Thermodynamics and Electromagnetic Force of a Voltaic Cell

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.

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Part 1

Thermodynamics enables us to connect variations in the electromagnetic force of a voltaic cell and a thermoelectric circuit (due to changes of temperature with heat effects) and to obtain similar relations in connection with the *electromagnetic fore of contact* or *potential difference of contact* between metals.

It seems desirable, however, first to allude to some elementary points in electrostatics. We regard it as proved experimentally that like electricities repel and unlike attract each other (or rather the material bodies on which these charges exist) with a force which is directly proportional to the product of charges and inversely to the square of the distance between them. If units are chosen properly (i.e. electrostatic units) the repulsion between two charges q and q^1 at a distance r is qq^1/r^2. If the charge q^1 moves from a point P which is at a distance r_p from q, supposed fixed, to another Q which is at a distance r_q from q, the work which must be done is algebraically $-qq^1\int r^{-2}dr$ or $qq^1(r_q^{-1} - r_p^{-1})$. When there are several fixed charges q the corresponding amount of work on q^1 is $q^1\sum q/r_q - q^1\sum q/r_p$ where summation is taken for each charge q and r_p denoting its distance from P and r_q its distance from Q. The number of charges q in any case is really infinite and each is infinitely small so that the sums in this expression are really integrals. The coefficient of q^1 in the first term $\sum q/r_q$ or $\int dq/r_q$ is called the electrostatic potential at Q and the corresponding coefficient in the second term is the electrostatic potential at P. Thus, the potential at Q minus the potential at P may be equally defined as the work done against electrical forces in carrying a unit positive charge from P to Q. The other charges must be supposed fixed or their units so small that their motion does not seriously affect their distribution. The above difference of potential is also called the ***Electromotive Force*** from Q to P. The above statement as to the law of force and, therefore, its mathematical consequences may be taken as correct even when the conductors are separated not by air or a vacuum but by a dielectric whose specific inductive capacity is no longer unity. In this case the electric force produces separation of positive from negative electricity (or polarisation as it is called) inside the molecules of the dielectric and, in determining the force that acts on any charged body, this polarisation and the force due to it must be taken into account. <u>The electric force in any direction on a unit positive charge at any point is the rate of decrease of potential in that direction.</u>

In the usual discussion of electrostatics inside the material of a conductor, the electricity is regarded as free to move under the influence of electric forces alone. Consequently, in a state of electric equilibrium there can be no electric force at any point in the body of a conductor and, therefore, the potential is the same at all points.in the material or on its surface. The value is called the potential of the conductor and leads mathematically to the result that the outer charge is on the surface. If we have two conductors (A and B) we may define the potential of B minus the potential of A to mean $\sum q/r_B$ - $\sum q/r_A$ where r_B is the distance of a charge q from some point in or on B with summation being taken for all charges for the first term and similarly for the second term. We may equally define it as the limit as e decreases indefinitely by e^{-1} times the work which must be done in order to carry a charge e from A to B. However, there are certain phenomena which show that when conductors are not all of one metal (and this includes a case where a conductor is not all of one homogeneous metal) or at the same temperature some modifications must be made in the preceding statements; that even in a conductor electricity is not quite free to move under electric attractions and repulsions.

Part 2

One of the phenomena from Part 1 is the fundamental fact of the generation of electricity between dry metals in contact (first observed by Volta). Two metals, for example zinc and copper, so long as they are in contact may have on the whole no charge of electricity but, when they are separated each is found to be charged – zinc positively and copper negatively. This is best shown by taking two flat discs – one of each metal and placing one on top of the other and, when pulled apart, if either is connected to the leaves of an electroscope it is shown to be charged. This is not the case, sensibly, for discs of the same metal. We, of course, infer that when the discs are in contact before being separated they are charged, zinc positively and copper negatively, with equal and opposite amounts of electricity. Now it would be impossible for these charges to be in equilibrium if the only forces acting on them were their mutual attractions and repulsions accordingly to the usually accepted law of inverse square of the distance. The opposing electricities would attract one another and the plates would discharge each other just as two plates of the same metal charged with equal and opposite amounts would do. The law of electrical force is modified in such cases or the electricity is acted on by other forces besides electrical ones. It is, of course, universally accepted that electricity is carried by exceeding minute corpuscular called electrons and it is supposed that these are subject to other forces than electrical. We can suppose that in the interior of any homogeneous metal these additional forces are themselves in equilibrium so that those due to electricity according to the unmodified law of inverse square are also so but that in in a layer near the surface this is not the case and that the electrons are in equilibrium under the joint influence of these other forces and electrical forces. (Such a statement cannot be made of any individual electron but must refer only to an average over an immense number. We consider that electrons are mobile and flying in all directions like molecules of a gas.) Mathematical attempts to explain contact difference of potential lead to the notion of a pressure acting on electrons that are the chief carriers of electricity. In a region in which this pressure is uniform it has no effect on electrons and they are forced to obey electric forces; but in a space in which the pressure is not uniform its effect can compensate out electric forces. We will adopt the view that electric forces obey the orthodox law but that electrons may be acted on by other forces. For the present purpose it is not necessary to understand the precise nature and origin of these non-electrical forces as they may be termed. (The idea of an electron becoming involved in a collision with another involves some modification of the law of force between electrons at very short distances.)

Part 3

Defining potential at a point as $\sum q/r$ where r is the distance of the point from a charge q we are led to the view that in electrical equilibrium, when no currents are passing, while it is very nearly true that te potential at all points in a given conductor has the same value, it need not and indeed in some cases cannot be accurately so. And we can no longer say without qualification that in equilibrium the difference of potential between two conductors or between two points is the work necessary to carry a unit charge from one to the other and meaning that the work must be done by some agent outside the system. We might alter the statement to a similar one about the work done against electrical forces. In the case of two metals in contact, when in electrical equilibrium electricity (ie electrons) can pass from one to the other without any work being done or by external bodies. The work done against or by electrical forces is being done by or against some other force or forces internal to the system. This is clear on considering that electrons are in equilibrium under electric forces. It is to be noted that in these cases difference of potential is not a quantity that lends itself easily to measurement and this constitutes one of the great difficulties of the subject. Also, variation of potential in the body of a conductor can be shown mathematically to require the existence of charges in the body; so we are led to the view that it is not necessary that the whole charge on the conductor should be on its surface. It should be realized that in electric equilibrium no ordinary method will detect such differences of potential between points which are connected by a conductor. For example, if the zinc and copper discs are in contact and one is connected to the leaves of an electroscope no sensible divergence is produced. If they are connected by copper wires, one to the fixed copper quadrants and the other to the insulated copper of a quadrant electroscope, no difference of potential can be measured. This is explained if we note that the zinc is now doubly connected to copper (ie to the copper disc and to the copper wire). If we assume that there is a definite difference of potential between zinc and copper in contact the movable and fixed quadrants will be at the same potential. And no current is obtained by voltaic forces round a closed circuit of conductors at a uniform temperature. The fundamental experimental fact is that when the zinc and copper discs are separated each is found to be charged.

Part 4

Before proceeding further with a discussion of Volta's contact difference of potential it seems necessary to mention another phenomena. It was discovered by Seeback in 1821 that, if a circuit consists of two metals and one junction is hotter than the other, an electric current is generated in the circuit; its direction depends on the metals and on the temperatures of the junctions but of the junctions only. If the metals are zinc and copper the current (ie electrons) flows from copper to zinc across the hot junction. If the current is interrupted by making a gap (eg in the copper) somewhere between the junctions and the ends are kept at the same temperature electricity tends to pass across this section. If the ends are connected to an electroscope or other form of potentiometer observation shows these ends are at different potentials that can be measured in the usual way. But although we regard this as proved by observation it should be realized that, as in the vast majority of measurements, there is a long chain of inferences connecting what we usually observe with what we say we have measured. It is a more immediate inference that the ends are charged with opposite electricities than that they are at different potentials. We have introduced already the idea that forces other than electrical may act on electricity (ie electrons) but we see reason why such forces should urge electricity from one to the other of two pieces of the same metal at the same temperature. We accordingly consider that the only forces acting on the charges at the ends of the gap are electrical attractions and repulsions of the ordinary type; if so, they are at different potentials. And it is the limit as e decreases indefinitely of e^{-1} times the work which must be done by internal forces in order to carry the quantity e across the gap from the negative side of the interrupted circuit to the positive side (or to the metal of the instrument in equilibrium with it). This is true independently of our notions as to contact differences of potential. Suppose for simplicity that a potentiometer is all of one metal that is uniform and of uniform temperature. We assume that the quantity measured is the difference of potential of the two points considered and, assuming further that the difference of potential at the two junctions between the copper and the metal of the potentiometer are the same, it is equally the difference of potential between the two ends of the gap.

From the existence of a current or of an electromotive force in such a circuit we may draw the following general inferences as to potential. In electrical equilibrium between 2 metals A and B at a temperature θ_1 there is a difference of potential. I shall use ${}^{A}S_{B}(\theta_1)$ to denote the excess of potential of A over B. We must be prepared to consider the question whether, in a mass of unequally heated homogeneous metal A, there may be differences of potential. It will be shown that an informative answer to this question fits in with more complicated laws of electrical contact than does a negative. But admitting the possibility of such potential difference let ${}^{1}S_{2}(A)$ denote the excess of potential at a place in the metal A where the temperature is θ_1 over the potential at a place where the temperature is θ_2, then ${}^{A}S_{B}(\theta_1) + {}^{1}S_{2}(A) + {}^{B}S_{A}(\theta_2) + {}^{2}S_{1}(B)$ or its equivalent ${}^{A}S_{B}(\theta_1) + {}^{1}S_{2}(A) - {}^{A}S_{B}(\theta_2) - {}^{1}S_{2}(B)$ is not equal to zero; its value is the electromotive force of the circuit. Experiment shows that there is no current and no electromotive force in any closed circuit of dry metals at a uniform temperature. We infer equations of the type ${}^{A}S_{B}(\theta_1) + {}^{B}S_{C}(\theta_1) = {}^{A}S_{C}(\theta_1)$ which we may write in the form ${}^{A}S_{B}(\theta_1) = {}^{A}S^{1}(\theta_1) - {}^{B}S^{1}(\theta_1)$ where S^1 is some other function. Experiment also shows that there is no current in any closed circuit of one unequally heated metal and so, we infer equations of the type ${}^{1}S_{2}(A) + {}^{2}S_{3}(A) = {}^{1}S_{3}(A)$.

Part 5

Now there is good reason, as will to some extent be explained, for believing that Volta's difference of potential is very different and much greater than that inferred from Seebeck's discovery. Volta's is of the order of a volt and the other is perhaps one thousand of a volt. Much more knowledge, both experimental and theoretical, is desirable on the subject. At present it seems reasonable to suppose, as Lord Kelvin does, all the surface of a metal is at the same potential and that all points well in the interior are at another but different potential and that the Volta difference is the difference between the potentials of the two surfaces. Seebeck difference is between the potentials of the two interiors. If this is so we may exhibit Volta's difference as the sum of three Seebeck differences by an equation of the type:

$${}^{A}V_{B} = {}^{\text{surface of }A}S_{A} + {}^{A}S_{B} + {}^{B}S_{\text{surface of }B}$$

When the copper disc lies on the zinc we can scarcely suppose that at actual points of contact the potential can have two different values but we may suppose that actual contact takes place over only a very small fraction of the area so that this difficulty, which arises whether we take Kelvin's view or not, is not a serious one. Now unless we assume that Seebeck's potential difference is the same as Volta's there is great difficulty in learning anything about the former directly. If we had plates of zinc and so long as the plates are in contact we have no evidence of electric charge. It appears only on separation. And even if we could have plates of different metals in contact under circumstances such that an appreciable part of the electricity is at the potential of either interior, the process of separation would cease to be so and the effect which we should obtain would be Volta's.

To return to the Volta effect Lord Kelvin considered it established that the potential of zinc exceeds the potential of copper in contact by about 0.7 volts with a difference varying from 0.63 to 1.13 according to the condition of the surface. It seems desirable to explain the method of measurement and to point out how the value was inferred. The discs were placed in parallel and opposite to each other with the zinc fixed and the copper movable but were not allowed to touch. The copper was connected by a wire to a pair of quadrants of an electrometer. The zinc was connected with the other pair of quadrants by a wire to an end P on the disc being of platinum. The copper disc was also connected by a wire to a fixed point O and the zinc disc could be connected through a wire both ends of which were tipped with platinum to a movable point X of the same wire. This last connection being made through the platinum piece P. The wire OX is a potential divider and the current from a known cell is passing through it so that when X is fixed the potential difference between O and X (in the same metal or on the surface of the same metal) is known. The measurement consists in finding the point X such that, when connection is made between X and the zinc disc through P and is afterwards broken at P, on moving the copper disc further away from the zinc no motion of the electrometer ensues. It will be seen that there is no attempt here to measure directly the difference of potential between the discs while in contact. We infer that when the point X is found in the subsequent motion the zinc disc gives no charge to the electroscope. And this could not happen if in the initial position the disc had a charge. If the zinc disc is charged electrical equilibrium requires an equal and opposite charge induced on the copper one. Therefore, this charge would have to remain constant during the motion. Its distance from the zinc disc increases. Its attraction would no longer suffice to retain all the opposing charge on the zinc disc and some would flow through the electrometer. Consequently, the discs are without charge and, therefore, at the same potential. Now the copper disc surface has the same potential as the copper surface at O. And the potential of the live disc surface exceeds that of the copper surface at X. By the Volta excess of zinc over copper this difference being made up of:

$${}^{\text{zinc surface}}S_{\text{zinc}} + {}^{\text{zinc}}S_{\text{platinum}} + {}^{\text{platinum}}S_{\text{copper}} + {}^{\text{copper}}S_{\text{copper surface}}$$

Thus the Volta excess in question is equal to the excess of potential of the copper surface at O over the similar potential at X <u>or</u> the excess of potential of the interior of the copper at O over the similar potential at X. And it will be seen that it is immaterial of what metals the wires and electrometer are composed. The essential point is to know accurately the difference in potentials in or on any one metal at O and at X. It is also essential that all connections should be truly metallic and dry avoiding on the one hand any partial insulation and on the other any electrolytic action as this would alter potential differences.

I do not know how far there is justification for supposing that, at a given temperature, these various difference of potential such as ${}^{A}S_{B}$ or ${}^{\text{surface }A}S_{A}$ are actually independent of the actual value of either potential. This appears to be assumed usually but it can scarcely be absolutely correct.

<u>Part 6</u>

When electricity passes through a conductor there is always a generation of heat (ie the temperature rises unless heat is abstracted). The time rate of abstraction which is necessary to maintain the temperature constant is equal to the resistance multiplied by the square of the strength of the current as was shown by Joule. Theory and experiment alike, however, lead us to believe that in many cases the passage of electricity is accompanied also by an absorption or evolution of heat of amount proportional to the strength of the current at the surface of a single metal, in the interior of an unequally heated metal, at the junction between one metal and another and in the case of a Voltaic cell probably at the junctions between the metals and the liquids. The effect at the junction between one metal and another was described by Peltier in 1834 and is known as the Peltier effect. The effect at the surface of a single metal (ie when electricity passes from the interior to the surface or vice versa heat is absorbed) was inferred theoretically by Lord Kelvin; although it is in some cases much greater than the Peltier effect (of the order of magnitude of a thousand fold) it does not seem to be so well known and I am not aware that its existence has been verified experimentally.

The effect at the interior and on the surface of an equally heated metal was also deduced theoretically by Lord Kelvin. In 1851 he showed that when electricity flows from one point of a metal to another at a different temperature heat is usually absorbed or liberated; its amount being for a given metal and a given temperature proportional to the quantity of electricity which flows. This may be expressed by the statement that electricity has a specific heat (positive or negative) and is different for different metals. It is reasonable to suppose it varies with temperature. This Thompson Effect as it is called has been verified experimentally. In the case of the Voltaic cell it has been verified experimentally that heat is absorbed or given out in addition to Joules' heat in the circuit as a whole but I think that it has not been located precisely.

The Voltaic cell is perhaps the most interesting case and it might be discussed without any special reference to the other cases but as they seem more fundamental I will consider them first.