in transferring electricity from conductor to conductor to the staid and classical methods of motion over the metallic surfaces or through the body of the metal. We may now extend our thermodynamic processes to cycles in which electricity is transferred from one conductor to another through the surface and the surrounding ether.

Richardson has developed by thermodynamic arguments many of the formulas connecting thermionic effects with those already discussed, but he has frequently made specific assumptions as to localized E.M.F.'s, and has further, it seems to me, confused or used interchangeably the thermodynamic quantities, quantity of energy, quantity of heat, and work, and has not sharply specified the conditions to which some of his quantities, notably the heat of vaporization of an electron, apply. A critical examination of his methods will suggest changes in his formulas.

The starting point is the observation that at high temperatures all metals emit electrons, and therefore, when in a state of equilibrium, are surrounded by an electron atmosphere. The density of this atmosphere becomes rapidly lower at lower temperatures, but we assume that it essentially exists at all temperatures, and obtain what information we can from the fact of its existence. The density of this gas is so small under ordinary conditions that the charge it carries does not affect its behavior, and it accordingly obeys the perfect gas laws. Richardson has given a qualitative argument for this, or it may be easily proved by writing down the equations of equilibrium of a gas in which there is a distributed volume charge proportional to the density, and finding the explicit solution for small densities.

The process of a metal surrounding itself with an electron atmosphere is analogous to the process of evaporation of a solid, and the same thermodynamic arguments apply to it. Any purely electrostatic action due to the isolation of the negative charge in the gas and a positive charge on the metal can be eliminated by evaporating only a small quantity of electrons, the electrostatic energy being proportional to the square of the charge. Assuming now the perfect gas law, we first find the relation between electron gas density and temperature.

Clapeyron's equation applies to this and gives

$$\frac{dt}{dp} = \frac{t\Delta v}{H},$$

where Δv is the change of volume when 1 gm. of electrons evaporates reversibly, and H is the latent heat of evaporation. Professor Hall has objected to the use of this equation, or the equivalent one by Richardson (Eq. 1, p. 28 of Richardson's book), and has published a statement to that effect in a recent number of the Proceedings of the National Academy of Sciences (17). He has later recognized, however, that the objection to Richardson's argument is not to be found at this stage, and is stating his revised position in a forthcoming note to the National Academy.

Returning now to Clapeyron's equation, since the perfect gas law holds, $p = nkt$, where n is the number of electrons per c.c., and k is the gas constant. The gas law now gives

$$dp = ktdn + nkdt.$$

Δv is obviously approximately equal to v, the volume of 1 gm. of electron gas. Making these two substitutions in Clapeyron's equation, we get

$$dt = \frac{tv}{H}(ktdn + nkdt),$$

which may be rewritten

$$dt = \frac{kt^2}{\frac{H}{nv}}\left(\frac{dn}{n} + \frac{dt}{t}\right).$$

Now nv is the total number of electrons per gm. of gas, and hence H/nv is the latent heat per electron. Denote this by η, and the equation becomes

$$\frac{\eta dt}{kt^2} = \frac{dn}{n} + \frac{dt}{t}. \tag{9}$$

An integration of this equation gives

$$n = At^{-1}e^{\int\frac{\eta dt}{kt^2}}, \tag{10}$$

in which A is not a function of t. This is the same as Richardson's equation 7, p. 29, noting that his φ is the energy change in the evaporation of one electron, so that $\eta = \varphi + kt$.

It is necessary to scrutinize pretty closely the conditions under which the η of this formula is to be determined. Clapeyron's equation, as used above, applies to an isolated system of metal with its electron vapor. We may imagine this system enclosed in a box provided with a piston working on the electron vapor, and so able to interchange work with the surroundings. The η in the formula above is the heat per electron which must be communicated to the box from outside during the evaporation of electrons and accompanying motion of the piston at constant pressure. Now during this process in which an electron is evaporated, a positive charge is left behind on the surface of the metal, so that during this process the surface charge is changing. We may split η into two parts. The first, η_ρ, is the latent heat which would be absorbed if the evaporation took place at constant surface charge. The second part of the heat is a heating effect due to the appearance of a positive charge on the surface; this is merely Lorentz and Kelvin's surface heat. If we put P_s for the heat absorbed by the system when unit positive charge is imparted to the surface, we have

$$\eta = \eta_\rho - \epsilon P_S, \tag{11}$$

where ϵ is the electronic charge, taken as a negative number.

These results may now be applied to contact difference of potential. Imagine two metals A and B together in a region at temperature t, in metallic contact. Each metal will sourround itself with an atmosphere of electrons by spontaneous emission, and these two atmospheres will in general be of different densities and pressures. The gas equilibrium is maintained by an electrostatic potential gradient accompanying the pressure gradient. Notice that this equilibrating electrostatic field, for gases of small densities, is due to charges outside the gas itself. The ordinary gas equations show that equilibrium demands the equation

$$\frac{n_A}{n_B} = e^{-\frac{\epsilon v}{kt}BA}, \tag{12}$$

where ϵV_{BA} is the work done against electrostatic forces in taking an electron from a point immediately outside B to a point immediately outside A, n_A and n_B are the number of electrons per c.c. immediately outside A and B respectively.

Under ordinary conditions it is doubtful whether two pieces of metal ever reach equilibrium in this way, because the emission of electrons at ordinary temperatures is so excessively slow. From data on page 69 of Richardson it may be computed that a sphere of tungsten 1 cm. in radius requires something of the order of 10^{55} years to charge itself to a potential of 1 volt by spontaneous emission of electrons at 0° C. It is to be considered, therefore, whether the Volta potential difference as measured under ordinary conditions is the same as it would be if measured after a time long enough for the attainment of equilibrium conditions. Now it is reasonable to suppose that the potential jumps at the surface of metal and ether or metal and metal are determined solely by forces operative at the surfaces, little if any affected by the presence of an electron gas outside. In a system of two metals in contact there may be jumps of potential at four places; at the three surfaces of separation of metal-ether or metal-metal, and through the ether between points outside the two metals. The sum of the four drops is zero, because the electrostatic field is conservative. Three of the drops are the same, probably, whether equilibrium is reached or not. The fourth drop, which is the Volta drop, is therefore also probably the same whether equilibrium is reached or not. We may therefore apply our thermodynamic reasoning to systems in which equilibrium has been attained with high probability that the Volta drop appearing in the formulas is the same as that measured under ordinary conditions.

We are now in a position to obtain V. Taking logarithms of the equation (12) above,

$$V_{BA} = \frac{kt}{\epsilon} \log \frac{n_B}{n_A}.$$

Substituting values of n

$$V_{BA} = \frac{kt}{\epsilon} \left\{ \log \frac{A_B}{A_A} + \int \frac{\eta_B - \eta_A}{kt^2} dt \right\}.$$

Now A_A and A_B are independent of t. Hence, differentiating the above equation,

$$\eta_A - \eta_B = \epsilon V_{BA} - \epsilon t \frac{dV_{BA}}{dt}. \tag{13}$$

It is to be noticed that during this differentiation all the other variables on which the quantities might conceivably depend are to be kept constant. In particular, if V_{BA} is possibly a function of the total charge on the surface, we should have to keep the surface density constant during the differentiation, and dV_{BA}/dt would become $(\partial V_{BA}/\partial t)_p$, as in the previous deduction by the condenser method.

We may obtain another relation by taking a gram of electrons around a closed cycle between A and B. This cycle may be performed in the following way. Imagine separate enclosures about A and B, containing the electron gas, and connected by a pipe in which there is a piston (see Fig. 2). The piston is to be pushed toward the enclosure about B and withdrawn by the corresponding amount from that about A. This transfers electrons from the gas about B to the gas about A. During the process of transfer of electrons from the atmosphere about B, through the metal, to the atmosphere about A, there has obviously been no change in the surface charges on A or B. The latent heats of vaporization involved in this process will therefore be the heats at constant charge. Now the process outlined above is isothermal and reversible, and therefore the total heat absorbed is zero. This gives

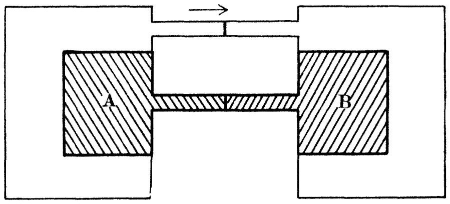

Fig. 2.

$$\eta_{\rho A} - \eta_{\rho B} + \epsilon P_{BA} + Q = 0.$$

P_{BA} is the ordinary Peltier heat at the junction. Q is the heat absorbed by the gas per electron in passing under equilibrium conditions from the gas about A to that about B. In this transfer the gas remains isothermal, and pressure and potential change simultaneously as equilibrium demands.

Now the analysis of the introduction shows that when a gas is displaced in this way in a potential field the mechanical work done by the pressures acting across the boundaries is zero. The first law of thermodynamics demands, therefore, that the heat inflow shall equal the change of energy. This change is composed of two parts, energy of position in the field, and intrinsic energy. But now the intrinsic energy of a gas does not change at constant temperature. Hence

$$Q = \epsilon V_{AB}.$$

We may apply our definition of E.M.F. given in the introduction and find the E.M.F. between two points in the electron gas outside A and B to be V_{AB}. In this particular case, therefore, electrostatic potential difference, local E.M.F., and heat locally absorbed are numerically equal.

The reason is that in this particular case (electron gas) the intrinsic energy of the electrons is a function of temperature only. We shall prove later that this equality cannot hold in general.

The Q found as above is the same as that which would be found from the ordinary formulas for a substance not in a field of force. This calculation gives

$$Q = \int_{p_A}^{p_B} \left(\frac{\partial Q}{\partial p}\right)_t dp = - \int_{p_A}^{p_B} t \left(\frac{\partial v}{\partial t}\right)_p dp.$$

For a perfect gas this becomes

$$Q = - kt \int_{p_A}^{p_B} \frac{dp}{p} = kt \log \frac{p_A}{p_B} = kt \log \frac{n_A}{n_B}.$$

But we have seen that the condition of equilibrium in a potential field is

$$\log \frac{n_A}{n_B} = - \frac{\epsilon V_{BA}}{kt}.$$

Substituting,

$$Q = \epsilon V_{AB},$$

as before.

We would not be justified, however, in assuming that the other formulas of thermodynamics are not affected by the presence of the potential field. In particular, the work done by a gas in expanding isothermally against the pressures exerted across its boundaries is Q when there is no potential field. We have just seen that this work is zero in a potential field. Work in a potential field is therefore not equal to $\int p dv$.

Instead of saying as above that the heat absorbed goes directly toward increasing the energy of position, we may, if we prefer, describe the phenomena by saying that the heat absorbed goes to the work which would normally be done by the gas in expanding out of a potential field, and that besides this work, additional work is received across the boundaries when expanding in a potential field, which goes to increase the energy of position.

Now substituting the value found for Q gives

$$\eta_{\rho A} - \eta_{\rho B} = \epsilon(V_{BA} - P_{BA}). \qquad (14)$$

An equation similar in appearance was given by Richardson, in which $\eta_{\rho A} - \eta_{\rho B}$ is replaced by $\varphi_A - \varphi_B$. He obtained the equation by identifying φ_A, φ_B and P_{AB} with the local E.M.F.'s, and by disregarding the difference between the heats of vaporization at constant surface density and with variable density.

In a recent paper, Langmuir (18), essentially following Richardson's point of view, has also failed to recognize the difference between the heat of vaporization at variable surface density, which appears in the thermodynamic analysis, and the heat under constant surface density, which may be measured experimentally. Langmuir's calculation of the magnitude of the heat of vaporization from the work done by an electron in escaping from the attraction of its image in the surface applies to vaporization with variable surface density, and not to the experimental conditions of vaporization at constant density. His argument for the probable non-existence of the double layer on the surface metal-ether would therefore seem to me to lose much of its force. This failure to distinguish between the two heats of vaporization would also seem to be involved in Langmuir's formulation (on page 172 of his paper) of the distinction between a potential difference and an E.M.F.

Combining the two equations (13), and (14), for $\eta_{\rho A} - \eta\rho_{\rho B}$, with (11) gives,

$$t\frac{dV_{BA}}{dt} = P_{BA} + P_{AS} - P_{BS}. \qquad (15)$$

Now if positive charge is passed from the surface of B to A through the metal, as in the condenser analysis previously given, negative charge appears on B and positive on A, and there may be accompanying heating effects in three places, at the two surfaces of separation of metal from ether, and at the surface metal-metal. The sum of these three heats is what was previously called P_{BA}'. Obviously

$$P_{BA}' = P_{BA} + P_{AS} - P_{BS}, \qquad (16)$$

and we have

$$t\frac{dV_{BA}}{dt} = P_{BA}', \qquad (17)$$

which is the equation (8) of Lorentz and Kelvin previously given. As already stated, it would be more correct, until more definite experimental evidence is at hand to write $\partial V_{BA}/\partial t$ instead of dV_{BA}/dt.

The deduction of this same equation by methods so different is pretty good presumptive evidence of its correctness.

The equation corresponding to the above given by Richardson is

$$t\frac{dV_{BA}}{dt} = P_{BA},$$

where P_{BA} is the ordinary Peltier heat. The surface heats do not appear in his equation, because, as already explained, he has neglected to distinguish latent at heats at constant from those at variable surface charge.

Assuming Richardson's formula to be correct, we may combine with the formulas for a thermo-electric circuit, obtaining the relation

$$\frac{dV_{AB}}{dt} = \frac{dE_{AB}}{dt}.$$

This consequence of Richardson's relation is frequently supposed to be correct,[1] but obviously is not correct if there is a surface heat.

The formula above as given by Richardson has never been verified experimentally. The failure of experimental verification may very well be due in large part to experimental difficulties. Recent work of Langmuir (19) has shown the enormous effect on a metal surface of a layer of adsorbed gas only one molecule deep. No experiments on this subject have ever been made in which this layer has been removed. Perhaps the most recent work is that of Compton (20), in which there is a large possible effect from residual gas, as he himself explicitly states. The experimental discrepancy has been reduced by this latest work of Compton from the thousand fold of Kelvin to fifty fold. There is still, however, as far as the best experimental evidence goes, ample room for the existence of the surface heat.

In view of the important rôle which the equation of Richardson plays in the subject of thermionic emission, the question of the existence of the surface heat assumes considerable interest. A direct experimental attack on the problem does not appear promising. Assuming in the most favorable case that the entire outstanding discrepancy in the formula

$$t\frac{dV_{BA}}{dt} = P_{BA}$$

is due to the hypothetical surface heats, the rise of temperature of a conductor on imparting to it a surface charge may be computed approximately. The greatest rise of temperature will be produced on thin conductors, such as wires or foil. But under these conditions the greatest effect to be expected is entirely overwhelmed by the heating effect due to the mechanical stress produced in the conductor by the mutual repulsion of the charges on the surface. (It is to be remarked that the η above does not include this electrostriction effect, which may be made vanishingly small by working with large enough conductors.) The best chance of detecting the existence of the surface heat is by an experimental determination of dV_{BA}/dt, improving the vacuum conditions as much as possible, or by a method to be suggested later.

Professor Hall in a recent paper (17) has stated his belief in the existence of the surface heats. He argues for their existence by giving such a picture of the mechanism involved in a redistribution of surface charges

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[1] See, for example, Langmuir, *loc. cit.*, page 182.

as to make a heating effect seem probable. His conception is that at every point within and on the surface of a metal there is a dissociation of atoms into positive and negative ions, whose relative number is determined by the mass law. A disturbance of equilibrium by the removal of electrons from the surface layer is followed by such a change in the surface dissociation as to again satisfy the mass law. This new dissociation, it is most natural to suppose, is accompanied by heating effects.

The introduction of the idea of a dissociation determined by the mass law is, I believe, a valuable addition to our stock of concepts of what may be taking place within a metal, and its application to the surface effects is one way of avoiding one very real difficulty. This difficulty is encountered in trying to picture the processes involved in giving a metal surface a positive charge. Let us suppose the surface initially uncharged, without surface layers. Then the surface may be given a negative charge by the mere addition of electrons, but to produce a positive charge, electrons must be removed from the interior of the atoms. These two processes are essentially different in character, and the last must almost of necessity involve a heating effect, which the first need not. There is thus a dissymmetry in the action of a positive and a negative charge which we are not willing to admit. The assumption of a continual supply of positive and negative ions in the surface, as Professor Hall suggests, avoids this dissymmetry, and to that extent has intrinsic probability. Nevertheless the extension of the concept of mass action to a surface layer seems questionable, and I believe the difficulty can be met in another way. If we suppose the surface is covered with a double layer, the electrons being on the side away from the metal, then a negative charge is added by adding electrons to the outer layer, and a positive charge is added by removing electrons from the outer layer. There is thus no difficulty from dissymmetry. I prefer, therefore, to regard the question of the existence of this surface heat as still open, to be settled by new experimental evidence, but incline to the opinion that it does exist.

We may now combine these thermionic formulas with those of the thermo-electric circuit. We introduce the following new quantities in addition to those already considered.

S_{AE} = potential jump at surface of separation of A and ether,
S_{BE} = potential jump at surface of separation of B and ether,
S_{AB} = potential jump at surface of separation of A and B,
Σ_{AE} = E.M.F. at surface of separation of A and ether,
Σ_{BE} = E.M.F. at surface of separation of B and ether,
Σ_{AB} = E.M.F. at surface of separation of A and B,
σ_A' = Thomson E.M.F. in A,

$\sigma_B{}'$ = Thomson E.M.F. in B,
$\sigma_A{}''$ = Thomson potential gradient in A,
$\sigma_B{}''$ = Thomson potential gradient in B.

It may of course be questionable whether there is any E.M.F. at the surface of separation of A and ether, and it is any event exceedingly improbable that the surface action can be completely represented by an E.M.F. It may be, however, that part of the action is properly so representable. We denote this part of the action by the letters above, and find what conditions it has to satisfy.

With regard to the Thomson potential gradient it is to be emphasized that this is entirely different in character from the surface jumps S_{AE} or S_{AB}. A jump of the potential at the surface necessarily involves a double layer at the surface; the jump is entirely determined by the double layer, and is unaffected by charges elsewhere. The surface jump is therefore probably determined by forces at the surface, which are probably characteristic of the surface and independent of the state of other parts of the system. The Thomson potential gradient (*i.e.*, the potential gradient in an unequally heated metal) is, however, affected by the distribution of charge throughout the system, and can therefore be characteristic of the system only under specified conditions. We shall in the following understand by σ'' the potential gradient in open circuit. The Thomson E.M.F. and Thomson heat are, on the other hand, probably determined merely by the local forces, independently of other parts of the system. We shall assume then to be of this character in the following.

We now have the following equations;

$$V_{BA} = \frac{1}{\epsilon}(\eta_{\rho A} - \eta_{\rho B}) + P_{BA}, \tag{18}$$

$$V_{BA} = S_{AE} - S_{BE} + S_{BA}, \tag{19}$$

$$V_{BA} = \Sigma_{AE} - \Sigma_{BE} + \Sigma_{BA}. \tag{20}$$

These three depend on the fact, already proved, that in the electron gas potential difference, E.M.F., and heat are locally equal. These three equations are obtained from the isothermal system by describing a closed path out of the ether into B, across the surface of separation of B and A, out into the starting point in the ether. By describing a closed path entirely within the metal, maintaining now the junctions of A and B at different temperatures, we may obtain the following three additional equations

$$\frac{dE_{BA}}{dt} = \frac{d\Sigma_{BA}}{dt} + \sigma_B' - \sigma_A', \tag{21}$$

$$\frac{dE_{BA}}{dt} = \frac{dP_{BA}}{dt} + \sigma_B - \sigma_A, \tag{22}$$

$$\frac{dE_{BA}}{dt} = \frac{dS_{BA}}{dt} + \sigma_B'' - \sigma_A''. \tag{23}$$

The last of these is the expression for the difference of potential between the ends of A and B on open circuit, assuming that the E.M.F. of a thermo-electric circuit is the same on open and closed circuit. This is matter for experimental examination; I do not know how carefully this examination has been made. Certainly the equality of E.M.F. on open and closed circuit is usually assumed without question, and in the absence of experimental evidence to the contrary, we shall make the same assumption here.

We also have the additional equations

$$\frac{P_{BA}}{t} = \frac{dE_{BA}}{dt} = \frac{dV_{BA}}{dt} - \frac{1}{t}[P_{AS} - P_{BS}]. \tag{24}$$

Now differentiating (18) and combining with (22) and (24) gives

$$\frac{d\eta_{\rho A}}{dt} + \epsilon\sigma_A - \frac{\epsilon}{t}P_{AS} = \frac{d\eta_{\rho B}}{dt} + \epsilon\sigma_B - \frac{\epsilon}{t}P_{BS}. \tag{25}$$

Similarly (20), (21), and (24) give

$$\frac{d\Sigma_{AE}}{dt} + \sigma_A' - \frac{P_{AS}}{t} = \frac{d\Sigma_{BE}}{dt} + \sigma_B' - \frac{P_{BS}}{t}, \tag{26}$$

and (19), (23), and (24) give

$$\frac{dS_{AE}}{dt} + \sigma_A'' - \frac{P_{AS}}{t} = \frac{dS_{BE}}{dt} + \sigma_B'' - \frac{P_{BS}}{t}. \tag{27}$$

Hence we have proved that

$$\frac{d\eta_\rho}{dt} + \epsilon\sigma - \frac{\epsilon P_S}{t}, \qquad \frac{d\Sigma_E}{dt} + \sigma' - \frac{P_S}{t}, \qquad \text{and} \qquad \frac{dS_E}{t} + \sigma'' - \frac{P_S}{t}$$

are all independent of the metal.

We may now obtain the universal value of $d\eta_\rho/dt + \epsilon\sigma - \epsilon P_S/t$ by an argument similar to that of Richardson. In this deduction we shall assume that the irreversible processes going on at the same time that we describe the various cycles are without effect.

Surround the two ends of the bar at difference of temperature by two chambers to contain the electron atmosphere (see Fig. 3), with pistons as shown. Electrons are first to be conveyed from one chamber to the other by operating the pistons as shown. The cycle then is to be completed in two steps. First, operate on the transferred gas under potential $V + \Delta V$, allowing it to expand to temperature t and to that pressure, $p + \Delta p'$, which is in equilibrium at t with gas at pressure p at a potential V. The second step consists in the transfer of gas at t from $V + \Delta V$ and $p + \Delta p'$ to V and p. During this second step V and p shall change together in such a way that they always have the simultaneous values to be found in an isothermal gas in equilibrium extendingfrom p, V to $p + \Delta p'$, $V + \Delta V$. To the first of these two steps all the ordinary formulas of thermodynamics apply, because the process is described at constant potential. During the second process, however, the potential is changing, and all of the ordinary formulas do not apply. In particular, we have shown that the work cannot be computed in the regular way, but is zero. We have, however, shown that the heat absorbed, and therefore the change of entropy, is not affected by the fact that the process is described in a varying potential field. The change of entropy may therefore be computed for these two steps together in the regular way, and therefore is independent of the precise way of passing from the initial to the final state.

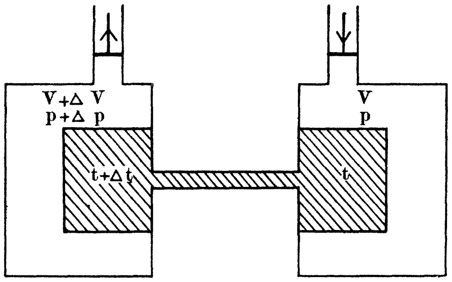

Fig. 3.

Applying the second law to the cycle now gives

$$\frac{1}{\epsilon}\frac{\eta_p}{t} + \frac{\sigma\Delta t}{t+\frac{\Delta t}{2}} + \frac{1}{\epsilon}\,\frac{\eta_p + \Delta t\frac{d\eta_p}{dt}}{t+\Delta t} + \frac{1}{\epsilon}\int d\psi = 0,$$

where $\int d\psi$ is the change of entropy of the gas per electron on being carried from $(t + \Delta t,\ p + \Delta p)$ to $(t,\ p)$, and may be computed by the ordinary thermodynamic formulas. Now

$$d\psi = \left(\frac{\partial\psi}{\partial t}\right)_p dt + \left(\frac{\partial\psi}{\partial p}\right)_t dp = \frac{C_p}{t}\,dt - \left(\frac{\partial v}{\partial t}\right)_p dp.$$

For a perfect gas, satisfying the equation $pv = kt$,

$$\left(\frac{\partial v}{\partial t}\right)_p = \frac{k}{p},$$

and

$$C_p = \frac{k\gamma}{\gamma - 1},$$

where γ is the ratio of C_p to C_v. Hence

$$\int d\psi = \frac{k\gamma}{\gamma - 1}\int\frac{dt}{t} - k\int\frac{dp}{p}.$$

Substituting in the equation above and taking the limit,

$$\frac{1}{\epsilon}\frac{d}{dt}\left(\frac{\eta_\rho}{t}\right) + \frac{\sigma}{t} - \frac{1}{\epsilon}\cdot\frac{k\gamma}{\gamma - 1}\cdot\frac{1}{t} + \frac{1}{\epsilon}\cdot\frac{k}{p}\cdot\frac{dp}{dt} = 0.$$

But we have already found that

$$\frac{1}{p}\frac{dp}{dt} = \frac{\eta}{kt^2} = \frac{\eta_\rho - \epsilon P_S}{kt^2}.$$

Hence the desired relation

$$\frac{d\eta_\rho}{dt} + \epsilon\sigma - \frac{\epsilon P_S}{t} = \frac{k\gamma}{\gamma - 1}. \tag{28}$$

Instead of this equation Richardson gives

$$\frac{d\varphi}{dt} + \epsilon\sigma = \frac{k}{\gamma - 1}.$$

It differs from that deduced above in the absence of the surface heat. Richardson uses the value of φ as given by this equation to get the thermionic current. His formula checks with experiment, but is of such a form that only very wide changes in the form of φ could be detected. Thus, using the value he gives for φ, there is a factor t^2 in the value of current (formula 17, page 33), but he states later that equally good agreement is obtained if a factor $t^{1/2}$ replaces t^2. Richardson's data do not, therefore, afford a check on his value for φ. The neglect of the surface heat in Richardson's equation would therefore seem to be indefensible, and until the order of the effect is known, we cannot tell whether Richardson's equation is even approximately correct. It is to be noticed that Richardson's formula would become the same as that developed above in case P_S should be proportional to t. The φ of his formula must then be understood to be the change of energy on evaporation at constant surface charge.

We may now obtain further information by applying the first law to the cycle, writing total work done in the complete cycle equal heat absorbed. Work is done in the cycle when the piston is pushed into the right hand chamber, when it is pulled out from the left hand chamber, and when the gas expands in the first of the two processes mentioned above, but no work is done in the second of the two steps. Heat is absorbed in all of the operations. The first law gives

$$\frac{d}{dt}(pv)\Delta t + \int_{t+\Delta t}^{t}\left(\frac{\partial W}{\partial t}\right)_p dt + \int_{p+\Delta p}^{p+\Delta p'}\left(\frac{\partial W}{\partial p}\right)_t dp$$
$$= \frac{d\eta_\rho}{dt}\Delta t + \epsilon\sigma\Delta t + \int_{t+\Delta t}^{t}\left(\frac{\partial Q}{\partial t}\right)_p dt + \int_{p+\Delta p}^{p+\Delta p'}\left(\frac{\partial Q}{\partial p}\right)_t dp - \epsilon\Delta V,$$

where

$$\int_{t+\Delta t}^{t}\left(\frac{\partial W}{\partial t}\right)_p dt = \int_{p+\Delta p}^{t} p\left(\frac{\partial v}{\partial t}\right)_p dt = -k\Delta t,$$

$$\int_{p+\Delta p}^{p+\Delta p'}\left(\frac{\partial W}{\partial p}\right)_t dp = \int_{p+\Delta p}^{p+\Delta p'} p\left(\frac{\partial v}{\partial p}\right)_t dp = \frac{\Delta p - \Delta p'}{n},$$

$$\int_{t+\Delta t}^{t}\left(\frac{\partial Q}{\partial t}\right)_p dt = \int_{t+\Delta t}^{t} c_p dt = \frac{-k\gamma}{\gamma - 1}\Delta t,$$

$$\int_{p+\Delta p}^{p+\Delta p'}\left(\frac{\partial Q}{\partial p}\right)_t dp = -\int_{p+\Delta p}^{p+\Delta p'} t\left(\frac{\partial v}{\partial t}\right)_p dp = \frac{\Delta p - \Delta p'}{n}.$$

Substituting these values, the left-hand side cancels out, leaving,

$$0 = \frac{d\eta_\rho}{dt} + \epsilon\sigma - \frac{k\gamma}{\gamma - 1} - \epsilon\frac{dV}{dt}.$$

But we found that

$$\frac{d\eta_\rho}{dt} + \epsilon\sigma - \frac{k\gamma}{\gamma - 1} = \frac{\epsilon P_S}{t}.$$

Substituting,

$$\frac{dV}{dt} = \frac{P_S}{t}. \tag{29}$$

This equation was also obtained by Lorentz (14) by an entirely different method.

Now dV/dt is the Volta difference per degree between different parts of the same unequally heated metal, provided that free circulation of the electrons from hot to cold through the electron gas is prevented. This is the Volta difference which would be observed at temperatures so low that the emission of electrons is negligible. We have here, therefore, a possible experimental method of detecting the existence of the surface heat P.

At temperatures so high that electron emission is not negligible there is no reason to expect that the free electron vapor is in equilibrium with an unequally heated metal, but there is a possibility that electricity may flow in closed circuits, as shown in Fig. 4, through the electron gas and the metal. I am not aware that the existence of such currents has been detected or suggested. If it should happen that such currents do not exist, we may obtain an additional relation. The electrons spontaneously emitted by different parts of the surface must in this case be of such densities as to be in equilibrium under the potential gradient given by $dV/dt = P_S/t$. This gives, together with (9),

$$\frac{\eta}{kt^2} = -\frac{\epsilon}{kt}\frac{dV}{dt},$$

or

$$\eta_p - \epsilon P_S = -\epsilon P_S,$$

or

$$\eta_p = 0.$$

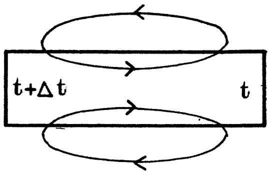

Fig. 4.

Now this condition is almost certainly not satisfied, so that it is exceedingly probable that closed circuits like those indicated do exist in an unequally heated metal.

Having found the value of dV/dt, we may now find the universal value of $d\Sigma_E/dt + \sigma' - P_S/t$ and $dS_E/dt + \sigma'' - P_S/t$. We may obtain the latter immediately by noting that the total change of potential in a closed circuit is zero. This gives

$$\frac{dS_E}{dt} + \sigma'' - \frac{dV}{dt} = 0.$$

Substituting for dV/dt,

$$\frac{dS_E}{dt} + \sigma'' - \frac{P_S}{t} = 0, \qquad (30)$$

the desired relation.

Next to obtain the value of $d\Sigma_E/dt + \sigma' - P_S/t$, we may write down the expression for the total E.M.F. encountered in going from the electron gas surrounding the metal at t, through the metal, to the electron gas at $t + \Delta t$. Our definition of E.M.F. is total change of energy plus work delivered to outside agencies. The change of energy of the electron gas is an intrinsic change ($= k\Delta t$) plus the change of electrostatic energy ($= \epsilon\Delta V$). The work delivered is $d/dt\cdot(pv)\Delta t$. Hence

$$\epsilon\left[\frac{d\Sigma_E}{dt}\Delta t + \sigma'\Delta t\right] = \epsilon\Delta V + k\Delta t + \frac{d}{dt}(pv)\Delta t.$$

Now

$$\frac{d}{dt}(pv)\Delta t = k\Delta t.$$

Hence

$$\frac{d\Sigma_E}{dt} + \sigma' = \frac{dV}{dt} + \frac{2k}{\epsilon},$$

or

$$\frac{d\Sigma_E}{dt} + \sigma' - \frac{P_S}{t} = \frac{2k}{\epsilon}, \tag{31}$$

the desired relation.

It is to be especially emphasized that the form of the formulas just obtained essentially modifies the point of view hitherto maintained. Our position up to this point in this paper has been one of agnosticism; we have been obliged to retain separate expressions for local E.M.F., heat, and potential difference because there seemed no necessity that these should be equal, although such equality is usually assumed. But now the fact that the formulas obtained for

$$\frac{d\eta_\rho}{dt} + \epsilon\sigma - \frac{\epsilon P_S}{t}, \qquad \frac{d\Sigma_E}{dt} + \sigma' - \frac{P_S}{t}, \qquad \text{and} \qquad \frac{dS_E}{dt} + \sigma'' - \frac{P_S}{t}$$

are of different form constitutes positive proof that local E.M.F., heat, and potential difference cannot be mutually equal, and that the assumption of such equality is in general positively incorrect. The assumption can be valid only in certain special cases, as in an electron gas.

Richardson has frequently set local E.M.F. and local heat equal to each other. This is in general incorrect, but will not necessarily lead to error in those processes in which a complete cycle is described.

Accepting now as proved that in general local heat, potential difference, and E.M.F. cannot be mutually equal, we will, in the next section, deduce additional relations between them.

THE GENERALIZED VOLTA LAW OF TENSIONS.

In a complete circuit composed of three metals in equilibrium at uniform temperature we have the following four relations:

$$V_{AB} + V_{BC} + V_{CA} = 0 \tag{32}$$

$$S_{AB} + S_{BC} + S_{CA} = 0 \tag{33}$$

$$\Sigma_{AB} + \Sigma_{BC} + \Sigma_{CA} = 0 \tag{34}$$

$$P_{AB} + P_{BC} + P_{CA} = 0. \tag{35}$$

The first of these is a statement that the total change in electrostatic potential in a closed path outside the metals is zero; the second is the same statement for a closed path within the metals; the third states that the total E.M.F. in a circuit in the metal is zero; and the fourth that the total heat absorbed in a cycle by electricity is zero. The first two are a mathematical consequence of the properties of an electrostatic distribution, and the last two are a consequence of the law of the conservation of energy, because in a system of solids all at one temperature there is no permanent source of energy. It is not possible that these relations should not be satisfied; the system must of necessity so adjust itself that they are.

Of the four relations above, the first is the ordinary Volta law of tensions. The point of the Volta law is not that the laws of electrostatics or of the conservation of energy are satisfied, but that each of the quantities in the above equations, V_{BC} for example, depends only on the two metals B and C, and is unaffected by the presence in the circuit of the third metal A. The proof of this fact is given by experiment.

Of the four equations, the quantities in only two of them, the first and the last, are susceptible of direct observation. It is proved experimentally that P_{BC}, for example, as well as V_{BC}, is independent of the presence in the circuit of the third metal. Therefore the Peltier heats satisfy the same conditions as the Volta difference of potential.

By the "generalized" Volta law of tensions we shall understand the correctness of the four equations above, and in addition a statement that any of the four types of action at the surface of two meals is independent of the presence of a third.

The quantities entering the second and third equations above are not directly measurable, and it is therefore pertinent to inquire whether the generalized Volta law holds; that is, whether S_{BC}, for example, is independent of the presence of A. The answer to this question is yes. Although a direct experimental proof is at present impossible, a theoretical proof may be given, because of certain relations holding between S and Σ and V.

It may be proved mathematically that the ordinary Volta law as partly expressed in the first of the above equations demands that each of the quantities may be split up into two quantities, each depending on only one of the metals at the junction. That is, it is possible to write $V_{BC} = V_C - V_B$, where V_B depends only on the properties of B and V_C only on those of C. This analysis is physically significant because it represents the action at the surface of B and C as the joint result of independent actions by B and C, each unaffected by the presence of the other. The proof of the generalized Volta law will be given by similarly splitting each of the quantities above into the difference of two quantities, each depending only on the properties of one of the metals at the junction.

This analysis is immediately effected from the expression for V_{AB}.

We have

$$\frac{n_A}{n_B} = e^{-(\epsilon V_{BA})/kt}.$$

Whence

$$V_{AB} = \frac{kt}{\epsilon} \log \frac{n_A}{n_B},$$

and we write at once

$$V_{AB} = V_B - V_A,$$

where

$$V_A = -\frac{kt}{\epsilon} \log n_A. \tag{36}$$

It is to be noticed that this analysis is not unique. We might equally write, for example,

$$V_A = -\frac{kt}{\epsilon} \log p_A,$$

which differs from the above by a quantity independent of A, but depending on the temperature.

We may now split up the other quantities with the help of equations (18), (19) and (20).

$$P_{BA} = V_{BA} + \frac{1}{\epsilon}(\eta\rho_B - \eta\rho_A) = P_A - P_B,$$

and

$$\left.\begin{aligned} P_A &= -\frac{kt}{\epsilon} \log n_A - \frac{1}{\epsilon}\eta_{\rho A} \\ S_{BA} &= V_{BA} - S_{AE} + S_{BE} = S_A - S_B, \end{aligned}\right\} \tag{37}$$

and

$$\left.\begin{aligned} S_A &= -\frac{kt}{\epsilon} \log n_A - S_{AE} \\ \Sigma_{BA} &= V_{BA} - \Sigma_{AE} + \Sigma_{BE} = \Sigma_A - \Sigma_B, \end{aligned}\right\} \tag{38}$$

and

$$\Sigma_A = -\frac{kt}{\epsilon} \log n_A - \Sigma_{AE}. \tag{39}$$

With regard to the last two it is to be said that it is mathematically conceivable that S_{AE} and Σ_{AE} should depend on the presence of the other metal, but physically it appears excessively improbable. Granting this assumption, this analysis shows that the generalized Volta law of tensions applies to the unmeasurable quantities S and Σ as well as to V and P.

Instead of the quantity Σ, we may, if we prefer, introduce the intrinsic energy of electricity, u, in the conductor. Taking the energy of a perfect gas to be zero at absolute zero of temperature, we obtain, on applying our definition of impressed E.M.F. between two points

$$\epsilon\Sigma_{AE} = \tfrac{3}{2}kt - \epsilon u_A + \epsilon S_{AE} + kt,$$

whence

$$\Sigma_{AE} = \tfrac{5}{2}kt - u_A + S_{AE}. \tag{40}$$

No simplification of the formulas is obtained on replacing Σ in terms of u. For theoretical discussions of the electron mechanism, however, it may be preferable to make this substitution.

The Effect of Hydrostatic Pressure on the Volta Effect.

The condenser analysis by which the effect of temperature on the Volta effect was determined may be modified to include the effects of hydrostatic pressure. The system of two metals A and B shall be characterized by the following variables.

t = absolute temperature,

ρ = positive charge per unit area on A (as before there is an equal opposite charge on B),

c = capacity per unit area,

π = hydrostatic pressure per unit area on the plate A (the symbol π is used for pressure to avoid confusion with p, the vapor pressure of the electron atmosphere).

There is no essential restriction in discussing the effect of a pressure applied to the plate A alone. After the formulas for this case have been developed, the effect of pressure on B alone may be found simply by interchanging the letters in the analysis, and then the effect of independently variable pressure on both A and B by adding the two effects.

The following dependent variables are to be discussed:

V_{BA} = Volta rise of potential on passing from B to A (see previous discussion for more detailed specification),

u = internal energy of system per unit area,

dW = work done by the system in any infinitesimal change,

dQ = heat absorbed by the system in any infinitesimal change,

v = volume of A per unit area.

Now, as before, we must have $(du + dW)/t$ an exact differential for reversible changes. We have

$$dW = \frac{\partial W}{\partial t}dt + \frac{\partial W}{\partial \rho}d\rho + \frac{\partial W}{\partial c}dc + \frac{\partial W}{\partial \pi}d\pi$$

and

$$du = \frac{\partial u}{\partial t}dt + \frac{\partial u}{\partial \rho}d\rho + \frac{\partial u}{\partial c}dc + \frac{\partial u}{\partial \pi}d\pi.$$

We are able to completely calculate dW from our knowledge of the mechanics of the system. We have

$$\frac{\partial W}{\partial t} = \pi\frac{\partial v}{\partial t},$$

$$\frac{\partial W}{\partial \rho} = -\left(\frac{\rho}{c} - V_{BA}\right) + \pi\frac{\partial v}{\partial \rho},$$

$$\frac{\partial W}{\partial c} = \frac{1}{2}\frac{\rho^2}{c^2} + \pi\frac{\partial v}{\partial c},$$

$$\frac{\partial W}{\partial \pi} = \pi\frac{\partial v}{\partial \pi}.$$

Substituting above,

$$\frac{1}{t}\left\{\left[\pi\frac{\partial v}{\partial t} + \frac{\partial u}{\partial t}\right]dt + \left[\pi\frac{\partial v}{\partial \rho} - \frac{\rho}{c} + V_{BA} + \frac{\partial u}{\partial \rho}\right]d\rho \right.$$
$$\left. + \left[\frac{1}{2}\frac{\rho^2}{c^2} + \pi\frac{\partial v}{\partial \pi} + \frac{\partial u}{\partial c}\right]dc + \left[\pi\frac{\partial v}{\partial \pi} + \frac{\partial u}{\partial \pi}\right]d\pi\right\}$$

must be an exact differential. This will give us six relations between the coefficients of the six possible pairs of differentials.

The work for finding these derivatives is entirely straightforward; only the results need be given here.

From the coefficients of dt and $d\rho$,

$$\frac{\partial V_{BA}}{\partial t} = \frac{1}{t}\frac{\partial Q}{\partial \rho} = \frac{1}{t}P_{BA}'. \tag{41}$$

From the coefficients of dt and dc

$$\frac{\partial Q}{\partial c} = 0. \tag{42}$$

From the coefficients of dt and $d\pi$,

$$\frac{\partial Q}{\partial \pi} = -\tau\frac{\partial v}{\partial t}. \tag{43}$$

From the coefficients of $d\rho$ and dc,

$$\frac{1}{t}\frac{\partial V_{BA}}{\partial c} = 0. \tag{44}$$

From the coefficients of $d\rho$ and $d\pi$,

$$\frac{\partial V_{BA}}{\partial \pi} = -\frac{\partial v}{\partial \rho}. \tag{45}$$

From the coefficients of dc and $d\pi$,

$$\frac{1}{t}\frac{\partial v}{\partial c} = 0. \tag{46}$$

Of these six relations the three which do not involve $d\pi$, (41, 42 and 44) are the same as those obtained by the previous analysis, except that the partial derivatives now involve the condition of constancy of π, a variable which did not enter in the previous work. Of the three remaining relations, 46 states that there is no change of volume on merely changing the distance between the plates, and 43 gives the ordinary thermodynamic relation for the heat absorbed during a change of pressure, it now being necessary to add the conditions of constant ρ and c to the ordinary condition of constant t during change of pressure. The remaining relation, 45, is the only one of the six which gives any essentially new information. This equation expresses the change in Volta difference between two metals, when one is subjected to pressure, in terms of the change of volume of that metal when unit positive charge is imparted to it. This change of volume is not an electrostriction effect, which varies as ρ^2 and depends on the shape of the metals, but is to be thought of as the effective volume of the electrons added or subtracted. There seems to be no experimental evidence for even the order of magnitude of $\partial v/\partial \rho$.

Within the range in which $\partial v/\partial \rho$ may be regarded as constant, this formula gives the Volta contact difference of potential between compressed and uncompressed metal.

$$V_{0\pi} = -\pi\frac{\partial v}{\partial \rho}. \tag{47}$$

The formula

$$\frac{\partial V_{BA}}{\partial \pi} = -\frac{\partial v}{\partial \rho}$$

may also be obtained by considering the effect of hydrostatic pressure in A on the pressure of the electron vapor in equilibrium with it through a stress resisting membrane. The formulas to be applied are well known; they may, for example, be obtained as special cases of formulas which I have given in a previous paper (21). The applicability of such formulas to such conditions as these becomes at least questionable, however, when one calculates that the density of the electron vapor in equilibrium with tungsten at 0° C., for example, is such that there is one electron in a sphere of radius 350 light years. The method of analysis used above makes no reference to the electron gas, and leads to the same results for those quantities not directly concerned with the vapor.

Effect of Pressure on Thermo-electric Properties.

A certain amount of information may now be obtained regarding the effect of pressure on thermo-electric properties other than the Volta effect. This may be obtained from the formulas previously given, taking as the metals A and B the same metal in two states, one without pressure and the other with it. The same double subscript notation as before may be used. Thus $S_{0\pi}$ denotes the potential jump in passing within the metal through the surface separating uncompressed metal from metal compressed to the pressure π.

For the Peltier heat in passing from uncompressed to compressed metal in terms of the E.M.F. of a couple composed of uncompressed and compressed metal, formula 3 gives

$$P_{0\pi} = t\frac{dE_{0\pi}}{dt}. \tag{48}$$

For the difference between the Thomson heats in the compressed and uncompressed metal, formula 4 gives,

$$\sigma_\pi - \sigma_0 = t\frac{d^2E_{0\pi}}{dt^2}. \tag{49}$$

For the effect of pressure on the density of an electron gas in equilibrium with a compressed metal formula 12, combined with formula 47 for the Volta difference of potential between compressed and uncompressed metal, gives

$$\frac{1}{n}\frac{\partial n}{\partial \pi} = \frac{\epsilon}{kt}\frac{\partial v}{\partial \rho}. \tag{50}$$

For the effect of pressure on the latent heat of vaporization of electrons under variable surface charge (total charge on metal and in the gas remaining constant) formula 13 gives

$$\eta_\pi - \eta_0 = \epsilon V_{0\pi} - \epsilon t\frac{dV_{0\pi}}{dt}. \tag{51}$$

For the effect of pressure on the latent heat of vaporization at constant surface charge formula 14 gives

$$\eta_{\rho\pi} - \eta_{\rho 0} = \epsilon(V_{0\pi} - P_{0\pi}). \tag{52}$$

For the effect of pressure on the surface heat, we get from 11 and 51 and 52

$$P_S(\pi) - P_S(0) = t\frac{dV_{0\pi}}{dt} - P_{0\pi}. \tag{53}$$

Of the six quantities treated in the last six equations, the first two, namely the effect of pressure on Peltier and Thomson heats, have been determined experimentally (1) from measurements on a "pressure" thermo-couple. The last four, namely the effect of pressure on electron gas density, the two latent heats, and the surface heat, cannot at present be determined numerically, because they involve the "pressure" Volta effect ($V_{0\pi}$) in addition to the "pressure" Peltier heat ($P_{0\pi}$). A determination of the pressure Volta effect, in addition to present knowledge, would give immediately all four of these quantities. Of course there are relations between the effects of pressure on these four quantities which may be obtained by eliminating $V_{0\pi}$ and $P_{0\pi}$ between the several equations.

In addition to the pressure effects 48–53, we may also obtain expressions for the effect of pressure on the various potential jumps and surface E.M.F.'s, but these can no longer be determined in terms only of $E_{0\pi}$ and $V_{0\pi}$, but involve an actual determination of some potential jump or surface E.M.F., which we are not yet in a position to make.

For the potential jumps, formula 19, gives

$$(S_{\pi E} - S_{0E}) + S_{0\pi} = V_{0\pi}. \tag{54}$$

For the surface E.M.F.'s, formula 20 gives

$$(\Sigma_{\pi E} - \Sigma_{0E}) + \Sigma_{0\pi} = V_{0\pi}. \tag{55}$$

For the Thomson potential gradient, formula 23 gives

$$\sigma_\pi'' - \sigma_0'' = \frac{dS_{0\pi}}{dt} - \frac{dE_{0\pi}}{dt}. \tag{56}$$

For the Thomson E.M.F., formula 21 gives

$$\sigma_\pi' - \sigma_0' = \frac{d\Sigma_{0\pi}}{dt} - \frac{dE_{0\pi}}{dt}. \tag{57}$$

Formulas 28, 30 and 31 give nothing new when applied to pressure effects.

With regard to the quantity $V_{0\pi}$ $(= -\pi\cdot\partial v/\partial\rho)$, we can possibly obtain an idea of the order of magnitude within 100 or 1,000 fold by assuming that all the change of volume on imparting a charge to a metal is the volume of the electrons added. Assuming that the radius of an electron is 1.8×10^{-13}, this gives for a lower limit

$$\frac{\partial v}{\partial \rho} = -1.7 \times 10^{-19} \text{ c.c.}$$

per coulomb. This is so excessively minute that the actual $\partial v/\partial\rho$ is probably forever beyond the reach of direct observation.

In view of the extreme smallness of the probable effect of pressure on the Volta potential difference it is natural to inquire whether we may not neglect this effect in comparison with the directly measurable $P_{0\pi}$, and so obtain an approximate idea of the order of the effect of pressure on the quantities given in equations 50–53. It turns out that this is probably not allowable. The experimental data give for molybdenum, for example, the value 1.5×10^{-18} for the effect of 1 dyne pressure on the Peltier heat. For most metals, the effect is of the order of 10 times greater, or 100 times the volume effect as calculated above from the volume of one coulomb of electrons. In view, however, of the extreme uncertainty in this latter value, I do not believe that a margin of 100 fold is sufficient, and that we would be justified in neglecting the effect of pressure on Volta effect in comparison with that on Peltier heat.

EFFECT OF MELTING OR CHANGE OF STATE ON THE VOLTA POTENTIAL DIFFERENCE AND THERMO-ELECTRIC PHENOMENA.

The Volta difference of potential between a metal in two states of aggregation, as for example solid and liquid, may be found by a slight modification of the preceding condenser analysis. This may be done by choosing for the independent variables t, ρ, c and volume, instead of t, ρ, c and pressure. The details of the work are the same as before. Six differential relations are obtained as before. The only essentially new one of these is

$$\left(\frac{\partial V_{BA}}{\partial v}\right)_{t,\rho,c} = \left(\frac{\partial \pi}{\partial \rho}\right)_{t,c,v}. \qquad (58)$$

If this equation is applied to melting or other change of state, we have the statement that the change in Volta contact difference of potential between B and A when A melts is equal to the change of volume on melting multiplied by the change in the melting pressure of A when unit quantity of electricity is added to the exterior surface of A at constant temperature, volume, and capacity. In virtue of the Volta law of tensions, this becomes, if we denote the two phases by subscripts 1 and 2,

$$V_{21} = (v_1 - v_2)\left(\frac{\partial \pi}{\partial \rho}\right)_{\tau}. \qquad (59)$$

The effect of a surface charge on melting point is one on which there seems to be no experimental evidence. It is not probable that a charge on the surface could change the equilibrium conditions between liquid and solid at points within the metallic mass, for there is no electric field at such points, and there is no real charge on a surface of separation of solid and liquid metal. It is possible, however, that a surface charge should have a surface effect on melting. For instance, the charged surface of a solid metal might possibly melt at a lower temperature than the interior, or conversely, the charged surface of a liquid might solidify at a higher temperature than the interior.

We may obtain partial information as to the effect of a change of state on the other thermo-electric and thermionic quantities by using the subscripts *A* and *B* of the first sections of this paper for the same metal in two different states of aggregation. The work is exactly similar to that of the section on pressure effects, and a series of formulas would be obtained parallel to 48–57.

Very little experimental work has been done in this field. So far as I know there are no measurements of the Volta potential difference between solid and liquid metal, so that there is no way at present of telling the order of magnitude of certain of the quantities in the above equations. Experiments have been made, however, on the thermal E.M.F. of closed circuits in which one of the metals passes through the melting point. There has been considerable disagreement about the facts, but the latest work (22) seems definitely to establish that there is a discontinuous change in the direction of the E.M.F. curve on melting. Attempts have been made to deduce from these data information as to the behavior of the Volta effect, etc., but all such attempts have involved some of the special assumptions about equality of local E.M.F.'s, heats, and potential differences which we are unwilling to admit.

Hitherto the electron theory has been unsuccessful in explaining the effects on melting, in most every case giving the wrong sign to the effect.

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