Physics. — "*On the Theory of* LIPPMANN'S *Capillary Electrometer*".
By Prof. W. EINTHOVEN (Communicated by Prof. T. ZAAIJER.)

In a paper on the capillary electrometer and on the action currents of the muscle HERMANN [1]) has put forward the statement, that the results obtained by BURCH [2]) and myself [3]) in the investigation of the motion of the mercury in the capillary electrometer are immediate consequences of his theory, and that since BURCH and I should have obtained empirically our results, they ought to be regarded as a „schöne Bestätigung" of his theory. An answer of BURCH [4]) hereupon has already appeared.

In answering HERMANN I will try by means of some new experiments to advance somewhat our knowledge of the laws governing the motion of the mercury in the capillary electrometer.

On a former occasion I have given the equation:

$$\frac{dy}{dT} = C\,(y^* - y) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where C is a constant, y the distance the meniscus has moved from its zero position at the time T and y^* the distance the meniscus would have moved if the P. D. of the poles of the capillary electrometer at the time T had been constantly applied.

In order to obtain for all capillary electrometers comparable values of the constant, we shall in this paper always measure the time T in seconds [5]), whereas y and y^* will be given in arbitrary but equal units. The value of C is apparently unaffected by a change of the unit in which y and y^* are measured. The constant C is, as I remarked on a former occasion, determined by the properties of the instrument, especially by the mechanical friction in the capillary and the ohmic resistance w in the circuit; the precise relation between C and w I did not mention till now, but it will be given in the following.

HERMANN thinks that the mentioned relation is very simple, and assumes that C varies as the inverse of w. The equation his theory

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1) PFLÜGER's Arch. f. d. ges. Physiol. 1896, Bd. 63, S. 440.
2) Philosoph. Transact. of the Royal Soc. London, 1892, Vol. 183, p. 81.
3) PFLÜGER's Arch. f. d. ges. Physiol. 1894, Bd. 56, S. 528 und 1895, Bd. 60, S. 91.
4) Proceedings of the Royal Soc. London, 1896, Vol. 60, p. 329.
5) In formerly given calculations of the constant, the time was given in twentieth to fiftieth parts of a second dependent on the velocity of the photographic plate, on which the normal curves were recorded, being 20 to 50 mm. per second.

arrives at, differs from formula (1), in having $\frac{h}{w}$ instead of C, h being an instrumental constant.

According to HERMANN formula (1) must be: [1])

$$\frac{dy}{dT} = \frac{h}{w} (y^* - y)$$

This formula represents the facts in so far as the *increment* of the resistance varies directly as the *increment* of $\frac{1}{C}$ in accordance with what I have said in a former paper and as will be discussed further on. This is occasioned by the fact, that the mechanical friction in the capillary has a similar influence on the motion of the mercury as the ohmic resistance in the circuit. HERMANN wrongly concludes that the constant must be proportional to $\frac{1}{w}$, whereas from the experiments is to be inferred only, that it is proportional to $\frac{1}{a + bw}$. Differently stated HERMANN wrongly assumes that $a = 0$.

The error of his formula is to be ascribed to a misconception of the action of the capillary electrometer.

He neglects entirely the influence of the mechanical friction in the capillary on the motion of the meniscus, whereas this mechanical friction is with most capillary electrometers of the foremost importance. This may be inferred from the following.

Using capillary G 103 and suddenly applying a P. D. remaining constant, a normal curve was described, no additional resistance being inserted in the circuit. This curve was measured and the constant, which we will call C_α [2]), determined according to formula (1). Then a normal curve was taken with the same instrument, a resistance of 0,1 Megohm now being inserted in the circuit, and the value of the constant, now indicated by C_1, was determined again.

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[1]) HERMANN's formula in his own symbols is:

$$\frac{\delta y}{\delta t} = \frac{h}{w} (kE - y);$$

kE being here identical with y^* of formula (1).

[2]) The manner in which the constant C is calculated from the normal curve was given formerly, vid. PFLÜGER's Arch. l. c.

$\frac{1}{C_\alpha}$ was equal to 0.0815

$\frac{1}{C_1}$ " 0.107

According to HERMANN's theory it must be possible to calculate from these data the internal resistance of the capillary electrometer.

Let the internal ohmic resistance of the capillary electrometer be denoted by w_i, the resistance intentionally inserted in the circuit w_u, then

$$w = w_i + w_u,$$

$$C_\alpha = \frac{h}{w_i}, \text{ and } C_1 = \frac{h}{w_i + w_u};$$

hence we must have

$$w_i \text{ (HERMANN)} = \frac{w_u}{C_\alpha \left(\frac{1}{C_1} - \frac{1}{C_\alpha}\right)}.$$

Substituting the values of C_α, C_1 and w_u we obtain

$$w_i = 0{,}320 \text{ Megohm.}$$

Now w_i may be calculated also from the dimensions of the capillary, in which case a knowledge of the dimensions of the sulphuric acid thread is principally necessary. Calculating the resistance from the dimensions, w_i was found 0,029 megohm; hence more then 11 times smaller than the amount required by HERMANN's theory.

Here follows a table with the correspondent calculations for four capillary electrometers.

TABLE I.

Number of the capillary.	w_i as calculated according to HERMANN's theory.	w_i as calculated from the dimensions of the capillary
G. 103	0,320 Megohm	0,029 Megohm
B. 101	1,545 "	0,124 "
B. 102	1,411 "	0,101 "
B. 103	0,665 "	0,026 "

We see that HERMANN's theory gives far too high values of w_i, with the above mentioned four capillary electrometers 11 to 25 times greater than is to be calculated from the dimensions of the apparatus [1]).

The value adopted for the length of the sulphuric acid thread in the calculations was one never exceeded in recording the curves, hence the figures in the last column of our table are maximum values. It seems difficult to misinterpret the results described above and they are certainly sufficient to refute HERMANN's theory.

That really the mechanical friction neglected by HERMANN is of primary importance with most capillary electrometers, will be clear from a series of experiments of entirely different character, in which the mechanical friction in the capillary was measured in a direct manner.

A capillary tube, after having been used for the recording of normal curves, is placed above a small glass vessel filled with mercury in such a manner that the end of the capillary is below the surface of the mercury.

For a short time the air above the mercury in the tube is highly compressed so that it flows in the vessel, the free air being admitted however immediately again. The mercury continues flowing if there has been but once a direct mercury connection between the interior of the tube and the vessel. The total quantity of the flow in a given time varies according to POISEUILLE's law directly as the pressure, in our case the difference of level between the mercury in the tube and the mercury in the vessel.

The flow is continued during some hours and the vessel is weighed before and after the experiment. From the difference of weight, q grams, the duration of the flow, T seconds, the mean difference of level, D centimetres, can be calculated how many grams of mercury G are pressed through the capillary tube under a pressure of 1 cm. in one second,

$$G = \frac{q}{TD} .$$

Let the radius of the capillary tube at its point be $= r$ cm., then the mean velocity in a section near the end is

1) In this communication a short account of our results must suffice, more particulars concerning the mentioned and yet to be given measurements and calculations will be published elsewhere.

$$v_0 = \frac{G}{r^2 \pi s}$$

centimetres per second under 1 cm. of mercury pressure; in this formula s is the density, whereas v_0 is dependent only on the mechanical friction.

Let us suppose that in a capillary electrometer the ohmic resistance in the circuit is reduced to zero, then in our formula (1) the constant C is determined only by the mechanical friction in the capillary [1]). We will call the constant, when this is assumed, k. For a given value of $y^* - y = u$ the formula can then be put [2]) in the form

$$\frac{du}{dT} = ku.$$

If u represents the displacement of the mercury meniscus for 1 cm. change of mercury pressure, then

$$\frac{du}{dT} = v_0 ,$$

hence also

$$v_0 = ku. \qquad \qquad (2).$$

The constant k is, as appears from formula (2), determined only by the magnitude of the displacement of the meniscus with a given change of pressure and the mechanical friction in the capillary; k can be calculated from u and v [3]).

Moreover k can be calculated in an entirely different manner viz: from 1st. the constants of the normal curves, recorded without and with resistance purposely inserted in the circuit, 2nd. the internal resistance of the capillary electrometer. For k is the con-

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[1]) Vid. on this point a former paper l.c.

We remind the reader that y and y^* denote the displacements from the zero position of the meniscus. In formula (1) we indicated as the cause of these displacements the change of P. D. between the poles of the capillary electrometer, the pressure in the capillary remaining constant. The formula remains unchanged if with a constant P. D. the displacements of the meniscus are caused by a change of pressure in the capillary.

[3]) In calculating k the difference between the friction of the sulphuric acid and of the mercury in the inferior part of the capillary has been neglected. It was supposed that the friction in the capillary electrometer equalled that in the capillary when totally filled with mercury. The error hereby introduced is but small and amounts only to a small percentage of the final result, see the more detailed publication.

stant of a normal curve that would have been recorded by a capillary electrometer if the internal resistance could have been annulled.

The double calculation of k has been made for two electrometers, and the results are united in Table II.

TABLE II.

Number of capillary-electrometer	$k=\frac{1}{a}=\frac{1}{\frac{1}{C_a}-p\cdot\frac{w_i}{0,1}}$ calculated from the normal curves and internal resistance of capillary electrometer.	$k=\frac{v}{u}$ calculated from friction in capillary and magnitude of displacement of meniscus by change of pressure
B. 102	4,59	4,95
B. 103	2,92	2,78

The agreement between the values of k in the two columns, obtained in so different a manner and which have required independent series of measurements is certainly quite sufficient.

According to HERMANN's theory we must have $C=\frac{h}{w}$, hence $k=\infty$.

Let us now consider more closely formula (1)

$$\frac{dy}{dT}=C(y^*-y)$$

and let us see in what manner the resistance in the circuit influences the value of C. Already on a former occasion [1]) the normal curves of capillary G 103 were examined, recorded with several resistances, purposely inserted in the circuit.

An increase of the resistance with 0,01 megohm gave an increase of $\frac{1}{C}$ 0,0025

An increase of 0,1 megohm increased $\frac{1}{C}$ . . 0,0255

An increase of 1 megohm increased $\frac{1}{C}$ . . . 0,2545

[1]) l. c. Bd. 60.

We see, that the increase of the value of $\frac{1}{C}$ varies directly as the increase of the resistance. Hence it follows immediately that,

$$\frac{1}{C} = a + bw ,$$

a and b being constants, determined by the properties of the instrument independent upon the internal ohmic resistance.

w represents the resistance in the circuit in megohms.

Hence our formula (1)

$$\frac{dy}{dT} = C(y^* - y)$$

now becomes

$$\frac{dy}{dT} = \frac{1}{a + bw}(y^* - y) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

For $w = 0$, is $\frac{1}{a + bw} = \frac{1}{a}$, hence the constant k is equal to $\frac{1}{a}$.

The constant b is the increase of $\frac{1}{C}$, when the resistance in the circuit is increased with 1 megohm.

In the subjoined table the values of a and b are given for four capillary electrometers.

TABLE III.

Number of the capillary.	a	b
G. 103	0,0741	0,225
B. 101	0,1599	0,1124
B 102	0,2181	0,166
B. 103	0,3429	0,5365

We may obtain a better insight into the action of the capillary electrometer in considering in which manner and to what amount the different forms of energy are transformed with a given displacement of the meniscus. For this purpose the following representation may prove of use in this connection.

Suppose that the drawn-out tube of the capillary electrometer, see fig. 1, is connected with two vertical tubes, *a* and *b*, filled with mercury and widened at the upper end. By means of the stop-cocks α and β the communication of *a* and *b* with the capillary tube can be stopped.

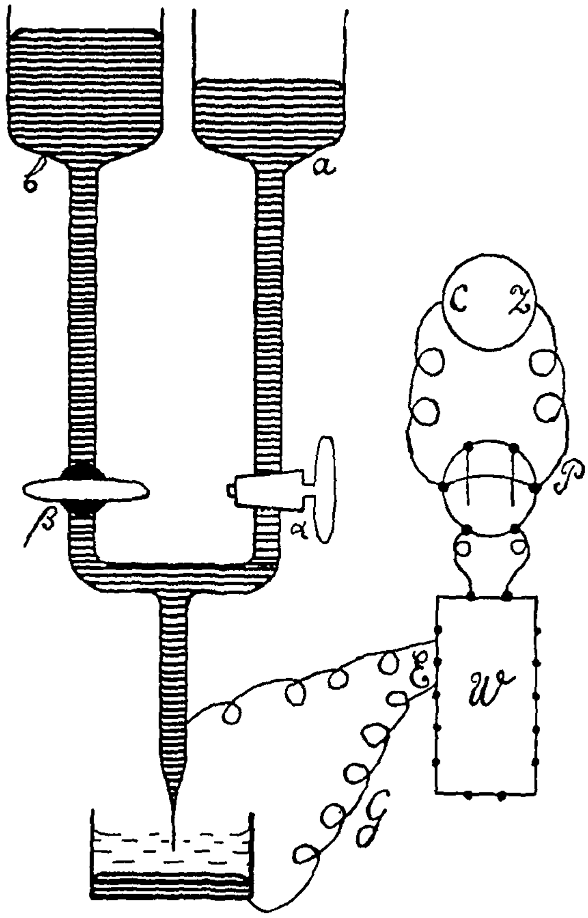

Fig. 1.

The poles of the capillary electrometer are connected by the conductor *G*. *W* is a resistance box, *CZ* a cell and *P* a POHL's mercury key insulating at the beginning the cell from the capillary electrometer, so that at *E* there is no P. D.

We think at the beginning stop-cock α opened, β closed: 1st position of stop-cocks. Let the meniscus have its equilibrium position at the height m_1 Suddenly the position of the stop-cocks is interchanged; 2d position of the stop-cocks. The meniscus will move, at first fast, then slower and will at last attain the equilibrium position m_2. If now the stop-cocks are placed again in their first position, then the meniscus will return also to its initial level m_1.

The work done in displacing the meniscus up and down is easily calculated. For the only final change in the apparatus is the passage of mercury from b to a. The quantity of mercury passed can be calculated from the section of the capillary tube d, the distance $m_1 - m_2$ and the specific gravity of the mercury s. This quantity is $M = ds(m_1 - m_2)$,

M being given in grams

d in square centimetres

and m_1 and m_2 in centimetres. Let the difference of level between a and b be n centimetres, then the work done is $A = nM$ gram-centimetres.

The potential energy of the displaced mercury is transformed into heat, partially by means of electric currents, partially by mechanical friction.

It merits attention that the amount A is not changed by changes in the resistance of the circuit G. An increase of the resistance causes retardation in the movement of the meniscus; the energy of mechanical friction is diminished, whereas that of electric currents is increased with the same amount.

If the stop-cocks have only changed the first for the second position and the meniscus has moved from m_1 to m_2, the energy of the heat produced is $= {}^1/_2\, A$; for the motion of the mercury in the capillary — viz. the cause of the mechanical friction and of the electric currents — is, while the meniscus returns from m_2 to m_1 in all phases perfectly equal — but of contrary direction — to the motion of the original displacement from m_1 to m_2.

Hence in first changing the position of the stop-cocks a quantity of energy must not have been transformed into heat, but must have accumulated as elastic tension in the meniscus. It is only in returning from m_2 to m_1, that the meniscus delivers its energy.

An analogous reasoning can be used if the meniscus is displaced by the sudden application of a constant P. D. between the poles of the capillary electrometer, the pressure in the capillary remaining unchanged.

If the P. D. E is applied by closing the key, see fig. 1, then there will be a temporary current in the circuit G. The work done by the current will be $Q = E \Sigma idT$ Joules, if E, i and T are, as usually, expressed in Volts, Ampères and seconds.

${}^1/_2\, Q$ is transformed into heat, whereas ${}^1/_2\, Q$ is accumulated in the meniscus as in a condensor in the form of an electric charge. If with circumstances as for the rest unchanged the applied P. D. — by opening of the key — is removed, the meniscus returns to its original position and delivers its energy, which once more is partially transformed into electric currents. The amount of $\Sigma\, idT$ in returning must be equal to $\Sigma\, idT$ in the original displacement. This was easily controlled experimentally.

The experiments which we have made with a sensitive high-resistance THOMSON-galvanometer, used as ballistic galvanometer, and kindly lent by Prof. KAMERLINGH ONNES, perfectly confirmed the statements given above.

The theoretical conclusions, that the value of the integral current increases directly as the P. D. used and that it remains unchanged with variation of the resistance of the circuit we could not rigorously prove by experiment because the time of oscillation of the galvanometerneedle was too small. The duration of a displacement of the meniscus was with some of the capillary electrometers a considerable part of the oscillation time of the galvanometer [1]).

Yet the results of the galvanometer experiments are far from unsatisfactory as may be proved from the data concerning capillary *B* 102 in the subjoined tables IV and V.

TABLE IV.

Difference of potential.	Mean deflection with suddenly applied P. D.	Mean deflection with suddenly removed P. D.	Mean deflection calculated per 1 millivolt. e_1.
40 millivolt.	10,5 mm.	10,6 mm.	0,264 mm.
100 "	28,5 "	28,5 "	0,284 "

TABLE V.

Resistances introduced in the circuit.	Mean deflection of the galvanometer with applied constant P. D.
6000 Ohm	35,5 mm.
0.4 Megohm	34 "
1	31,5 "

[1]) It proved unpracticable to arrange the galvanometer for large period. The damping soon became excessive.

The columns 2, 3 and 4 of Table IV give the mean values, obtained from experiments with the mercury as positive pole and the sulphuric acid as negative pole and reciprocally. Usually the deflections, calculated for 1 millivolt at first slightly increased with increasing P. D. then reached a maximum and further decreased.

On account of the above mentioned relatively too short oscillation time of the galvanometer, the maximum value of e_1 probably will be the most accurate for calculating the work done, we therefore will make use only of the maximum.

The values in column 2 of Table V are obtained only with mercury as the positive pole, sulphuric acid as negative pole. They represent the means of observations with suddenly applied and suddenly annulled P. D.

For three capillary electrometers I have calculated the work necessary for the motion up and down of the meniscus, the difference of potential being $E = 1$ millivolt.

The calculation always was made in two different manners, in the first place from mechanical principles using the difference of pressure, necessary for the displacement and the dimensions of the capillary; in the second place from electrical principles using the deflections of the galvanometer, see Table VI.

TABLE VI.

Number of the capillary.	Work done as calculated from dimensions of the capillary-electrometer and the manometer readings		Work done calculated from galvanometer readings in Joules.
	in gram-centim.	in Joules.	
B. 101	$1,282 \times 10^{-9}$	$1,258 \times 10^{-13}$	$1,405 \times 10^{-13}$
B. 102	2,209 " "	2,162 " "	2,137 " "
B. 103	8,05 " "	7,9 " "	6,16 " "

The agreement between the values of columns 3 and 4 of the given Table VI, though not very beautiful may yet be called satisfactory considering the different measurements necessary in calculating the result.

Concluding, we will see what part of the work done is spent in surmounting the mechanical friction, what part for the production of electric currents.

Let the total quantity of heat developed in a complete up and down motion of the meniscus by the sudden application and annulling of a given P. D. be A, the heat produced by mechanical friction A_1, by electric currents A_2, then

$$A = A_1 + A_2 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

Let the initial velocity of the meniscus after the application of the given P. D. be v_0, then is

$$v_0 = \frac{dy_0}{dT}.$$

Formula (3) reading

$$\frac{dy}{dT} = \frac{1}{a + bw} (y^* - y),$$

becomes for $y = 0$

$$v_0 = \frac{dy_0}{dT} = \frac{1}{a + bw} \cdot y^* .$$

A_1 varies directly as v_0 hence with a given value y^*, also as $\frac{1}{a + bw}$. Therefore we write

$$A_1 = \zeta \cdot \frac{1}{a + bw} \quad . \; . \; . \; . \; . \; . \quad (5)$$

ζ being a constant.

For $w = 0$ the heat produced by mechanical friction becomes equal to the total work. The last remains the same for every value of w, hence we may put

$$A = \zeta \cdot \frac{1}{a} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (6)$$

From the formulae (5) and (6) follows

$$\frac{A_1}{A} = \frac{a}{a + bw} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (7)$$

and from (6) and (7)

$$\frac{A_2}{A} = \frac{bw}{a + bw} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

In the subjoined table are given for a few capillary electrometers, examined without purposely inserted resistance the values of A_1 and A_2 in percentages of A.

TABLE VII.

Number of the capillary.	$100 \times \frac{A_1}{A}$	$100 \times \frac{A_2}{A}$
G. 103	91	9
B. 101	92	8
B. 102	93	7
B 103	96	4

In the course of these experiments valuable assistance has been given by Mr. H. W. BLÖTE and Mr. H. K. DE HAAS.

Botanics. — Prof. BEIJERINCK speaks: "*On the Formation of Indigo from the Woad (Isatis tinctoria)*" [1]).

Some years ago I wished to become acquainted with the so-called "indigo-fermentation", about which nearer particulars had been communicated by Mr. ALVAREZ. He examined *Indigofera* and says:[2]).

"If a decoction of the plant is prepared and sterilised atfer passing it into test-tubes or PASTEUR's-flasks, the reddish colour of

[1]) It was first my intention to treat „On the function of enzymes and bacteria in the formation of indigo." I have declined this plan for the moment, and give now only part of my experiments, because I see that also Mr. HAZEWINKEL, of the Experimentstation for Indigo at Klaten, Java, has obtained important results about that very subject, which results, for particular reasons, have however been imparted till now to a few experts only. Yet I cannot avoid mentioning some facts, found by me, the priority of which perhaps pertains to Mr. HAZEWINKEL, without my being able to acknowledge his claim. One indiscretion, however, I am obliged te commit: Mr. HAZEWINKEL has, already before me, established the fact, that by the action of the indigo-enzyme and of acids on indican, indoxyl is produced.

[2]) Comptes rendus T. 105, pag. 287, 1887.