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$$v - b' = v - b_1 - x_2 \Delta_2 b + v \cdot \frac{1}{2} x_2.$$

In this the infinitesimal quantity  $x_2 \Delta_2 b$  (also when  $\Delta_2 b$  is finite) may be neglected by the side of  $b_1$  and the also finite quantity  $v \cdot \frac{1}{2} x_2$ , and we get:

$$b' = b_1 - v \cdot \frac{1}{2} x_2,$$

identical with (3) of § 3. For  $v \cdot \frac{1}{2} x_2$  the value  $R : C_2$  follows then again from ( $\epsilon$ ), and the conclusions are further as in the cited paragraph.

*Fontanivent sur Clavens.*

**Chemistry.** — “*Current Potentials of Electrolyte solutions*”. By Dr. H. R. KRUYT. (Communicated by Prof. ERNST COHEN).

(Communicated in the meeting of June 27, 1914).

1. For a proper understanding of the reciprocal action between electrolytes and colloids the knowledge of the capillary-electric phenomena is indispensable<sup>1)</sup>. Researches on the influence of the electrolyte concentration in these phenomena have indeed been carried out of late years; PERRIN<sup>2)</sup> and ELISSAFOFF<sup>3)</sup> studied the electric endosmose of electrolyte solutions, BURTON<sup>4)</sup> determined the influence of electrolytes in various concentrations on the cataphoresis whilst there already exists a vast material on the capillary-electrometer and the dropping electrode<sup>5)</sup>. The recent investigations were, therefore, chiefly concerned with the measurement of the phenomena of motion in consequence of a supplied electric tension; the reverse phenomenon, however, namely the occurrence of an electric tension in consequence of a moving electrolyte solution has been but little studied<sup>6)</sup>. The former investigations on these current potentials (generally, though less accurately, called “Strömungsströme”) are restricted to pure water. True, CHWOLSON<sup>7)</sup> states that electrolyte solutions cannot produce current potentials, but from the quoted treatises of GOURÉ DE VILLEMONTÉE<sup>8)</sup> it appears that the latter only

<sup>1)</sup> For full details of this problem see H. FREUNDLICH, *Kapillarchemie*, Leipzig 1909 in very condensed form H. R. KRUYT, *Aanteekeningen Prov. Utr. Gen.* 3 June 1913 p. 9 and *Chem. Weekbl.* 10, 524 (1913).

<sup>2)</sup> *Journal de Chimie physique* 2, 601 (1904).

<sup>3)</sup> *Z. f. physik. Chem.* 79, 385 (1912).

<sup>4)</sup> *Phil. Mag.* [6] 11, 425; 12, 472 (1905) and 17, 583 (1909).

<sup>5)</sup> Detailed literature statements in CHWOLSON, *Lehrbuch der Physik* IV 1.

<sup>6)</sup> The most important investigations of recent times are those of CAMERON and OETTINGER, *Phil. Mag.* [6] 18, 586 (1909); GRUMBACH, *Ann. de chim. et de phys.* [8] 24, 433 (1911) and RIÉTY, *ibidem* [8] 30, 1 (1913).

<sup>7)</sup> *l. c.* note 5.

<sup>8)</sup> *Journ. de phys.* [3] 6, 59 (1897).

investigated solutions of  $\text{CuSO}_4$ ,  $\text{ZnSO}_4$  and  $\text{NiSO}_4$  in the concentration of 10 grams per litre. Because current potential and electro-osmosis are so to say each other's reflected image <sup>1)</sup>, one may rather expect that the electrolyte concentration will make itself felt in a similar manner in regard to those two phenomena. As ELISSAFOFF (l. c.) found that even exceedingly feeble electrolyte concentrations strongly diminish or suspend\* the electro-osmotic transport, we can only assume from the negative result of GOURÉ DE VILLEMONTÉE that in the concentrated solutions used by him the potential is already lowered to about zero. RIÉTY's result <sup>2)</sup> have also confirmed this conclusion.

GRUMBACH <sup>3)</sup>, who investigated the influence of non-electrolytes on the current potential, has not used pure water as comparison liquid but a KCl-solution of the concentration 1 millimol. per litre and in this manner obtained positiv results. In the investigation here described I have made use in many respects of the experimental methods mentioned in GRUMBACH's paper.

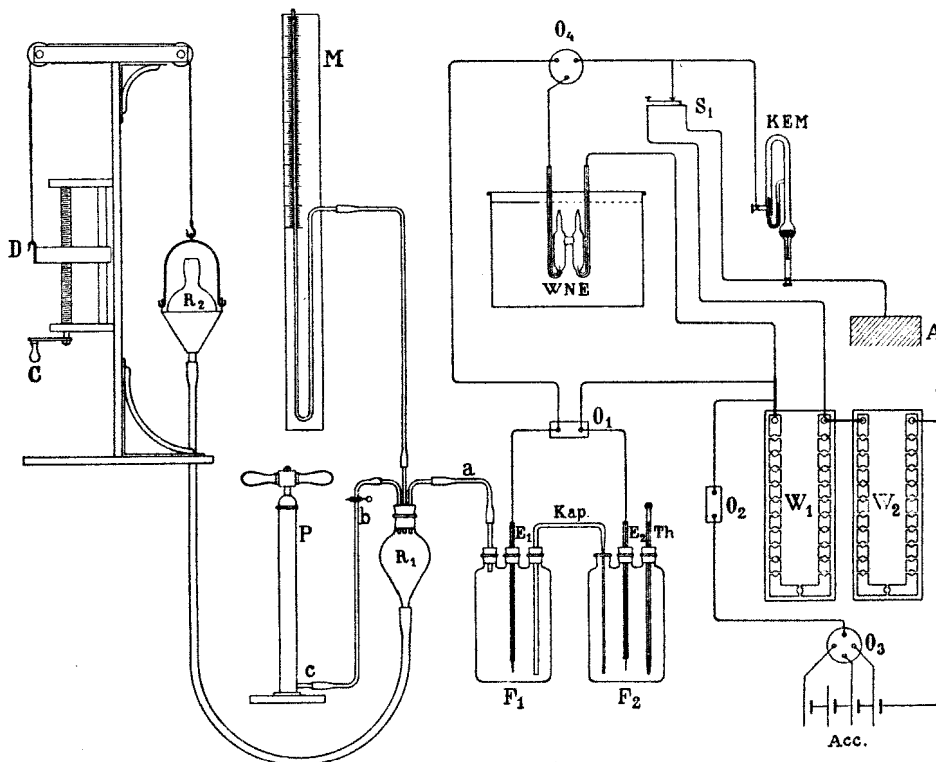


Fig. 1.

<sup>1)</sup> Vgl. SAXÉN, Wied. Ann. 47, 16 (1892).

<sup>2)</sup> l. c.

<sup>3)</sup> l. c.

2. *Apparatus.* In fig. 1 the apparatus used is represented schematically. The liquid serving in the experiment runs from flask  $F_1$  into flask  $F_2$  through a doubly bent glass tube  $Kap$ , which is partly drawn to a capillary. Into the three-necked WOLFF flask  $F_1$ , which is closed by means of rubber stoppers with copper wire ligature, arrives also (1) a tube  $a$  through which air can be pressed and (2) an electrode  $E_1$ . In the other flask  $F_2$  is found an electrode  $E_2$  and a thermometer  $Th$ . The electrodes are Ag-AgCl electrodes. A silver wire is fixed into a glass capillary by means of CAILLETET-wax. The protruding end is electrolytically covered with AgCl according to the indications given by JAHN<sup>1)</sup>.

A constant pressure above the liquid in flask  $F_1$  is obtained as follows: by means of a cycle foot-pump mercury can be pressed from the reservoir  $R_1$  into  $R_2$ ; the pressure thereby generated is read off on the open mercury manometer. As owing to the transferring of the liquid from  $F_1$  to  $F_2$  the pressure would diminish a little during the experiment, it is kept constant by means of the arrangement  $CD$  by turning the handle  $C$ .

The measurement of the potential differences between the electrodes  $E_1$  and  $E_2$  was carried out by the compensation method of POGENDORFF-DU BOIS REYMOND. A galvanometer could not be used as a zero instrument because the strength of the current passing through the instrument is exceedingly small in consequence of the enormous resistance in the battery  $F_1F_2$ . Hence, a capillary electrometer ( $KEM$  in fig. 1) was used, which was fixed to the object table of an ordinary microscope; the axis of the microscope was, of course, placed horizontally. The readings were made using of an ocular-micrometer, objective 4c (REICHERT) and HUYGENS ocular 1.

The following serves to further explain the figure.  $S_1$  is a key for cutting off the short circuit of the capillary electrometer;  $A$  indicates that this is connected with the earth. As working element are used one or more accumulators  $Acc$  whose tension was determined by comparison with a WESTON standard-cell, which was placed in a thermostat at 25° (WNE). By  $O$  the different current interrupters are indicated; by  $O_1$  the electrodes  $E_1$  and  $E_2$  can be brought into short circuit, which was always done during the time that no observations were made. By  $O_2$  the current of the working cell is twitched in;  $O_3$  annables to introduce at will one, two or four accumulators as a compensation battery.  $O_4$  renders it possible to take up in the circuit either the standard cell or the battery  $F_1F_2$ .

1) Zeitschrift f. physik. Chem. 33, special page 556 (1900).

In order to protect the Ag-AgCl-electrodes from the light, the flasks  $F_1$  and  $F_2$  are externally coated with a film of red gelatin obtained by inserting them in a solution of gelatin to which a little eosine had been added and which had just started to gelatinise. Moreover, they were always protected from direct daylight.

3. *Method and preliminary experiments.* The measurements were made a few minutes after the pressure had set in. A number of measurements at different pressures were always made. When between two measurements the liquid had to be pressed back from flask  $F_2$  to flask  $F_1$  (for which at  $a$  the connection with the pressure arrangement could be broken off and an oil suction pump attached), no measurements were executed at suction pressure.

From GRUMBACH'S experiments we notice that the value of the current potentials varies a little during the first days after the construction of a battery  $F_1F_2$ . I repeated one of his observations, also with the object of comparing the results obtained with his and my own apparatus.

Table I contains the results of a series of measurements carried

TABLE I.

$P$ cm mercury	$E$ millivolts	$\frac{E}{P}$	$P$ cm mercury	$E$ millivolts	$\frac{E}{P}$
11 March	$t = 14^\circ$		62.2	253	4.1
61.2	271	4.4	51.2	218	4.3
86.4	367	4.2		average	4.1
54.8	236	4.3	14 March	$t = 16^\circ$	
70.8	315	4.4	82.2	310	3.8
	average	4.3	85.2	323	3.8
12 March	$t = 13^\circ$		72.2	280	3.9
48.2	201	4.2	60.8	236	3.9
57.2	240	4.2		average	3.9
68.1	280	4.1	16 March	$t = 14^\circ$	
	average	4.2	86.2	341	4.0
13 March	$t = 14^\circ$		70.2	284	4.0
85.2	350	4.1	58.8	240	4.1
73.2	302	4.1		average	4.0

out with a solution of the concentration 1 m. Mol.  $KCl$  per Liter. The battery was filled March 11<sup>th</sup>.  $P$  indicates the pressure,  $E$  the current potentials.

From this we notice that the apparatus acted splendidly. The potential per cm. mercury pressure has each day a constant value, but varies the first two days. On the third day the terminal value is attained.

4. *Measurements.* In this paper a series of measurements is communicated, the object of which was to ascertain the influence of some solutions which differed in the valency of the cation. Therefore solutions of the chlorides of  $K'$ ,  $Ba''$ , and  $Al'''$  were used. As solvent was always used so-called "conductivity water". The very dilute solutions were made by diluting a standard solution. All measures used in this investigation were carefully calibrated or recalibrated.

In order to shorten the time of these tedious measurements they were all executed 20 hours after filling the cell. True, the constant terminal value is then not yet attained, but the difference is comparatively small and the error introduced is the same in all measurements. Moreover, the inaccuracy caused thereby is without influence on the tendency of the conclusions presently to be drawn, in itself a good reason for proceeding to this measure of enormous time saving. Moreover, several sets of flasks were used, in such a manner however that, for instance, all the  $KCl$  solutions were measured in the same set. Finally, the sets were compared mutually in which the solution of 100  $\mu$  Mol. (micromol =  $1/1000$  millimol)  $KCl$  p. L. served as comparison liquid. With both apparatus was found exactly the same value for the potential per unit of pressure.

In the subjoined tables, the concentrations in the first column are given in  $\mu$  mols. p. L.; in the second column is found the current potential  $E$  in millivolts per unit of pressure (cm. of mercury) under which the liquid was forced over. This value is always the mean of two or more measurements whose differences were of the order of those in Table I (generally much less than those).

When in the tables no sign is indicated at the potential value, the condition (as with pure water) is such that the electrode  $E_1$  in fig. 1 is negative. In the  $AlCl_3$  solutions a change of poles took place, hence the potentials following are indicated by  $+$ .

The results of the tables II, to IV are represented graphically in fig. 2. Fig. 3 also gives the curve for  $AlCl_3$  on a larger scale.

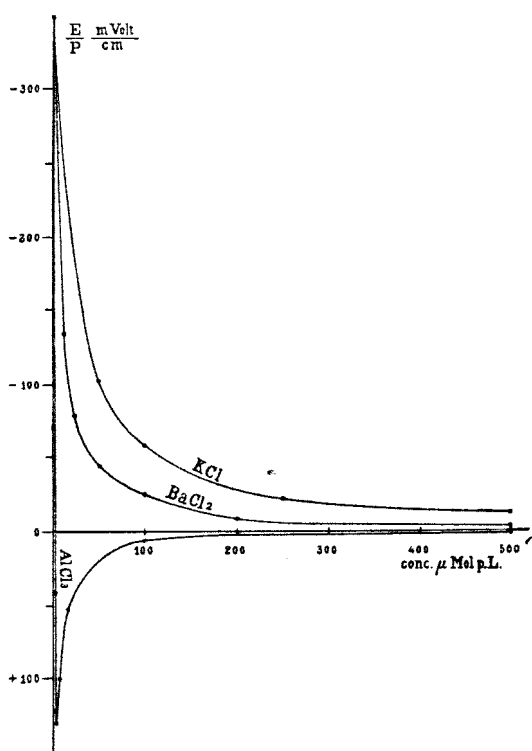


Fig. 2.

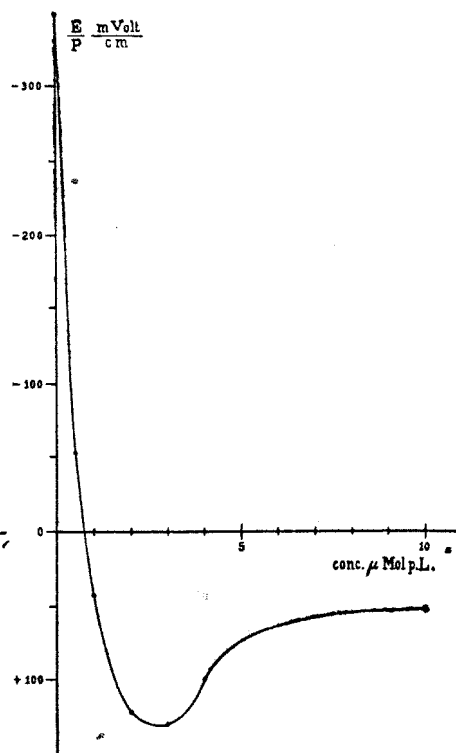


Fig. 3.

TABLE II

KCl	
Conc. in $\mu$ Mol p. L.	$\frac{E}{P}$
0	about 350
50	102
100	57
250	23
500	12
1000	4

TABLE III

BaCl <sub>2</sub>	
Conc. in $\mu$ Mol p. L.	$\frac{E}{P}$
10	139
25	79
50	44
100	25
200	9
1000	1
40000	no exchange of poles

TABLE IV

AlCl <sub>3</sub>	
Conc. in $\mu$ Mol p. L	$\frac{E}{P}$
0	about 350
0.5	52
1	+ 42
2	+ 122
3	+ 129
4	+ 100
10	+ 52
100	+ 6
500	+ 1.4

5. On considering these results we notice, of course, first of all the great influence of the valency of the cation; as this gets higher the capillary gets more strongly discharged at an equal concentration. This had also been observed by ELISSAFOFF when measuring the electric endosmose and may be noticed with RIÉTY from his experiments with uni- and bivalent ions. The latter has observed a change of poles only once, namely with copper nitrate and that only at a high concentration<sup>1)</sup>. In the case of AlCl<sub>3</sub> about 0.8  $\mu$  mol. or *about 0.1 mg. per liter appears to be sufficient* to lower the current potential from about 350 mV. to zero. It seems remarkable that this charge reversal does not take place with BaCl<sub>2</sub> (see Table III) neither with ZnSO<sub>4</sub> or CuSO<sub>4</sub> (RIÉTY) nor with substances with a univalent cation.

Still more striking is the fact that according to ELISSAFOFF, the electro-endosmotic transport requires, in a glass capillary, 100 micromols of Al<sup>+++</sup> to be reduced to 0 without a reversal occurring, whereas the same investigator, although attaining the zero point, with a quartz capillary, at about the same concentration as required in our research [he found 1.6  $\mu$  mol.  $\frac{1}{2}$  Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>] could not even then notice a reversal of the transport direction. This creates the impression that

<sup>1)</sup> The exact concentration cannot be made out from his experiments. In any case, however, it lies above 900  $\mu$  mol p. L.



in that research secondary influences come to the fore; perhaps the powerful electric field in which the measurements are executed is not without influence on the capillary itself. Only the quadrivalent Th<sup>4+</sup>-ion was capable of causing a charge reversal.

The results obtained here are in harmony with the general theoretical points of view. The electric double layer in the capillary, in the case of pure water consists of 'OH-ions at the side of the glass wall and 'H-ions at the side of the liquid in consequence of the selective ion adsorption of the glass wall which always adsorbs the 'OH-ion more strongly. From the electrolyte solutions the cations are absorbed more eagerly than the anions so that the charge gets lowered. If this adsorption for KCl, BaCl<sub>2</sub> and AlCl<sub>3</sub> is such that solutions of the same molecular concentration are absorbed about equally, it is conceivable that the three times more active Al<sup>3+</sup>-ion requires a much lesser concentration than the K<sup>+</sup>-ion in order to attain an equal potential reduction.

If once the capillary is charged reversely the adsorption of the Cl<sup>-</sup>-ion, which carries a charge now opposite to that of the capillary, seems to predominate. The positive charge now soon attains (at 3  $\mu$  mol.) a maximum value, and then decreases, but only slowly, because the discharging ion is univalent here.

In agreement with the theory are also the results of RIÉTY<sup>1)</sup>, for instance that the salt of a heavy metal has a stronger discharging action than that of a lighter one (Cu and Zn, at least in the small concentrations). A cation of a heavy metal is known to be adsorbed more strongly than that of a light one.<sup>2)</sup>

Moreover, the behaviour in the case of CuSO<sub>4</sub> and of Cu(NO<sub>3</sub>)<sub>2</sub> is in agreement with investigations as to the adsorbability of those salts<sup>3)</sup>. The influence of the anions is also observable in RIÉTY's results and appears to have an effect corresponding with that in the case of AlCl<sub>3</sub> just described.

The question whether the organic cations also behave according to the theoretical expectations is being considered. Several other solutions of electrolytes in water as well as in mixed solvents<sup>4)</sup> will be investigated.

*Utrecht, June 1914.*

*VAN 'T HOFF-Laboratory.*

<sup>1)</sup> l. c.

<sup>2)</sup> MORAWITZ, Koll. Beih. 1, 301 (1910).

<sup>3)</sup> FREUNDLICH and SCHUCHT, Z. f. physik. Chem. 85, 641 (1913).

<sup>4)</sup> Of these have also already been measured a few series in connexion with the researches of KRUYT and VAN DUIN, Koll. Beih. 5, 269 (1914).