



XLVIII. On galvanic currents occasioned by differences of concentration—Inferences from the mechanical theory of heat

Professor Helmholtz

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zero, and went up to 2 or 3 U.S., making irregular vibrations. The weight was replaced and additional shot poured in very slowly. The deflection almost instantaneously changed to about 2 S.U., which increased slightly until the wire broke.

Experiment 11.—A copper wire .24 millim. diameter. $\Theta = 15^\circ$. Initial deflection 1 S.U.

M.	D.
0	1
3	1
6	3
9	3
12	3
15	4
18	4
21	2.5
24	2.5
27	2
30	1.5
33	1.5
36	1.5
39	1.5
42	1.5

The direction of the current was S.U. Several small weights were added to the can; but the deflection remained steady at 1.5. In copper wire, no fall in the deflection was observed when the weight was left suspended for some time.

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XLVIII. *On Galvanic Currents occasioned by Differences of Concentration—Inferences from the Mechanical Theory of Heat.* By Professor HELMHOLTZ*.

WE will regard as the electro-chemical equivalent of an ion that amount of it which is separated at the corresponding electrode, in the unit of time, by the chosen unit of current.

The transport-number n , referred to the cation (Hittorf's $\frac{1}{n}$), gives, as with Wiedemann, that fraction of the equivalent of the cation in question which is carried by the unit of current, during the unit of time, through each cross section of the current's path in the solution, to the cathode. On the other hand, the quantity $(1-n)$ of the anion goes in the opposite direction,

* Translated from the *Monatsbericht der königlich preussischen Akademie der Wissenschaften zu Berlin*, Nov. 1877, pp. 713-726.

by which $(1-n)$ of the cation at the cathode becomes free—which, combined with the amount n of cation brought to this side, gives the quantity 1 set free at the cathode. In like manner the quantity n of the cation is conveyed away from the other side, by which n of the anion is set free. To this is added $(1-n)$ of the anion brought over. Now, when the cation is a metal which can deposit itself on the electrode, $(1-n)$ of the metal disappears there from the solution, and $(1-n)$ of the salt-forming acid is conveyed away; consequently from there $(1-n)$ of the salt is removed. On the other side the liberated anion combines with the metal of the electrode; and therefore 1 equivalent of new metal here enters the solution, while n of the metal is carried away and $(1-n)$ of the anion is brought over. This gives here an increase of the quantity of the salt by $(1-n)$ of the equivalent for the unit of time and unit of current. If the metal of the electrode is the same as that which is contained in the solution, the total result of the electrolysis is the same as if one equivalent of metal were carried from the anode to the cathode, and $(1-n)$ equivalent of salt in the solution from the cathode to the anode.

If, then, the salt-solution is more concentrated at the cathode than at the anode, the difference of concentration is equalized by the transfer. Therewith the liquid approaches the state of equilibrium to which the forces of attraction between the water and salt tend even in the processes of diffusion, namely the state of uniform distribution of the salt. Thus the chemical forces acting in this direction will also in turn assist the electric current acting in their direction.

That the work of the chemical forces which herewith comes in acts in this case as an electromotive force according to the same laws as other electrolytic chemical processes, can be deduced from the mechanical theory of heat.

A reversible process without changes of temperature, such as is required for the application of Carnot's law, we can institute in the following manner:—

(1) We let the quantity E of positive electricity slowly enter the anode in a constant current, and in return take away the quantity $+E$ from the cathode; or, what leads to the same result, we admit $+\frac{1}{2}E$ into the anode, and, inversely, discharge $-\frac{1}{2}E$ at the cathode. If P_k and P_a are the values of the electrostatic-potential function for the two electrodes, then is

$$E\{P_a - P_k\}$$

the work which must be done in order to bring about this through-current. If the duration of the current is equal to t , the current-intensity according to electrostatic measure is given by the equation

$$Jt = E.$$

(2) Under the influence of this through-current, in the electrolytic cell, which we suppose provided with two electrodes of the same kind of metal and filled with a solution of that metal, there is brought about a transfer of the salt in the electrolyte. The alteration hereby produced in the state of the liquid we can get rid of by evaporating, from all the layers of the liquid where the current attenuates the liquid, as much water as is conveyed thither, and, conversely, where the current produces concentration, introducing the corresponding amount of water by precipitation of vapour. If in this way the state within the liquid be maintained perfectly constant, the anion must remain wholly in its own place, because at neither end is any thing withdrawn from it, and nothing is added to it. From the cation, on the contrary, an amount perfectly equivalent to the current-intensity must pass through each cross section of the path of the current, since a full equivalent is dissolved at the anode, and precipitated at the cathode. Now, since the displacement of the anion against the water is to that of the cation against the water as $(1-n):n$, the water must move forwards with a velocity amounting to $(1-n)$ of that of the cation. Consequently, if 1 electrolytic equivalent of the salt is combined with q parts by weight of water, and through a portion $d\omega$ of the surface the current of density i is to be led, and, expressed in equivalents, the quantity $id\omega$ of the cation, then must $q(1-n)i \cdot d\omega$ parts by weight of water pass through the same in order to keep the parts of the anode in their place.

This quantity of water, amounting to $q(1-n)i \cdot d\omega$, carries with it as dissolved constituents $(1-n)i \cdot d\omega$ equivalents of the cation as well as of the anion. Electrolysis impels through the same cross section $ni \cdot d\omega$ of the cation forwards, and $(1-n)i \cdot d\omega$ of the anion backwards; hence, on the whole, one equivalent of the cation goes forwards, and the anion remains in its place.

Therefore, if u, v, w denote the components of the electric flow parallel to x, y, z , reckoned according to the quantity of electricity which passes the unit of surface in the unit of time, the increase in the amount of water in the volume-element dx, dy, dz is, according to known hydrostatic laws, for the unit of time,

$$\begin{aligned}
 & - \left\{ \frac{\partial}{\partial x} [q(1-n)u] + \frac{\partial}{\partial y} [q(1-n)v] + \frac{\partial}{\partial z} [q(1-n)w] \right\} dx \cdot dy \cdot dz \\
 & = - \left\{ u \frac{\partial}{\partial x} [q(1-n)] + v \frac{\partial}{\partial y} [q(1-n)] + w \frac{\partial}{\partial z} [q(1-n)] \right\} dx \cdot dy \cdot dz, \quad (1)
 \end{aligned}$$

since in the stationary current

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} = 0. \quad . \quad . \quad . \quad . \quad (1A)$$

On the contrary, at the surface of the electrodes the required inflow of water through the surface-element $d\omega$ would be

$$q(1-n)[u \cos a + v \cos b + w \cos c]d\omega, \quad . \quad . \quad . \quad (1B)$$

if a, b, c denote the angles between the normal, directed to the liquid, of the element $d\omega$ and the positive coordinate-axes.

Integrating over the entire volume of the liquid the above expression which is multiplied by dx, dy, dz , we obtain, by known methods of partial integration, the same value that the last expression (multiplied by $d\omega$) gives when integrated over the surface.

The water, then, which collects in the whole interior, and, according to our supposition, is to be removed by evaporation, will exactly suffice, when again precipitated at the surfaces of the electrodes, to give the supply required there. Of course the collection of the water within the liquid, as well as its precipitation on the surface, may in places have also negative values.

(3) The evaporation, or, where it is negative, the precipitation of the vapour, can be managed thus:—By conveying heat to each of the volume-elements the temperature is kept constant during the evaporation. As long as water is to be extracted from a volume-element of the liquid, the vapour is left in contact with it; finally the two are separated, and the vapour, under a further supply of heat, is permitted to expand at constant temperature until it has reached a constant pressure p_1 . Where the evaporation is to be negative, of course the vapour is withdrawn from the pressure p_1 , and giving up heat at constant temperature is compressed at first out of, and afterwards in, contact with the liquid, until it turns to water. Since the vapour which is in contact with the more concentrated portions of the liquid has less pressure than that which is in contact with the more dilute portions, work will be gained in this evaporation when water is carried over from the more dilute to the more concentrated portions, lost when the reverse is the case.

(4) The electric current can be made to pass so slowly that the heat-development (proportional to the square of its intensity) on account of the resistance of the conductor becomes vanishingly little in comparison with those actions which we have hitherto discussed, and which are proportional to the first power of the intensity.

In like manner the diffusion which takes place between the

differently concentrated portions of the solution could be reduced to a minimum by inserting narrow connecting tubes, without altering the electromotive force of the apparatus, which we wish to calculate.

We can, on account of this, neglect these two irreversible processes, and apply Carnot and Clausius's law to the reversible ones. Since all the bodies taking part in the process are each to have the same constant temperature, no heat can be converted into work, nor can any work be converted by the reversible processes into heat. The sum of the work gained and lost must therefore, taken by itself, be equal to *nil*, as must also the sum of the heat withdrawn and supplied. Hence result two equations.

The one, which refers to the heat, expresses nothing but what can be obtained without consideration of the electrolytic process—namely, that the same amount of heat is generated when the metal of the electrodes comes into a concentrated salt-solution which is gradually diluted as when it enters directly into the dilute solution.

The second equation expresses that with the above-described reversible process the mechanical work must be equal to *nil*. Work is expended, partly,

(1) for the collection of the electricity. If P_a and P_k are the values of the potential-function in the anode and cathode, and in the time t the electricity $+E$ is collected in P_a and taken out of P_k , the work for the unit of time is, as already remarked,

$$\frac{E}{t}(P_a - P_k) = J(P_a - P_k).$$

(2) Partly, work is performed by the expanding vapour. This vapour is first evolved under the pressure p , which corresponds to the degree of saturation of the liquid with salt; it then expands at a constant temperature up to the pressure p_1 . Naming the work for the unit of mass W , and the volume of the unit of mass V , both referred to the given constant temperature,

$$W = pV + \int_v^{v_1} p \cdot dv. \quad \dots \quad (1c)$$

The total quantity of this work, \mathfrak{M} , is found, by means of the values shown in equations (1) and (1B) of the current, to be equal to

$$-\iiint dx \cdot dy \cdot dz \cdot W \left\{ u \frac{\partial}{\partial x} [q(1-n)] + v \frac{\partial}{\partial y} [q(1-n)] + w \frac{\partial}{\partial z} [q(1-n)] \right\} \\ - \int d\omega \cdot W q(1-n) \{ u \cos a + v \cos b + w \cos c \} = \mathfrak{M}. \quad (2)$$

By partial integration of the triple integral, and taking into account equation (1A), we find

$$\mathfrak{W} = \iiint dx \cdot dy \cdot dz \cdot q \cdot (1-n) \left\{ u \frac{\partial W}{\partial x} + v \frac{\partial W}{\partial y} + w \frac{\partial W}{\partial z} \right\}. \quad (2A)$$

Here n and W are functions of q . Consequently, if we put

$$q(1-n)dW = d\Phi, \quad . \quad . \quad . \quad (2B)$$

where Φ denotes a function of q , or

$$\Phi = \int_{p_0}^p q(1-n) \frac{dW}{dp} dp, \quad . \quad . \quad . \quad (2C)$$

in which p , the pressure of the vapour above the salt-solution, is likewise a function of q , we get

$$\mathfrak{W} = - \int d\omega \cdot \Phi \{ u \cos a + v \cos b + w \cos c \}. \quad (2D)$$

The parenthesis in this expression denotes the component of the current perpendicular to the limiting surface of the electrolyte. This differs from *nil* only at the parts of the limiting surface turned to the electrodes. If the concentration of the liquid, and therefore q , u , p , Φ , along each single electrode is constant, then becomes

$$\mathfrak{W} = J(\Phi_k - \Phi_a), \quad . \quad . \quad . \quad (3)$$

and the equation of the work becomes

$$P_k - P_a = \Phi_a - \Phi_k = \int_k^a q(1-n) \frac{dW}{dp}. \quad . \quad . \quad (3A)$$

But $P_k - P_a$ is the value of the electromotive force produced by the electrolytic cell in the direction from the anode to the cathode, consequently in the direction of our assumed current.

This equation therefore indicates the existence of an electromotive force, the amount of which depends only on the concentration of the liquid at the two electrodes, not upon the distribution of more concentrated and more diluted layers in the interior of the liquid—a conclusion which is confirmed by the experiments of Dr. J. Moser, recently communicated to the Academy.

At the temperature of the apartment, the diminution of pressure shown by the vapour over the solutions of most of the metallic salts is very inconsiderable; and on this account the quantity $\frac{\partial W}{\partial p}$ may be supposed approximately constant within these narrow limits of the pressure. It can therefore be placed before the symbol of integration. On the other hand,

according to Wüllner's experiments the diminution of the vapour-pressure is to the amount of salt dissolved in the constant quantity of water directly, and therefore to our q inversely proportional. If we use p_0 , hitherto left undefined, to denote the vapour-pressure of pure water at the temperature of the experiment, we may put

$$p_0 - p = \frac{b}{q}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where b denotes a constant depending on the kind of the salt. Consequently

$$P_k - P_a = b \frac{\partial W}{\partial p} \int_{p_k}^{p_a} (1-n) \frac{dp}{p_0 - p}. \quad . \quad . \quad (4A)$$

In intervals in which $(1-n)$ has a constant value this would become

$$P_k - P_a = b(1-n) \frac{\partial W}{\partial p} \log \frac{p_0 - p_k}{p_0 - p_a} \quad . \quad . \quad (4B)$$

$$= b(1-n) \frac{dW}{dp} \log \left(\frac{q_a}{q_k} \right). \quad . \quad . \quad . \quad . \quad . \quad (4C)$$

The quantity $\frac{\partial W}{\partial p}$, here occurring, has at all events a positive value. If we suppose Mariotte's law valid for the inconsiderable densities possessed by the aqueous vapour at the temperature of the apartment, and if V denotes the volume of the mass-unit of the vapour under the pressure p , then (as noted above in equation 1c) is

$$W = pV + \int_v^{v_1} p \cdot dv.$$

According to Mariotte's law,

$$V = \frac{V_1 p_1}{p},$$

$$dV = -V_1 p_1 \frac{dp}{p^2},$$

$$\int_v^{v_1} p dv = V_1 p_1 \log \left(\frac{p}{p_1} \right),$$

$$W = p_1 V_1 \left\{ 1 + \log \frac{p}{p_1} \right\},$$

$$\frac{\partial W}{\partial p} = \frac{p_1 V_1}{p} = V \quad . \quad . \quad . \quad . \quad . \quad (4D)$$

as an approximately correct value.

Hence it follows that the electromotive force of the cell is positive if the liquid is more concentrated at the cathode and consequently $q_k < q_a$ and $p_k < p_a$, which is likewise confirmed by a great number of observations by Dr. J. Moser.

For inconsiderable concentrations, and correspondingly slight diminutions of the pressure of vapour above the solution, formulæ (4c) and (4d) give also the law of the increase of electromotive force with rising concentration of the solution, since the value of $(1-n)$ is, according to Hittorf's investigations, nearly constant for slight concentrations, but rises for greater ones.

The S of the following Tables is the quantity of water (proportional to q) which is combined with the anhydrous salt in the solution; A is the electromotive force, according to the observations of J. Moser, stated in thousandth parts of a Daniell element (Cu, CuSO₄, ZnSO₄, Zn). The quantity

$$\eta = \frac{1}{A} \log \frac{S_k}{S_a}$$

should, according to equation (4c), be constant.

For a cell with sulphate-of-copper solution and copper electrodes the following values are found.

Sulphate of Copper.

S_k .	S_a .	A observed.	A calculated.	η .	Value of $1-n$ according to Hittorf.
128.5	4.208	27	27	0.0550	0.724 for $S = 6.35$
—	6.352	25	23.75	0.0552	
—	8.496	21	21.45	0.0562	
—	17.07	16	15.94	0.0548	
—	34.22	10	10.45	0.0575	0.644 for $S > 39.67$

As calculated values of A those are given which are obtained when the value of q from the first observation is retained for the others also. With sulphate and chloride of zinc, which can be employed in more concentrated solutions, greater deviations in these values occur* simultaneously with great increase in the values of $(1-n)$.

* Note added Jan. 1878.—More recent experiments by Dr. Moser show, indeed, that with zinc chloride the quantity $\frac{\partial W}{\partial p} = V$ increases to half as much again with greater concentrations, and can no longer be regarded as approximately constant.

Sulphate of Zinc.

S_k	S_a	A observed.	A calculated.	η .	Value of $1-n$ according to Hittorf.
163	1.972	36	29	0.0543	
—	2.963	28	26.4	0.0635	0.778 for $S = 2.524$
—	4.944	22	23.1	0.0707	0.760 for $S = 4.052$
—	10.889	18	18.0	0.0673	0.636 for $S = 267.16$

Chloride of Zinc.

99	19	21.5	24.7	0.0333	0.70 for $S = 332.87$
—	9	40.4	36.0	0.0258	
—	5.66	42.9	42.9	0.0290	
—	2.33	67.1	56.2	0.0243	1.08 for $S = 2.774$
—	1.22	120.9	65.9	0.0158	
—	0.67	200.0	0.0108	

The great deviations which occur, especially with the higher concentrations, may probably be accounted for partly by the rise in the value of $(1-n)$ for the denser solutions, and partly by the more considerable diminution of the vapour-pressure. As the laws of both alterations for these salts have not yet been investigated, I could not institute a more detailed calculation.

Respecting the *calculation of the absolute value of the electromotive force* we have further to remark as follows:—The current-intensity J hitherto used is measured electrostatically; likewise the electromotive force $P_k - P_a$ is determined in electrostatic units. Measured in electromagnetic measure the current intensity J will become

$$J = \frac{1}{\mathfrak{C}} J,$$

and the electromotive force

$$\mathfrak{A} = \mathfrak{C}(P_k - P_a),$$

where \mathfrak{C} is the velocity determined by W. Weber. According to the determinations of Friedrich Weber the electromotive force of a Daniell's element (Cu , CuSO_4 , ZnSO_4 , Zn) is, in electromagnetic measure,

$$\mathfrak{A}_D = 109540000 \frac{\text{centim.}^{\frac{3}{2}} \text{gram.}^{\frac{1}{2}}}{\text{second}^2}.$$

Now W. Weber's electromagnetic current-unit, the unit of which is

$$\frac{\sqrt{\text{milligr. millim.}}}{\text{second}} = 0.01 \frac{\sqrt{\text{gram centim.}}}{\text{second}},$$

decomposes, according to R. Bunsen, 0.0092705 mgr. of water and $\frac{159.5}{18}$ times as much sulphate of copper—that is, 0.082147 mgr.

If, then, as in the numerical Tables, we denote by S the amount of water contained with one part by weight of anhydrous salt in the solution, for the experiments with sulphate of copper

$$\mathfrak{E}q : S = 0.0082147 \text{ sec.} \sqrt{\frac{\text{gram}}{\text{centim.}}} : 1.$$

Now, if the diminution of the vapour-pressure by the salt-solution employed is known, we obtain the constant b from the equation

$$p_0 - p = \frac{\mathfrak{E}b}{\mathfrak{E}q},$$

in which the pressure p is also to be reckoned in absolute force-measure as $\frac{\text{gram}}{\text{centim. sec.}^2}$.

Our equation (4c) becomes

$$\mathfrak{A} = \mathfrak{E}(P_k - P_a) = (\mathfrak{E}b) \cdot V(1-n) \log \left(\frac{S_a}{S} \right).$$

Consequently the value of the constant \mathfrak{E} need not be known for the calculation of the \mathfrak{A} 's in electromagnetic measure.

Since we have assumed for the vapour the validity of Mariotte's law, the product

$$\mathfrak{E} \cdot b \cdot V = \mathfrak{E}q \cdot p_0 \cdot V_0 \cdot \frac{p_0 - p}{p}.$$

The ratio $\frac{p_0 - p}{p}$ is, from Wüllner's experiments, in many salts nearly constant with changed temperature; while the product $p_0 \cdot V_0$ increases approximately in proportion to the absolute temperature, which, within the limits of the temperature of the apartment, is not of much consequence. In fact the experiments do not show any considerable influence of the temperature upon the electromotive force of the cells; at least it by no means varies in so great a proportion as the pressure of the saturated vapour.

For testing the accordance of the absolute value of the electromotive force of our series with that given by the formula, sufficient data on the vapour-tension of the salt-solutions used are still wanting. If we employ equation (4c) in order to calculate, from the electromotive force found by J. Moser for

cells with sulphate-of-copper solutions, the quantity $\frac{p_0 - p}{p_0}$ for the one-per-cent. solution at 20° C., we find this quantity equal to 0·00082, while M. Wüllner* has found the same quantity,

For cane-sugar	= 0·00070,
For nitrate of potass...	= 0·00229,
For sulphate of soda...	= 0·00236.

From the chemical properties of sulphate of copper it is probable that, in this respect, it takes its place between cane-sugar and the alkali-salts†. Experiments are in preparation in the laboratory here for the purpose of obtaining more accurate determinations. Meanwhile this calculation shows already at least so much, that the consideration instituted gives a theoretic value of the electromotive force which is of the same order of magnitude as the observed.

Since, moreover, factors obtained from the most various kinds of physical investigations, and one of which amounts to above a hundred millions, must be eliminated from both sides of the equation, this preliminary result is still of some importance.

XLIX. *Rate of Earthquake-wave Transit.*

By R. MALLET, F.R.S.‡

I PRESUME that I have been indebted to the politeness of General Abbot, U.S. Engineers, for a copy of a paper by that officer, published in the 'American Journal of Science' for March 1878. In this paper the writer recurs to his account of the experiments made at Hallet's Point on the occasion of the great explosion there, on the rate of seismic-wave transmission as described in General Abbot's paper read before the American National Academy of Sciences, October 18, 1876, and also published as one of the papers of the Essayons Club of the Corps of U.S. Engineers. Upon the results there recorded I deemed it necessary to publish some remarks in the Philosophical Magazine for October 1877, in which I pointed out their anomalous character and their entire discordance with each other. If I rightly gather General Abbot's meaning from his last paper above alluded to, he considers that the

* Poggendorff's *Annalen*, vol. ciii. p. 556.

† *Supplementary Note* (Jan. 1878).—Dr. J. Moser has since effected determinations of the quantity in question, employing water and dilute solutions instead of mercury. He obtained 0·00086 as the mean value from three experiments.

‡ Communicated by the Author.