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Physics. — „*On an asymmetry in the change of the spectral lines of iron, radiating in a magnetic field*”. By Dr. P. ZEEMAN.
(Will be published in the Proceedings of the next meeting).

Physics. — *The HALL-effect in electrolytes.* By Dr. E. VAN EVERDINGEN JR. (Communication N^o. 41 from the Physical Laboratory at Leiden, by Prof. H. KAMERLINGH ONNES).

1. The researches on the HALL-effect and the increase of resistance in the magnetic field for bismuth, communicated to the Academy in the Meetings of 30 May 1896, 21 April and 26 June 1897¹⁾, and afterwards treated more at large in my dissertation, induced me to put the question, whether these phenomena may justify a choice among various theories about the nature of the electric current and the resistance of metals. A first step towards answering this question was the deduction of a formula for the HALL-effect in electrolytes, with the aid of simplifying suppositions. Indeed it is generally assumed that in electrolytes the electric current consists in a convection of charges by the ions; the velocities of this motion are known in many cases, hence all the data for the calculation are present. This research, already begun in Chapter VIII of my dissertation, being concluded for the present, I wish here briefly to communicate the results.

2. Several physicists have tried to observe the HALL effect in liquids. They succeeded indeed in observing differences of potential, caused by a magnetic field in solutions of sulphate of zinc and copper which were traversed by currents, and changing their signs on the reversal of the magnetic field or of the current. Whereas however in most metals the HALL-effect is proportional as well to the strength of the current as to the field, and in all metals the difference of potential appears immediately on closing the magnetizing current, in the liquids this difference increases more than the current and less than the magnetic field, and after the applying of the field it grows slowly towards a maximum. Chiefly on account of the last named fact ROTTI²⁾, FLORIO³⁾ and CHIAVASSA⁴⁾ refused to acknowledge the differences of potential observed also by themselves as

¹⁾ Communications from the Phys. Lab at the Univ of Leiden. N^o. 26, 37 and 40.

²⁾ Atti della R. Acc. dei Lincei 12 p 397, 1882; Journ. de Phys. 1883.

³⁾ Il nuovo Cimento, Ser. 4, T. 4, p. 106, 1896.

⁴⁾ Elettricista 6, 1897.

proofs of the existence of the HALL-effect in liquids, and attributed those differences rather to ponderomotive forces, exerted by the magnetic force on the particles of salt, to differences of concentration or to differences of temperature. The two physicists first mentioned confined themselves to experiments, in which disturbances of this kind were avoided, and the HALL-effect had really disappeared; CHIAVASSA however also demonstrated the existence of differences of temperature and of concentration, determined the influence of these differences on the readings of the electrometer, and proved that in a non homogeneous magnetic field vortical motions occur in the liquid, which depend on the strength of the current, the magnetic field etc. in the same manner as the observed apparent HALL-effect.

BAGARD¹⁾ on the contrary believed to have avoided all disturbances in his experiments and was therefore convinced of the reality of the HALL-effect in liquids.

The observations of CHIAVASSA were made in the same manner as those of BAGARD; hence the greater part of the difference of potential observed by BAGARD was very likely due to disturbances. In the controlling experiments however, which were to prove that without disturbances no difference of potential appears at all, strongly concentrated solutions were always used; so it was still possible that in the diluted solutions used by BAGARD a part of the observed effect would remain even in the absence of disturbances. Hence the question has not yet been solved by experiment.

3. We proceed to the theory of the phenomenon and for the present confine our attention to the state of matters in the inner part of the liquid, i. e. far from the lateral borders. If we put for the E. M. F. in the direction of the axis of X E_x , and for the velocities of the ions caused by a slope of potential of 1 C. G. S. unit per cM. U and V , then the velocities are

$$E_x U \text{ and } E_x V$$

respectively in the directions of the positive and the negative axis of X . We assume with LORENTZ²⁾ that an ion, moving with the velocity v in a magnetic field of intensity H is acted upon by a force represented by the vector product $[v. H.]$ for each unit of elec-

¹⁾ C. R. T. 123, p. 77 and 1270, 1896. Journ. de Phys. Sér. 3, T. 5, p. 499, 1896.

²⁾ See f. i. Versuch einer Theorie der electrischen und optischen Erscheinungen in bewegten Körpern. Leiden, 1895.

tricity. In real cases the numerical value of this product is small as compared with unity; the variation in the direction of motion is only slight; hence we are allowed to assume this force to be always perpendicular to the axis of X . If the magnetic force is along the axis of Y , the ions will obtain an additional velocity in the direction of the axis of Z ¹⁾.

These velocities will cause differences of potential and of concentration. When the state of equilibrium has been reached it is not necessary that the velocities should be zero, but it will be sufficient if

1^o. The velocities of positive and negative ions are equal.

2^o. As much of the dissolved material wanders back by diffusion in the molecular state as is transported in the form of ions by the said velocities.

For completing the image formed in this way we ought to imagine at the borders of the liquid, or at all events outside the space now considered, on one side molecules dividing into ions, on the other side ions combining again into molecules. For the moment we suppose the reaction-velocities for these processes to be infinitely great.

We will now work out the two conditions.

If we call the E. M. F. in the direction of the axis of Z E_z , the ions obtain velocities in the direction of this axis equal to

$$(UH E_x + E_z) U \text{ and } (VH E_x - E_z) V.$$

Writing c_1 for the concentration of both ions and c_2 for the concentration of the salt, we may represent the velocities of diffusion of the ions by

$$\frac{A}{c_1} \frac{dc_1}{dz} \cdot U \text{ and } \frac{A}{c_1} \frac{dc_1}{dz} \cdot V$$

and that of the salt by $\frac{B}{c_2} \frac{dc_2}{dz} \cdot U$.

Here A is a constant closely related to the diffusion constant of completely dissociated electrolytes; B has a similar signification for the diffusion of a non dissociated salt.

¹⁾ A calculation which takes into account the irregular thermal motion of the ions leads to the same results.

The first condition reads

$$\left(U H E_x + E_z - \frac{A}{c_1} \frac{dc_1}{dz} \right) U = \left(V H E_x - E_z - \frac{A}{c_1} \frac{dc_1}{dz} \right) V \quad (1)$$

the second

$$\frac{B}{c_2} \frac{dc_2}{dz} \cdot U c_2 = \left(U H E_x + E_z - \frac{A}{c_1} \frac{dc_1}{dz} \right) U c_1 \quad (2)$$

Taking into account that the difference of concentration will be very small, and that we supposed the reaction-velocities to be infinitely great, we shall put $c_1 = k c_2$, k being a constant.

(2) may now be written

$$\frac{B}{c_1} \frac{dc_1}{dz} = \left(U H E_x + E_z - \frac{A}{c_1} \frac{dc_1}{dz} \right) k.$$

so

$$\frac{1}{c_1} \frac{dc_1}{dz} = \frac{(U H E_x + E_z) k}{B + A k}$$

Substituting this in (1) and writing a for $\frac{A k}{B + A k}$ we obtain

$$\begin{aligned} (U H E_x + E_z) (1 - a) U &= \{ (V H E_x - E_z) - a (U H E_x + E_z) \} V. \\ E_z \{ U + V - a (U - V) \} &= - E_x H \{ U^2 - V^2 - a (U^2 - U V) \} \\ \frac{E_z}{E_x} &= - H (U - V) \cdot \frac{U (1 - a) + V}{U (1 - a) + V (1 + a)} \end{aligned}$$

and

$$\frac{1}{c_1} \frac{dc_1}{dz} = E_x H \cdot \left\{ U - (U - V) \cdot \frac{U (1 - a) + V}{U (1 - a) + V (1 + a)} \right\} \frac{a}{A}.$$

The limiting cases are $k = 0$ and $k = \infty$.

First case (very slightly dissociated) $a = 0$.

$$\frac{E_z}{E_x} = - H (U - V) \quad \frac{dc_2}{dz} = 0 \quad \dots \quad (3)$$

Second case (completely dissociated) $a = 1$.

$$\frac{E_z}{E_x} = - \frac{H}{2} (U - V) \quad \frac{1}{c_1} \frac{dc_1}{dz} = E_x H \cdot \frac{U + V}{2 A} \quad \dots \quad (4)$$

Both these results may be deduced directly. If c_1 tends to zero, no differences of concentration of the free ions are possible and the velocities must be equalised by the action of electromagnetic and electric forces alone.

The equation

$$(E_x U H + E_z) U = (E_x V H - E_z) V$$

immediately gives the relation (3).

In a completely dissociated solution on the contrary no molecules of salt can go back by diffusion, so the velocities of the ions in the direction of the axis of Z should both become equal to zero; hence

$$E_x U H + E_z - \frac{A}{c_1} \frac{dc_1}{dz} = 0 \quad \text{and} \quad E_x V H - E_z - \frac{A}{c_1} \frac{dc_1}{dz} = 0$$

from which the relations (4) follow immediately.

As a matter of fact, the reaction-velocities are not infinitely great. By supposing these velocities to be equal to zero we may however perceive that the result is not very much altered by this. In this case no decomposition or combination occur; the concentration of the molecules of salt is not altered, these have therefore no influence at all upon the phenomenon. So we then find, whatever the real degree of dissociation may be, the same result as in the case of complete dissociation.

Hence it is very likely that the HALL-effect in liquids may generally be represented by

$$\frac{E_z}{E_x} = -\mu H(U - V)$$

μ lying between 1 and $\frac{1}{2}$.

This result gives the rotation of the equipotential lines in the inner part of the liquid. The question rises, whether this is what has been observed in the experiments. In these namely the difference of potential between two electrodes of metal is read; if these electrodes are immersed in liquids of different concentration, another difference of potential will appear, the value of which may be

estimated by means of the formula of HELMHOLTZ ¹⁾

$$V_2 - V_1 = \frac{2 p_0}{\varepsilon} \cdot \frac{V}{U + V} \cdot l \frac{c_2}{c_1}$$

Here p_0 means the osmotic pressure for a concentration of 1 gram-ion per cm^3 , ε the charge of a gram-ion in electromagnetic units.

We take a definite case for this estimation, namely a solution of sulphate of copper with the concentration $c_1 = 3.10^{-5}$, the lowest value we find among the numbers of KOHLRAUSCH ²⁾ for this salt. We shall suppose that, in this case, applies the formula for completely dissociated solutions.

$$U = 218.10^{-14} \quad V = 373.10^{-14}$$

so — $(U - V) = 155.10^{-14}$. Taking $E_x = 1$ volt or 10^8 C. G. S., $H = 10^4$, we find $E_x H = 0,78$.

This is the difference in C. G. S. units between two points on the axis of Z , 1 cM. apart.

The difference of concentration is determined by

$$\frac{1}{c_1} \cdot dc_1 = E_x H \cdot \frac{U + V}{2 A}$$

Comparing our formula for the velocity of diffusion with that of NERNST ³⁾, it appears that $A = \frac{p_0}{J} \frac{u}{U}$ where $\frac{J}{u}$ = force required to move a gram-ion, with migration-velocity u , with the velocity of 1 cM. per second through the solution.

$$l \frac{c_2}{c_1} = l \left(1 + \frac{dc_1}{c_1} \right) = \frac{dc_1}{c_1} - \dots$$

We retain only the first term, so

$$l \frac{c_2}{c_1} = E_x H \cdot \frac{U + V}{2 A}$$

¹⁾ Wied. Ann. 3. p. 201, 1878. In this form the formula is given by NERNST, Zeitschr. f. ph. Chem. 4, p. 129, 1889.

²⁾ Wied. Ann. 50, p. 404, 1893.

³⁾ Zeitschr. f. ph. Chem. 2, p. 619, 1888.

$$\begin{aligned}
 V_2 - V_1 &= \frac{2 p_0}{\varepsilon} \cdot \frac{V}{U + V} \cdot E_x H \cdot \frac{U + V}{2 p_0 u} \cdot J \cdot U = \frac{E_x H}{\varepsilon} \cdot J \frac{U V}{u} \\
 &= \frac{10^8 \cdot 10^4}{10^4} \cdot 0,89 \cdot 10^{10} \cdot \frac{110}{10^8} \cdot 373 \cdot 10^{-14} = 3,6
 \end{aligned}$$

These calculations are sufficient to show that this difference of potential is of the same order of magnitude as the HALL-effect.

If the electrodes are placed in little vessels communicating through long tubes with the points on the axis of Z , as frequently occurred in the experiments, then no difference of concentration exists at the electrodes, and the last mentioned difference of potential disappears.

4. Comparison of theory and experiments.

For this comparison we choose the experiments of BAGARD with a half normal solution of sulphate of copper. We find for this solution $V - U = 11 \cdot 10^{-13}$ 1).

The experiments of BAGARD however in a field of 385 C.G.S. give for $\frac{E_z}{E_x} : H$ a value of $13 \cdot 10^{-7}$.

Taking the sixteenth normal solution in the strongest field, 962, the theory gives $14 \cdot 10^{-13}$, the experiment $35 \cdot 10^{-7}$.

If we moreover consider, that even the sign of the apparent effect, which agrees here with the theoretical sign, in the experiments of CHIAVASSA with sulphate of zinc proved to be variable, it will appear that we may safely conclude that the hitherto observed galvano-magnetic differences of potential in liquids are *not* caused by the phenomenon of HALL.

Researches much more accurate than have been attempted till now 2) should decide whether the weak theoretical effect can be observed. It may be doubted however whether the disturbances, which can assume such large proportions, will ever be completely avoided.

5. So the result of this research is: for the present we can not

1) In the dissertation the factor 10^{-8} (ratio of volt and C.G.S. unit) has been omitted. As moreover the accurate researches of CHIAVASSA had not yet appeared then, the experiments of BAGARD were, at that time, trusted more than they now appear to deserve. Also mr. F. G. DONNAN at Holywood (Ireland) has noticed the omission and has been so kind as to tell me so.

2) The smallest observable difference of potential was in the experiments of CHIAVASSA $5 \cdot 10^{-5}$ volts. The largest effect calculated above would give for a slope of potential of 1 volt per cM in a field of 10000 C.G.S. units $1,4 \cdot 10^{-8}$ volts.

yet use the phenomena in electrolytes in order to get a better insight into the nature of the electric current in metals. In this respect more may perhaps be expected from researches as those published lately by RIECKE ¹⁾ under the title „Zur Theorie des Galvanismus und der Wärme,” where relations are sought between the different thermic, galvanic, thermo-magnetic and galvano-magnetic phenomena in bismuth. I. a. RIECKE calculates with the aid of certain suppositions U and V for bismuth and finds

$$U = 0,05.10^{-5} \quad V = 7,21.10^{-5}.$$

I intend shortly to publish the results of measurements of the various phenomena in the *same* plate of bismuth, and to compare those results with RIECKE's theory.

¹⁾ Gött. Nachr. 1898.

(June 24 1898).