Electromotive Force of a Thermoelectric Circuit

Editor's Note: this article is based on hand-written notes in the archives of William McFadden-Orr FRS, Professor of Mathematics in the Royal College of Science. CGS unit system is used. The time of drafting is unknown but was probably before 1900. Parts of the document are difficult to read due to fading but no part has been added or amended. Editorial changes are confined to general lay-out and paragraph structures.

Brian Patrick McArdle, The Library, Royal Irish Academy.

Part 1

Thermodynamics enables us to connect the variations in the electromotive forces of a galvanic cell and of a thermoelectric circuit (due to changes of temperature) with heat effects which occur in them. It seems necessary first to define what one means by electromotive force in these cases. Dealing first with the cell suppose the circuit is left open with the metallic connection between the poles not being made. The metals which usually dip into the liquid or liquids of the cell are, of course, different but we will suppose that they are provided with terminals of the same metal. Consider the difference in potential between these terminals. This means e times the work which it would be necessary to do in order to carry the quantity e, supposed small, of electricity from the negative pole to the positive one, the transfers taking place outside the battery. The charge e might be supposed to be on a small detachable piece of one pole which can be carried bodily to the other. The difference of potential may be measured by a quadrant electrometer or any form of potentiometer. In this definition and in the measurement it is immaterial whether the poles remain connected with the battery or are isolated. In the former case during the supposed carriage of e from the negative pole to the positive one an equal quantity would pass through the battery from the positive to the negative but this would not appreciably affect the forces on the moving charge. In the latter case the definition is, of course, is the same as applies to two pieces of metals which have no connection with any battery. The same reading of the measuring instrument will be obtained whether or not the terminals of the cell are of one metal. If the positive is of one metal A and the negative of another B the quantity measured is not the difference of potentials of the poles but the excess of the potential of the positive pole over the that of metal A placed in contact with the negative pole. It is assumed that the whole system is at the same temperature.

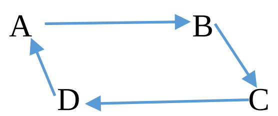
Part 2

The difference of potential as defined above is what is meant by the electromotive force of the cell. It depends on the liquids of the cell and on the metals which dip into them and, to some extent, on the temperature but not on the dimensions of the metals of the terminals. If a current is allowed to pass for some time through a cell and the circuit interrupted and its EMF measured again it is generally found to be less than the original by an amount which depends on the nature of the cell and on the time during which it has been in action. When the circuit is kept open the EMF gradually rises again. More knowledge, experimental or theoretical, of these phenomena is desirable. To simplify matters in what follows that we deal with an ideal cell where measured with the circuit open the EMF remains constant at its original value no matter how long it has been in action. It is necessary to explain how an electric circuit may be made to transverse a cell reversibly under ideal circumstances. The ordinary passage of an electric current is, of course, irreversible. If the system is not in equilibrium the passage of the current is accompanied by a generation of heat (ie temperature rises) unless the system is allowed to give out heat or, in order to maintain the temperature constant, heat must be abstracted. The time rate of such abstraction is equal to the resistance of the circuit multiplied by the square of the strength of the current and was found by Joule. A reversible current with open circuit may be obtained as follows (ref: Parker – thermodynamics treated with elementary mathematics). Let each pole piece be connected by a flexible wire to one of two plates of considerable capacity and with these plates being placed opposite to one another like the plates of a condenser. The wires and plates should be of the same metal as the terminals of the cell. The plates become the terminals. To simplify matters suppose the plates, identical in size and shape are placed parallel and opposite to one another, and altering the distance between the plates by moving one or both a current will pass through the cell. The difference of their potentials remain constant but the capacity of the condenser which they form (ie the charge on either divided by the difference of potential) depends on their relative positions and so, therefore, must the charges. The current may be made to pass in either direction and if we suppose that the motion of the plates takes place indefinitely slowly while the temperature is kept constant we obtain, as a limit, a reversible current of electricity. The system is at any point in equilibrium or indefinitely nearly so; this is not the case when a current flows under ordinary circumstances. And it should be noted that as the speed of motion of the plates diminishes indefinitely so too does the strength of the current and that the rate of generation of Joulean heat, since it is proportional to the square of the strength of the current, diminishes indefinitely compared to the current.

Part 3

The first object of the present discussion is to show that, when a current passes reversibly through a cell as explained above and the temperature of the system remain constant at θ, heat is absorbed according to the equation: $JH = \theta(dV/d\theta)$ where V is the EMF either in electrostatic or electromagnetic units and H is the quantity of heat absorbed (regarded as negative if heat is given out) when unit quantity of electricity passes through the cell from the negative pole to the positive (ie in the same direction as the ordinary current obtained by closing the circuit). This heat must not be confounded with Joules' heat effect already alluded to; H may be of either sign and the rate of absorption or emission of heat expressed by the above equation is proportional to the strength of the current whereas Joules' heat effect always consists, as has been stated already, in the emission of heat and at a rate which is proportional to the square of the current. To obtain the result stated the system will be supposed to undergo a cycle in which the relative positions of the pole plates are varied. We may for convenience suppose that the negative plate is fixed and only the positive moved, but so as to be always parallel and opposite to the negative, that corresponding to every position which it takes up there is a definite position of the flexible wire. The mutual capacity of the plates and the complete state of the system at a given temperature and pressure depend now only on one other co-ordinate and that a co-ordinate of position is the distance between the plates which will be denoted by x.

Let the system now undergo the following Carnot Cycle of ABCD



where the y co-ordinate represents V and the x co-ordinate represents Q as the positive pole plate and the equal negative charge on the negative. The circuit is to be left open throughout.

1. Slowly and reversibly at constant temperature θ bring the positive plate nearer to the negative. By so doing the capacity of the condenser which they constitute is increased and thus, since V remains constant, positive electricity flows, reversibly in the limit, through the cell from the negative plate to the positive. Let the motion terminate after some definite and finite quantity q has passed.
2. Make adiabatically a very small alteration in the distance of the plates. Supposing, as we have supposed, that V is found experimentally to alter with θ, the temperature will be altered in this process. We will at present assume this and justify the assumption afterwards. Therefore, the EMF is altered also; let this new temperature be (θ – dθ) and the new EMF be (V – dV). In this operation there passes through the cell a very small quantity of electricity of the same order of magnitude as dV.
3. Slowly and reversibly at constant temperature (θ – dθ) move the positive plate away from the negative.
4. By making adiabatically the very small change necessary to regain the original position of the positive plate the system recovers its original temperature. The cycle is now complete.

During these processes, in order to keep the system virtually in equilibrium, in addition to the uniform pressure there must be applied from outside to any part of it which is charged forces to balance the electrical attractions on it. We may conveniently suppose that the capacity of the flexible wire is negligible. Thus, we may anticipate that the system does work, positive to negative, on external bodies. In order to obtain the result that we desire we proceed to obtain an expression for this work. In any position of the plates the force between them is, of course, unaffected by the fact that when either moves their charges alter and is also unaffected by the wires.

We suppose that the wires do not exert tension; their sole function being to conduct electricity. The forces on the plates in any position are, in fact, the same as if in that position the wires were severed and the plates became two ordinary charged plates of metal. When the distance between the plates is x and their capacity C the force in question is $1/2V^2dC/dx$ tending to increase x. The force is, of course, one of attraction but the direction of the force is reconciled with this expression through the fact that C decreases as x increases. This formula is well known to students of electrostatics but it may be proved as follows. Since Q=CV it is equivalent to $1/2Q^2C^{-2}dC/dx$ or $-1/2Q^2(dC^{-1}/dx)$. It therefore suffices to show that, if the movable plate passes from a position x1 in which the capacity is C1into another x2 in which it is C2 the work which can be done on external bodies is $1/2Q^2(1/C_1 – 1/C_2)$ since by dividing the work by $(x_2 - x_1)$ and taking the limiting value of the quotient as x diminishes indefinitely one obtains the force. Now the work which the plates could do in this displacement is equal to the of the work which they could do in being discharged in the first position over that which they could do in being discharged in the second, since they might be free from charge in the first position by moving the positive plate to the second position discharging the plates in that position and moving the positive plate back discharged to the first position; for the work done in the last displacement is zero and when dealing as here with conductors of the same metal the work done by electrical forces depends only on the initial and final states of the system and not on its history in the interval. This last statement is true whether or not the temperature varies in the interval and is true also if the system includes conductors of different materials provided the temperature is kept constant. But it is usually not accurate if the system includes conductors of different materials (which may transfer charges to one another) and the temperature is allow to vary. The fact that a current can be caused in a circuit composed of two metals by maintaining the two junctions at different temperatures shows this.

And the work that the plates can do in being discharged is $Q^2/2C$. Suppose they are discharged by carrying in succession exceedingly small quantities of electricity from the positive plate to the negative keeping each fixed and therefore C constant. Set the charge on each and any stage be +/-yQ where y lies between 0 and 1. Since in any given position the difference of potential varies as the charge their difference of potential is consequently yQ/C. If, now, this difference be further decreased by carrying a small quantity $Q(\delta y)$ from the positive to the negative the work which can be done on external bodies is $Q(\delta y)yQ/C$. Thus the work which can be done in discharging the plates completely is $C^{-1}Q^2\int ydy$ between 1 and 0 or $Q^2/2C$. The statement that the repulsive force between the plates is $1/2V^2(dC/dx)$ has been proved.

In this connection the student of electrostatics will recall the following but here again the conductors must be of the same material and at constant temperature. The electrostatic potential energy of the plates means the work that could be done by the electric forces on the plates while they are discharged by the electricity on them being scattered to infinity (but on conductors of the same material and at the given temperature). In this case, since the charges are equal and opposite they may equally be discharged into each other. In any case of two conductors at potentials V_1 and V_2 this energy E is expressible in the form:

$$E = 1/2(q_{11}V_1^2 + 2q_{12}V_1V_2 + q_{22}V_2^2)$$

Where q_{11} and q_{22} are called the coefficients of capacity of the first and second conductors and q_{12} is called their mutual coefficient of induction. These coefficients depend on the dimensions and relative positions of the plates. The charges on the conductors are respectively $(q_{11}V_1 + q_{12}V_2)$ and $(q_{12}V_1 + q_{22}V_2)$. Since in the case under discussion we have $V_2 = V_1 = -V/2$ and $q_{11} = q_{22}$, then

$$E = (q_{11} - q_{12})V_1^2 = (q_{11}-q_{12})V^2/4$$

so that the capacity C is $(q_{11} - q_{12})/2$. If the conductors are moved while their charges are constant the work which they can do is the decrease of electrostatic potential energy. If, on the other hand, they are moved while their potentials are kept constant, which requires electricity to be supplied to them as by a battery, the work which they can do is the increase in electrostatic energy so that while they do work their potential energy increases; the battery or other apparatus for altering their charges supplies energy. And, as a mathematical proposition, the rate of decrease of electrostatic potential energy E with regard to a displacement in a given direction by either conductor (-dE/dx in the present case) obtained on the supposition that the charges remain constant is equal to the rate of increase of E obtained on the supposition that the potentials remain constant; and each is resolved part in that direction of the force which acts on that conductor owing to the charges.

The repulsive force between the plates being $1/2V^2(dC/dx)$ the work which they can do in any displacement or series of displacements $1/2\int V^2dC$ the integral being taken for the displacements considered. Now since $d(V^2C)/du = V^2(dC/du) + C(dV^2/du)$ where u is any quantity on which the functions depend we have

$$V^2C = \int V^2dC + \int Cd(V^2) \quad \underline{\text{or}} \quad \int V^2dC = V^2C - \int Cd(V^2)$$

The last equation is merely a special application of the well-known formula for integration by parts. This is equivalent to the equation:

$$\int V^2dC = V^2C - 2\int CVdV = V^2C - 2\int QdV = V^2C – 2(QV - \int VdQ) = -V^2C + 2\int VdQ$$

so that we may write:

$$1/2\int V^2dC = -1/2V^2C + \int VdQ.$$

For any cycle since V^2C has the same value at last as at first:

$$1/2\int V^2dC = \int VdQ.$$

Thus the work done by the plates in any cycle whatever is $\int VdQ$ taken round the cycle. And, if the cycle is represented by a closed curve in which x corresponds to Q and y to V, this is its area described in the negative direction (clockwise if they are as usual). In the particular case of the Carnot Cycle described above this is qdV. Using the equation:

$$Jd\theta/\theta = \text{work done by the system in the cycle/heat taken in at } \theta$$

$$= qdV/qH \quad \underline{\text{or}} \quad \theta dV/d\theta = JH \qquad (1)$$

where H is the quantity of heat absorbed by the system while unit electricity passes reversibly from the negative plate to the positive through the cell with its circuit open, the temperature being maintained constant and equal to θ.

Part 4

In obtaining this result it was assumed in connection with operations of the Carnot Cycle that an adiabatic change in the capacity of the pole-plates is accompanied by a change in temperature and, therefore, of EMF. The differential coefficient $dV/d\theta$ of the last equation presented itself, in fact, as $(dV/dx)/(d\theta/dx)$ and the argument would be reduced if each of these differential coefficients were zero. The cycle would be replaced by a horizontal straight line described backwards and forwards. In operations electricity does pass through the cell and, if it can be shown that this Carnot takes place at constant temperature without absorption or emission of heat and when it takes place adiabatically, there must be a change of temperature. The discussion above obtains an expression for the amount of heat so absorbed but it assumes that there is an effect in that the passage of electricity at constant temperature is, in fact, accompanied by absorption or emission of heat. It may be shown as follows. Let the system undergo the following reversible cycle at constant pressure and with the circuit open.

1. As in (1) of the former cycle bring the positive plate slowly and reversibly nearer the negative while the finite quantity q of positive electricity passes from the negative plate to the positive, the temperature being kept constant at θ_1.
2. Cool the system from θ_1 to θ_2 moving the positive plate slowly and reversibly and if necessary, as usually will be the case, so that no electricity passes from one plate to the other.

3. Take the positive plate further from the negative while the same quantity q, as in (1) of positive electricity passes slowly and reversibly from the positive plate to the negative keeping the temperature constant at θ_2.
4. Heat the system to θ_1 slowly and reversibly moving the positive plate to its original position. In this operation no electricity will, on the whole, pass through the cell for the final temperature being the same as the initial so, therefore, must also be the electromotive force and, therefore, the positions being the same so too are the charges on the plates.

Now the work done by the system in this cycle is $\int VdQ$ taken round the cycle and this is equal to $q(V_1 - V_2)$ where V_1 is the EMF at θ_1 and V_2 at θ_2. By supposition this is usually not zero since V depends on θ. By the First Law, therefore, the heat taken in by the system Carnot Cycle is zero. And the heat taken in at (4) is equal to that given out in (2). In (4) the system occurs a different position from that in (2) but this makes no difference in its thermal capacity. The only other difference between the states at instants when the temperature is the same in (4) as in (2) is that in (4) the positive plate has a charge of positive electricity and the other plate a charge of negative electricity with each greater by q than in (2). In consequence of this the heat given out by the positive plate alone in (2) is, for most materials, not quite equal to that which it absorbs in (4) for the thermal capacity of a body charged with electricity usually depends slightly on its charge. In fact, electricity has a specific heat (positive or negative) and this specific heat depends on the material of the charged body but the sum of the thermal capacities of equal amounts of positive and negative electricities on bodies of the same material at the same temperature is zero. Otherwise the specific heat of a body without charge would be different according as we consider it uncharged or charged with equal amounts of opposite electricities. Thus the thermal capacity of the whole system in (2) at any temperature is the same as in (4) at the same temperature and the whole heat given out in (4) is equal to that absorbed in (2). If, then, operations (1) and (3) both took place without heat being absorbed or emitted, the system would neither absorb or emit heat in the cycle as a whole and we have seen that this cannot be the case. In one at least of the operations (1) or (3) heat must be taken in or given out. Evidently this will usually be so for both. It must, therefore, be the amount given by equation (1) and can vanish only when $dV/d\theta$ is zero when the temperature is such that V is a maximum or minimum.

Part 5

When an electric current passes through a cell some chemical and physical actions usually occur. It is mainly energy liberated by such action which maintains the current that flows when the circuit is closed. And in addition to equation (1) there are in the ideal cell of constant EMF at constant temperature quantitative laws connecting th EMF with the heat effect of the chemical action and connecting each with the heat given out when a current passes with the circuit closed and the plates fixed. In the circumstances no work is done or on the system and it is a fact of experience that, if the chemical and physical changes are brought about in any other fashion in which work is done by or on the system, the amount of heat given out will be exactly the same. This fact justifies the use of the term heat equivalent of these changes or some similar term. Similar facts and correlated ones relating to systems which do work or have work done on them justify the doctrine of the Conservation of Energy and the First Law of Thermodynamics.

The total heat given out in the flow of electricity around a closed circuit may be said to be the heat equivalent of the chemical and physical changes which accompany it no matter how complicated these changes may be; but this I repeat asserts no more than that, no matter how the system passes from the same initial to the same final state, provided it does no work and has none done on it, the heat which it gives out is always the same.

Let the ideal cell be one of Daniell type to take a definite example. Suppose that after the passage of a quantity e of electricity through the cell with closed circuit at temperature θ and pressure P the only changes which can be detected are that:

1. a quantity ez of zinc disappears from the positive plate and the quantity of zinc which exists as zinc sulphate is increased by ez where z is a quantity found to be constant in such experiments and called the electrochemical equivalent of zinc;
2. a quantity of copper ec is deposited on the negative pole while the quantity of copper sulphate is decreased by the equivalent amount.

An important test which must be satisfied in order that one would be justified in asserting that the above are the only changes is that V should remain unaltered and it has been supposed already that this is the case. The heat that would be given out in these changes supposed to take place at θ and P whether so described above or in any other manner which affects external bodies in no other way than by giving heat to them may be denoted by eΓ. It may be that there does not readily occur any other convenient way of causing these changes so as to obtain an independent value of Γ. We may however write $\Gamma = (\Gamma_z - \Gamma_c)$ where Γ_z is the heat that would be given out by the dissolution of the quantity z of zinc in sulphuric acid, thus forming zinc sulphide and liberating hydrogen. And Γc is the heat that would be given out by the dissolution of the quantity c of copper in sulphuric acid, thus forming cupric sulphate and liberating an equal amount of hydrogen. Both reactions take place at θ and P and these quantities of heat may readily be measured. The other quantitative law additional to equation (1) is that expressed by the equation:

$$J\Gamma = V - \theta(dV/d\theta) \qquad (2)$$

the units being either electrostatic and P or electromagnetic. At one time it was supposed that the equation is simply JΓ = V. The correct form was given by Helmholtz, by Gibbs and by Parker. In order to establish equation (2) consider the following irreversible cycle at θ.

1. Set a quantity of electricity e to pass round the cell with circuit closed and the plate fixed.
2. Open the circuit and move the positive plate further from the negative until a quantity e of electricity passes (reversibly) through the cell in the opposite direction. Assume that in this ideal cell the only changes which occur in 2 are that the chemical changes described in (1) and (2) are reversed, that the position of the positive plate is altered and that the charge on it is decreased by e while the negative charge on the negative plate is also decreased by e. In order to complete the cycle of operations it is still necessary to bring the positive plate back into the first position and, unless we are further to complicate the argument, this must be done without passing current through the cell.
3. Let us move the positive plate slowly to the original position. Suppose that as this is being done equal and opposite quantities of positive and negative changes are brought from infinity in exceedingly small amounts and discharged on the plates so that each is maintained at constant potential without any electricity passing through the cell. The cycle is now complete.

By the First Law the heat which is given out in 1 is ($e\Gamma_z - e\Gamma_c$) or $e\Gamma$; the heat given out in 2 is $e\theta(dV/d\theta)$ as has been proved; no heat is given out in 3. Thus the heat given out in the cycle is $[e\Gamma+e\theta(dV/d\theta)]$.

Considering, now, the work done on the system, the constant pressure does zero work in any cycle. The work done on the system against electrical forces in 1 is zero since the plates do not move and the work done on the system against these forces in 2 is annulled by the work which the attraction between the plates enables the system to do in 3. The amount of this work is now required. It is, however, $-0.5\int V^2 dC$ between 2 and 1 where the suffix 1 refers to the original state and the suffix 2 to the state after 2. But in 3 a quantity e of positive electricity is brought from an infinite distance to the positive plate and an equal quantity of negative to the negative plate, the difference of potential between the plates being V. This requires work eV to be done on the system. The same work would be necessary if the electricity, instead of being brought from infinity, is simply separated inside some body in the neighbourhood. Thus we obtain the equation:

$$eJ\Gamma + e\theta(dV/d\theta) = eV$$

$$J\Gamma = V - \theta(dV/d\theta) \qquad (2)$$

This is with electrostatic or electromagnetic units. If, however, the quantity of electricity is measured in coulombs and V in volts it becomes $10^{-7}J\Gamma = V - \theta(dV/d\theta)$ and (1) similarly becomes $10^{-7}JH = \theta(dV/d\theta)$. Equation (2) was verified very satisfactorily for cells of various types by Jahn in 1886.

Part 6

It was discovered by Seebeck in 1821 that, if a circuit consists of two metals and one of the junctions is hotter than the other, an electric current is generated in the circuit; its direction depends on the metals and also on the temperatures of the junctions only. Peltier discovered in 1834 that, when an electric current crosses a junction of two metals, in addition to the heat which the current generates throughout the circuit according to Joule's Law, there is usually an absorption or liberation of heat at the junction; the amount being for given metals and a given temperature proportional to the quantity of electricity which flows. And in 1851 Lord Kelvin showed that also when a current traverses a metal whose temperature varies from point to point heat is usually absorbed or liberated throughout. Its amount, again, for a given metal and a given length, whose ends are kept at given temperatures, being proportional to the quantity of electricity which flows. This may be expressed by the statement that electricity has a specific heat, positive or negative; thia specific heat is different for different metals and it is reasonable to suppose that it varies with the temperature.

Thermodynamics enables us to connect not quite satisfactorily the Peltier and the Thomson effects, as they are respectively called, with the EMF of the circuit and with each other. This is my personal object. If the metals are denoted A and B (antimony and bismuth form a good example) we will suppose that when the circuit is closed the current flows from B to A across the hot junction. The electromotive force V is defined in a manner analogous to that of the voltaic cell. A gap is made in made in one of the metals (say A) and the two ends are kept at any but the same temperatures. The EMF of the circuit means that the difference of potential of these ends (e^{-1} times the work necessary to carry a small quantity e of positive electricity across the gap from the side adjoining the cold junction to that adjoining the hot.

If plates of the metal A are connected by flexible wires of A to the sides of the gap, by moving one or both with the circuit open a current may be made to pass as slowly as we please and in either direction as with the voltaic cell discussed above. But, unlike that case, this process is not completely reversible even in the limit. Owing to the differences in temperatures heat is conducted from the hot junction towards the cold and this effect cannot, of course, be reversed by reversing the motion of the pole plates. Also, the more nearly reversible are the conditions of the current (ie the more nearly is there electrical equilibrium at every instant) the slower is the motion of the plates and the longer the time required for the transfer of a given quantity of electricity and, therefore, the greater the effect of this heat conduction during the transfer. And we cannot evade this difficulty by supposing the metal to be an absolute non-conductor of heat. For there is reason to consider that the terms 'absolute non-conductor of heat' and 'conductor of electricity' are mutually contradictory. In the case of metals theory connects the two conductivities and, indeed, infers that the ration of the thermal to electrical is the same for all metals at the same temperature and varies directly as the absolute temperature, results that are true in most cases to a rough order of approximation. Heat conduction through metals is attributed chiefly to the free electrons (which are negative). These electrons, whether or not in the neighbourhood of a particular point, have a general velocity of drift which would constitute an electric current possess velocities of agitation in all directions. The average kinetic energy of an electron due to this velocity of agitation is, chiefly for theoretical reasons, believed to be proportional to the absolute temperature. These electrons diffuse in all directions. This diffusion and also collisions between them and the molecules (nearly stationary) gradually diffuse kinetic energy of agitation or heat from places of higher temperature to places of lower. And the electric current in metals consists (chiefly at any rate) of electrons having, in addition to their motion of agitation, an average drift in the opposite direction to that of the EMF. Thus low conductivity of heat requires a body with few free electrons and, therefore, low conductivity of electricity.

When a current passes in a thermoelectric circuit the temperature of which is kept at each point constant as regards time but, of course, varying from point to point the heat which is given out involves, as we have seen, four terms. One represents the Joule heating effect; this is always positive and proportional to the square of the current strength; two others represent respectively the Peltier and Thomson effects of which the former exists at the junctions only; each of these may be of either sign and is proportional to the current; the fourth represents the effect of heat conduction along the circuit and is independent of the current. When the circuit is open we can, as with the voltaic cell, make the first negligible compared with the second and third by supposing the motion of the pole plate to be indefinitely slow; the fourth term, however, becomes the most important of all. It appears to be the case that, even with currents so small that the first term is negligible with the second and the fourth term also is very small compared with the second and third. Thermodynamics, up to the present, has deduced very few, if any, quantitative results wherever it is necessary to apply the Second Law to irreversible cycles. So the usual investigation neglects the fourth term altogether or rather considers that, if we corrected observed values of the Peltier Effect and Thomson Effect for the effects of heat conduction, we may use the same equations for the corrected values as would hold for a very slow current with open circuit as reversible. And on this unsatisfactory basis I proceed.

We consider a cycle in which a current passes with circuit open and, as just stated, we ignore or allow for the irreversible conduction of heat in the metals but, as the Thomson Effect liberates or absorbs heat at all temperatures which occur we cannot have a cycle so simple as one of the Carnot type, for that would allow the system to interchange heat with external bodies at two different temperatures only. A suitable cycle is as follows: the temperature of each part being kept constant and the pressure constant and uniform.

1. Slowly move the positive plate from the negative until a quantity e of electricity has passed from the positive plate to the negative.
2. Move the plate slowly back to its original position but, instead of allowing the quantity e of electricity to pass back through the wires, maintain the system in electric equilibrium by bringing from a very great distance equal and opposite quantities of electricity in exceedingly small amounts and discharging them on the plates. The total amount of each so brought will, of course, be e. This completes the cycle.

The work done on the system by the constant pressure is zero in the cycle and, as regards electrical forces, the work done on the system in (1) is annulled by the work which the moving plate does in (2); but in (2) work of amount eV is done on the system in bringing the charges from infinity. This, then, by the First Law must be the equivalent of the heat given out in the cycle. I use the symbol ${}_BP_A(\theta)$ to denote the absorbed at a junction of two metals A and B at temperature θ while unit quantity of electricity crosses from B to A. I use the term $\sigma_A(\theta)$ to denote the specific heat of electricity in the metal A at θ. In other words the limiting value as δθ diminishes indefinitely of $(\delta\theta)^{-1}$ times the heat (positive or negative) which must be given to a piece of metal A at θ in the circuit to keep the temperature unaltered while unit quantity of electricity flows into it very slowly from another piece of A which is at temperature (θ – δθ) and, if necessary, corrected for the corresponding quantity due to heat conduction. The specific heat of electricity in A is $-\sigma_A(\theta)$. Let θ_1 denote the temperature of the hot junction and θ_2 of the cold. In the first process of the cycle, remembering that electricity passes from A to B across the hot junction, the system gives out heat of amount algebraically equal to $e\left\{{}_BP_A(\theta_1) - {}_BP_A(\theta_2) - \int\sigma_A(\theta)d(\theta) + \int\sigma_B(\theta)d\theta\right\}$ between θ_1 and θ_2. Thus we obtain the equation:

$${}_BP_A(\theta_1) - {}_BP_A(\theta_2) - \int\left\{\sigma_A(\theta) - \sigma_B(\theta)\right\}d(\theta) = J^{-1}V \qquad (1)$$

Now V depends on θ_1 and θ_2 as well as on the metals and it must be of the form $[F(\theta_1) - F(\theta_2)]$ with the form of F depending on the metals. In other words, if $\theta_1>\theta_2>\theta_3$ and if V_{12} denote the EMF in a circuit whose junctions are at θ_1 and θ_2, the current with closed circuit being from B to A across the hotter, then keeping to the same two metals

$$(V_{12} + V_{23}) = V_{13}. \qquad (2)$$

I think the most satisfactory proof of this is experimental. We may see, however, that if equation (2) were untrue the three equations of type (1) for the three circuits would be inconsistent. Assume that σ for a given metal and ${}_BP_A$ for given metals depend only on the temperature at the plate. We might also connect equation (2) with the experimental fact that a current cannot be caused to flow in a circuit composed of a single metal by heating it unequally but as it does not seem easy to make this connection quite satisfactorily I do not pursue the matter. If we now differentiate equation (1) with respect to θ_1 and afterwards omit the suffice 1 we have

$$d({}_BP_A(\theta))/d\theta - \sigma_A(\theta) + \sigma_B(\theta) = J^{-1}(dV/d\theta) \qquad (3)$$

and in this the right hand member depends only on the metals and θ but not at all on the temperature of the other junction, the colder. Also neglecting as we do the irreversible transfer of heat along the circuit by conduction and treating the cycle as reversible, Clausius' Theorem for reversible cycles gives:

$${}_BP_A(\theta_1)/\theta_1 - {}_BP_A(\theta_2)/\theta_2 - \int \left\{ \left[\sigma_A(\theta) - \sigma_B(\theta) \right] / \theta \right\} d\theta = 0 \qquad (4)$$

Differentiating this with respect to θ_1 and omitting the suffice 1 we have:

$$d({}_BP_A(\theta)/\theta)/d\theta = (\sigma_A(\theta) - \sigma_B(\theta))/\theta \qquad (5)$$

<u>or</u>

$$\theta^{-1}d({}_BP_A(\theta))/d\theta - \theta^{-2}{}_BP_A(\theta) = \theta^{-1}\{\sigma_A(\theta) - \sigma_B(\theta)\} \qquad (6)$$

and using equation (3) we deduce:

$${}_BP_A(\theta) = J^{-1}\theta(dV/d\theta) \qquad (7)$$

and this enables us to replace (5) by:

$$\sigma_A(\theta) - \sigma_B(\theta) = J^{-1}\theta(d^2V/d\theta^2). \qquad (8)$$

These important equations (7) and (8) are in their simplest forms. These units may be either electrostatic or electromagnetic. If, however, the derived electromagnetic units are used they become:

$${}_BP_A(\theta) = 10^7J^{-1}\theta(dV/d\theta) \qquad (9)$$

$$\sigma_A(\theta) - \sigma_B(\theta) = 10^7J^{-1}\theta(d^2V/d\theta^2). \qquad (10)$$

Of these equations (9) has been verified satisfactorily in most cases and, although in the case of (10) the agreement between values obtained for the two sides is not very good the discrepancy probably lies within the limits of experimental error, having regard to the nature and magnitudes of the quantities involved.

<u>Part 7</u>

It may be noted that the heat absorbed in the galvanic cell is analogous to the Peltier Effect; it is, indeed, sometimes stated that it is due to Peltier effects at the surfaces between the metals and the liquids.

It seems of interest to see how the recognition of the Peltier Effect and Thomson Effect modify the expression for the energy and the entropy of a system changed with electricity and to trace the connection between the expressions. In a non-electrified system at rest and consisting of a number of phases (or a single phase) each of which is under uniform pressure and of uniform temperature (though these may differ from phase to phase), the energy can be expressed in terms of these pressures and temperatures and other co-ordinates which express the constitution and amount of each phase. When the system contains electric charges at rest, to obtain the energy we must add to the above expression the electrostatic potential energy (ie the work which can be obtained in carrying the charges to some standard position which is usually taken to be infinity). Supposing that the medium surrounding the conductors is air or simply the aether of space this electrostatic potential energy is under certain conditions of the form $\sum\sum ee^1/r$ where e and e^1 are two charges supposed to occupy an exceedingly small volume and r is the distance between them. (The summation is taken for every pair of charges in the system. The sum $\sum e^1/r$ where r is the distance of a charge e^1 from a particular point is the electrostatic potential V at that point; so $\sum\sum ee^1/r$ may be written in the form $0.5\sum eV$ with V being the potential at the point occupied by the charge e; the 0.5 occurs because in $\sum eV$ each term ee^1/r occurs twice.) If such transfers are contemplated other terms must be included in the expression for the energy; the Peltier Effect and the Thomson Effect demand this. These additional terms are of the form $\sum\sum e_A F_A(\theta)$ where e_A denotes a charge on a metal A at a temperature θ and $F_A(\theta)$ is a function which depends on A and θ; summation is to be taken for the different metals and different temperatures. Thus the complete expression for the energy E may be written in either of the forms:

$$E = E_0 + \sum\sum ee^1/r + \sum\sum e_A F_A(\theta) \quad (1)$$

$$E = E_0 + 0.5\sum\sum e_A V_A + \sum\sum e_A F_A(\theta) \quad (2)$$

where E_0 denotes the energy which the system would have at the same temperatures and pressures but uncharged and VA denotes the potential of metal A, the sign of double summation denoting summation for all conductors and all temperatures.

Similarly the expression for the entropy is of the form:

$$\xi = \xi_0 + \sum\sum e_A \xi_A(\theta) \quad (3)$$

where ξ_0 is the entropy of the system at the same pressures and temperatures but without charge. It will be noticed that potential at a point is still taken as $\sum e^1/r$ at the point considered without any reference to the nature of the conductor. This is not inconsistent with the existence of two finite difference of potential between two metallic surfaces in close contact. Such a difference does not in reality require two different values of potential at the same point. We may and usually do explain this difference by supposing that the layer between the materials is polarized (ie there is a positive charge on the surface on one metal and a negative on the other). This would cause a finite change in potential in an exceedingly small distance, just as the potential of a thin magnetic shell experiences a finite alteration at the point at which it is measured passes through the shell.

The above modified forms of E and ξ were given by Helmholtz, Duhem and Parker. Suppose, now, that a portion of A which carries a charge e_A has its temperature raised from θ to (θ+δθ). To simplify matters we ignore any charge in its dimensions and, therefore, any change in the terms $\sum\sum ee^1/r$ or their equivalent $0.5\sum\sum e_A V_A$ due to change of r. Thus the increase in energy is $[\delta E_0 + e_A \delta F_A(\theta)]$ where δE_0 is the increase of energy which would accompany the same rise of temperature in the absence of electric charge. As the work done against against pressure is the same whether charged or uncharged we see that $e_A \delta F_A(\theta)$ denotes the additional heat taken in consequence of the charge e_A. Thus, by supposing δθ diminishes indefinitely we have:

$$\sigma_A(\theta) = dFA(\theta)/d\theta. \quad (4)$$

Again since the heat taken in under the same circumstances use θδξ we easily obtain:

$$\sigma_A(\theta) = \theta\left\{d\xi_A(\theta)/\, d\theta\right\}. \quad (5)$$

Also since the heat taken-in in a reversible transfer across a junction is θ multiplied by the accompanying increase in entropy we have:

$$_BP_A(\theta) = \theta\left\{\xi_A(\theta) - \xi_B(\theta)\right\}. \quad (6)$$

Returning again to the *Contact Difference of Potential* between terminals A and B in the sense of the potential of A minus the potential of B it may, as in previous analogous cases, be defined as the limit when e diminishes indefinitely of e^{-1} times the work necessary to carry a small charge from B to A when they are in contact and in electrical equilibrium. [The student may possibly have difficulty in realizing that electricity can be in equilibrium on A in contact with B if work can be done by its passage from B to A. The writer at any rate has felt this a difficulty. It must be borne in mind, however, that the system may exchange heat as well as work with external bodies and this makes the conditions of equilibrium more complicated. Ordinary Dynamics is not Thermodynamics. The conditions of equilibrium is not, in fact, that no work can be gained by a transfer of electricity, nor again that no energy can be lost but may be expressed by stating that a transfer makes no alteration in which is technically called the *Thermodynamic Potential*. This, however, constitutes no explanation of the difficulty, if there is one. The ultimate fact appears to be that, in equilibrium, the transfer in one direction gives out less heat and in the other absorbs more than when there is no equilibrium. The system is somewhat analogous to one which consists of a liquid and its vapour; these can co-exist in equilibrium though work would be done if the liquid wholly evaporates.] And the difference is equally the excess of $\sum e^1/r$ at a point in A over the similar sum at a point in B when A and B are in contact and in equilibrium.

In equilibrium the transfer of the small quantity e from B to A being reversible we have for such a transfer:

θ x Increase of Entropy = Heat taken-in
= Increase of Energy – J^{-1} x Work done by systems

<u>or</u>

$$\theta\left\{\xi A(\theta) - \xi B(\theta)\right\} = F_A(\theta) - F_B(\theta) - J^{-1}(V_B - V_A)$$

<u>or</u>

$$J^{-1}(V_A - V_B) = F_B(\theta) - F_A(\theta) - \theta\xi_B(\theta) + \theta\xi_A(\theta) \quad (7)$$

It may be well to emphasize that this holds only for the equilibrium difference of potential, also to point out that, though this equation indicates a definite value for the equilibrium difference at θ, either potential may have any value whatever. Differentiating with respect to θ and using equations (4) and (5) and their analogues for B we obtain:

$$J^{-1}\left\{d(V_A\text{-}V_B)/d\theta\right\} = \xi_A(\theta) - \xi_B(\theta) \quad (8)$$

and using equation (6) gives:

$$J^{-1}\left\{d(V_A-V_B)/d\theta\right\} = \theta^{-1}{}_B P_A(\theta) \quad (9)$$

which is identical with equation (7) where the V in that equation (ie the EMF of the circuit there discussed) is identical with $\left\{(V_A-V_B) \text{ at } \theta_1 - (V_A-V_B) \text{ at } \theta_2\right\}$. Summing up results we have the important equations:

$$J^{-1}\left\{d(\text{EMF of Circuit})/d\theta_1\right\} = \theta_1^{-1}{}_B P_A(\theta_1) = \xi_A(\theta_1) - \xi_B(\theta_1)$$

$$J^{-1}\left\{d^2(\text{EMF of Circuit})/d\theta_1^2\right\} = d\left\{\theta_1^{-1}{}_B P_A(\theta_1)\right\}/d\theta_1 = d\left\{\xi_A(\theta_1) - \xi_B(\theta_1)\right\}/d\theta_1$$

$$= \theta_1^{-1}\left\{F_A(\theta_1) - F_B(\theta_1)\right\} = \theta_1^{-1}\left\{\sigma_A(\theta_1) - \sigma_B(\theta_1)\right\}$$