would be smaller than for the movement under constant force. The observations are too rough for quantitative calculations, but the differences of $m_{calc.}$ and $m_{meas.}$ are too great and too much in one direction to be attributed to errors of observation.

Amsterdam.   *Physical Laboratory.*

Chemistry. — *"Current Potentials of Electrolyte solutions."* (Second Communication). By Prof. H. R. KRUYT. (Communicated by Prof. ERNST COHEN).

(Communicated in the meeting of January 27, 1917.)

1. In a former paper [1]) I communicated a series of measurements with respect to the influence of dissolved salts on the current potential, after having made investigations with solutions of the chlorides of potassium, barium and aluminium. These salts were chosen, because they are electrolytes with resp. a monovalent, a bivalent and a trivalent cation. In Tables 2 and 3 similar results are given for investigations made with hydrochloric acid and the chloride of p-chloro-anilene. A standard solution of HCl was prepared by conducting gaseous hydrochloric acid in "conductivity water"; to get the solution of $p\,ClC_6H_4NH_2 . HCl$ KAHLBAUM's $p\,ClC_6H_4NH_2$ was dissolved in water containing the equivalent quantity of HCl from the solution first mentioned.

The results given in Tables 2 and 3 show the decrease of the current potential to be here much larger than in the case of potassiumchloride (cf. Table 1, columns 1 and 2). This result is in perfect agreement with the investigations on electric endosmosis (for literature, see my first communication), and it can be easily understood when we suppose, as FREUNDLICH does, that these phenomena are in close relation with the adsorption of the ions: the H-ion, and also the organic ions (especially aromatic ones) are adsorbed in a greater amount than those of the light metals. A comparison of Tables 2 and 4 shows, that the monovalent H-ion and the bivalent Ba-ion bring about nearly the same lowering of the current potential.

2. A comparison between the electric charges of the capillary tube is still of more importance than that of the current potentials especially with regard to the problems of colloid-chemistry [2]).

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[1]) These Proceedings 17, 615 (1914).
[2]) See H. R. KRUYT, These Proceedings 17, 623 (1914).

According to HELMHOLTZ' theory the electric charge is proportional to the product of the current potential and the conductivity of the flowing liquid [1]. This electric charge ε is dependent on the electric

TABLE 1.

Potassiumchloride (K)			
Conc. μ Mol p. L.	$\dfrac{E}{P}$	$\varkappa \cdot 10^5$	$\varepsilon \cdot 10^3$
0	ca. 350	—	—
50	102	0.65	19.9
100	57	1.3	22.4
250	23	3.2	23.0
500	12	6.4	23.3
1000	4.0	12.7	15.4

TABLE 2.

Hydrochloric acid (H)			
Conc. μ Mol p. L.	$\dfrac{E}{P}$	$\varkappa \cdot 10^5$	$\varepsilon \cdot 10^3$
0	ca. 350	—	—
25	77	0.95	22.1
50	43	1.9	24.8
100	22	3.8	25.4
250	7.7	9.5	22.1
500	3.1	18.8	17.5
1000	1.2	37.6	13.6
50000	0 no change of pole	—	—

TABLE 3.

p Chloro-Anilenechloride (An)			
Conc. μ Mol p. L.	$\dfrac{E}{P}$	$\varkappa \cdot 10^5$	$\varepsilon \cdot 10^3$
0	ca. 350	—	—
31	114	0.4	13.9
62	65	1.0	19.6
124	26	2.1	16.6
310	12.2	3.9	14.5
500	4.9	8.0	11 8
1000	1.8	14.7	9.7

TABLE 4.

Bariumchloride (Ba)			
Conc. μ Mol p. L.	$\dfrac{E}{P}$	$\varkappa \cdot 10^5$	$\varepsilon \cdot 10^3$
0	ca. 350	—	—
10	139	0.24	10
25	19	0.60	14.2
50	44	1.20	16.0
100	25	2.4	18.1
200	9	4.7	12.7
1000	1.1	23.1	7.6

[1] I seize this opportunity to make a slight emendation to p. 625 of the paper mentioned above. In the equation (2) I confounded the letters b and k; in the conclusion, printed in italics, "inversely" should be omitted (or "conductivities" should be read instead of "resistances"). The calculations in the paper are however correct in respect to this alteration.

moment M of the double layer, according to:

$$\varepsilon = 4\,\pi M$$

and

$$M = \frac{E}{P} \cdot \eta \cdot \varkappa$$

where η is the viscosity and $\varkappa$ the specific conductivity of the flowing liquid. We can consider the viscosity of the liquids used to be equal to that of water; the conductivity $\varkappa$ has been measured in each case. The results showed a discrepance with those calculated from KOHLRAUSCH' data of only 1 to 2×10^{-6} Ohm^{-1}; as I measured the conductivity of the water I found it to be from 9×10^{-7} to 2×10^{-6} Ohm $^{-1}$. In the Tables 1, 2, and 4 the conductivities are those calculated according to KOHLRAUSCH; only in Table 3, for p ClC$_6$H$_4$NH$_2$HCl, I give the results of my own measurements. [1])

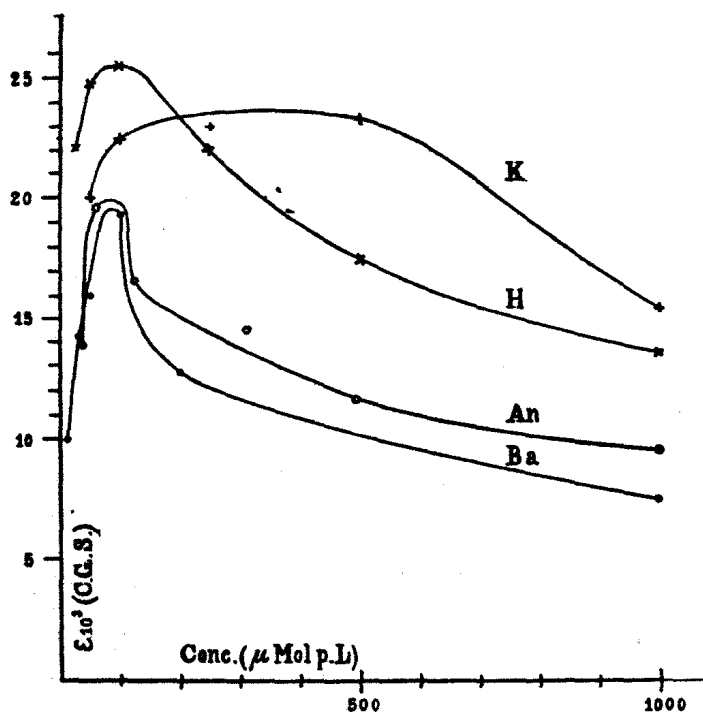To calculate ε, I reduced all the values to c.g.s.-units; therefore I had to multiply:

Fig. 1.

65*

$$\frac{E}{P_{\iota}} \text{ in } \frac{\text{millivolt}}{\frac{\text{cm.Hg}}{\text{cm}^2.}} \quad \text{by} \quad \frac{10^{-3} \times \frac{1}{3} \times 10^{-2}}{13.6 \times 981}$$

$$\varkappa \text{ in Ohm}^{-1} \text{ by } 9 \times 10^{11}$$

η was put to 0.0108 dyne.

In the last column of the Tables 1--4 the electric charge of the capillary tube is given per cm² in c.g.s.-units. Fig. 1 represents the relations between this charge and the concentration of the liquid flowing through the capillary tube.

3. From these results we may infer that each of these four electrolytes can effect a greater charge to the capillary tube than pure water can; only when an optimum charge is reached, higher concentrated solutions lower the charge.

In .the chemistry of colloids much attention has been paid until now to the fact that electrolytes lower the potential of contact; this now appears to be true only for solutions of higher concentration. It is remarkable that in all four cases, mentioned in the Tables 1— 4, the current potentials are lowered by the electrolytes, but that the contact potentials are modified in the peculiar way with an optimum value. [1]

A short time after the publication of my previous paper on this subject, FRANK POWIS [2] of DONNAN's laboratory communicated (Nov. 1914) a most interesting investigation about the influence of electrolytes on the cataphoresis of oil-emulsions. The similarity of our results is striking; therefore we came in many respects to the same conclusions [3]. When calculating the contact-potential for oil and water resp. for glass and water, Powis found an optimum only in the case of the monovalent cation of potassium, but it is clear from our Fig. 1 that he could not have observed such a value as regards Ba as he has made no measurements of solutions with a concentration below 200 μ Mol BaCl₂. We may now draw the conclusion that the difference between a monovalent and a bivalent cation is only quantitative and not qualitative.

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[1] It is impossible to make out if the optimum is present in the case of AlCl₃. As $\frac{E}{P}$ has reached the value zero at 0.8 μ Mol, the optimum should appear at a still smaller concentration. I regard the data to be insufficient to decide whether we are dealing here with an optimum or not.

[2] Z. f. physik. Chem. **89**, 91 (1915).

[3] We gave a.o. the same criticism on the theory of irregular series of floculation. With regard to the way in which the final value is reached in each case, I found the same progress, as Powis describes (l.c p. 179).

The less recent researches of ELLIS[1]) do not clash with my results either; he found an optimum only in the case of NaOH, but if we pay attention to the concentrations of his experiments it is clear again that it was impossible for him to have observed the other maxima.

The relation between the four curves in our fig. 1 is most remarkable from the point of view of colloid chemistry. It is well known that all anorganic ions are adsorbed in nearly the same molecular concentration with exception only of the ions H and OH (and those of the heavy metals). Considering that the Cl-ions have a tendency to give a higher charge to the adsorbing surface, we can easily understand that the ion of potassium causes much less resistance to the increase of the negative charge than the highly absorbative ions of H and $pClC_6H_4NH_2$ and the Ba-ion, which is absorbed in a normal way, but bears the double electric charge. Therefore we find with KCl a plain optimum, which is noticeable even in rather strongly concentrated solutions; with the other three ions the optimum is reached at a concentration from $50-100\,\mu$ Mol and the curve is rather pointed, especially with the anilene- and the Ba-ion. POWIS' results regarding the influence of the anions and ELLIS' regarding that of the OH-ion are in agreement with these conclusions.

It is worth observing that the charges of contact for the different electrolytes at a certain concentration show the same sequence as the corresponding limit values with colloids, but only at concentrations somewhat higher than those of the maxima. The descending branches e. g. at a concentration of $1000\,\mu$ Mol. p. L. show the sequence K·, H·, An· and Ba··; the limit values[2]) for the floculation of the As_2S_3 sol are (m. Mol p. L.)

$$KCl50 \quad HCl\ 31 \quad pClC_6H_4NH_2HCl\ 1.08$$

$$BaCl_2\ 0.69.$$
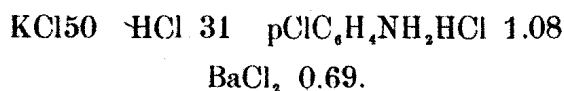
To test a quantitative relation between electric charge and limit value (as I tried to do in a previous paper) it is necessary to make use only of the values of the descending branches of fig. 1. For that purpose a close investigation of these branches will be necessary but cannot be made with the apparatus I have used till now. I hope that I shall be able before long to continue these researches with an apparatus fit for experiments at higher pressures.

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[1]) Z. f. physik. Chem. I **78**, 321 (1912); II **80**, 597 (1912); III **89**, 145 (1915).
[2]) FREUNDLICH, Kapillarchemie p. 351 (Leipzig 1909).

4. In the chemistry of colloids one often meets with facts which can be explained by the result of these investigations, viz. that the contact potential in a very diluted solution is higher than in pure water.

The stability of suspensoids is a function of the electric change of the suspended particles [1]. In literature "stabilising ions" are often mentioned; it is well known that a suspensoid sol free from all electrolytes has but little stability, a long dialyzing often causes floculation. [2] The importance of these traces of electrolytes can now easily be understood in connexion with this investigation: though greater amounts of electrolyte lower the potential of contact and so cause floculation, when the critical potential is reached, extremely low concentrations increase the electric charge and at the same time the stability. Of course they are absolutely necessary when the contact potential in pure water is lower than the critical potential of the sol and when the optimum in the potential curve is higher than that critical value. As the presence of some electrolyte generally seems to be necessary for a stable sol, we may conclude the potential in pure water to be ordinarily rather low. The current potential, it is true, may be high, this is only a consequence of the enormous electrical resistance of this liquid. In the Tables above-mentioned we have not calculated ε for pure water as the value $\dfrac{E}{P}$, ca 350 m.V., is not exact, the enormous resistance in the cell lowering the exactness of the measurement too much. When we put $\varkappa$ to 9×10^{-7} (this was indead the case with the water when freshly prepared) the electric charge of the tube would be less than 0.01 c.g.s units.

5. The result of this investigation, that an optimum in the curve for the contact potentials may be generally received, draws our attention to the change of our knowledge about the iso-electric phenomenon. In fig. 2 A, B, and C the concentrations are given as abscissae, the contact potentials being ordinates. The axis of ordinates is erected in the iso-electric point, so we have the alcalic liquids on the left, acid liquids on the right. Fig. 2 A

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[1] I think Powis [Z. f. physik. Chem. **89**, 186 (1914)] is quite right when he concludes that spontaneous floculation does not occur at the potential zero but at a certain "critical" value. In fig. 1 of my communication [these Proceedings **23**, 623 (1914)] the same supposition is represented graphically.

[2] A great many examples may be found in Svedberg's work: Methoden zur Herstellung kolloider Lösungen anorganischer Stoffe (Dresden 1909).
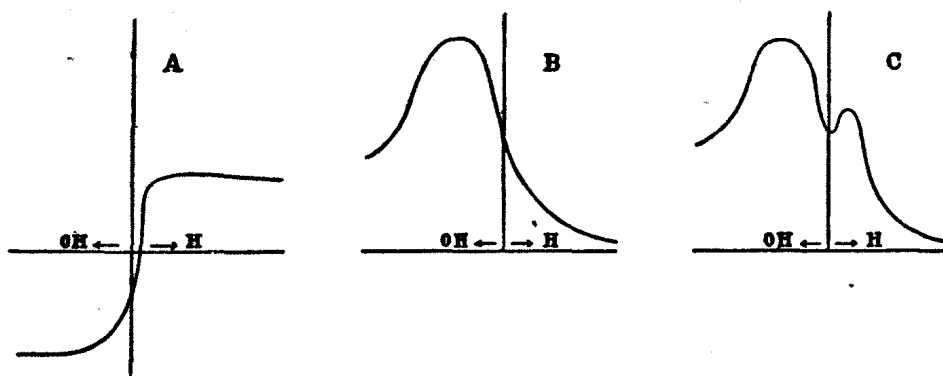
Fig. 2.

illustrates Perrin's [1]) results, as he measured the electro endosmosis of a naphtalene membrane. Fig. 2B shows the results of Ellis' investigations [2]) and Fig. 2C completes that representation by adding the results of this communication. It is still difficult to give a decision whether the minimum lies exactly at the iso-electric point or not.

6. Finally we must inquire into the cause of the increase of the electric charge in diluted solutions and we have to look for points of agreement with the theory of selective adsorption of ions. Powis [3]) too discussed this question.

The adsorption of ions by a surface with an electric charge of the same sign as that of the ions does not form an exceptional case. Lately Freundlich and Poser [4]) mentioned a similar phenomenon when studying the adsorbents with positive and negative electric charge. [5])

They found bolus (negative charge) did not adsorb dye-anions but that aluminium oxide did adsorb cations, some of them (chrysoidin, malachit green) even to a high degree.

"Dies erklärt sich unserer Meinung nach einfach damit, dass die adsorbierende Oberfläche keineswegs mit dem aktiven Elektrolyten, der die Ladung bedingt — gesättigt zu sein braucht; sie kann also sehr wohl neben diesem Stoff noch weitere adsorbieren, genau wie etwa Kohle, die eine nicht zu grosse Menge Benzoesäure adsorbiert hat, noch Oxalsäure aufzunehmen vermag" (p. 318).

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[1]) Journ. de chim. phys. **2** 601 (1904).

[2]) loc. cit. spec. I p. 348 and II p. 606.

[3]) Z. f. physik. Chem. **89**, 103—105, (1915).

[4]) Koll. Beih. **6**, 297 (1914).

[5]) Michaëlis and Lachs, Z. f. Elektrochemie **17**, 1 (1911), as well as Kruyt and van Duin, Koll. Beih. **5**, 269 (1914) found that negatively charged charcoal adsorbed more Cl than K out of a KCl solution.

The same could be the case with the surface of the glass tube. In the iso-electric point only a minimal concentration of anions (the OH ions of water) is present; the concentration of anions becomes larger by adding alkali, chlorides, even acids to water. Evidently the charge given to the tube by the OH ions and the silicic acid of glass is not so large that it cannot increase any more.

The potential increases more as the added anion is better adsorbed; this explains why we meet with such a great increase towards the side of the OH-ions in Fig. 2C and why Powis found that the optimum on the right side is higher when the anion is more adsorbed or polyvalent[1]. Of course a cation always accompanies the anion and the former resists a continuous increase of the electric charge, as it is adsorbed itself and gets in a more favourable condition for electro-adsorption because it bears an electric charge of opposite nature. Consequentely a lowering of the charge must occur at higher concentration.

Still it is curious that the concentration of anions *really* present plays an important part; for *potentially* there is in water an amount of OH-ions, which is nearly unlimited and we are accustomed in questions of this sort to consider as decisive the concentration of potential ions. The phenomenon of hydrolysis (e. g. with solutions of $AlCl_3$) is usually of no importance[2]. These results warn us however to be prudent with all theory on this account, though on the other hand the condition of the ions of water is not always quite comparable with that of salts in solutions.

POSTSCRIPT.

Just now a paper appeared of HERSTAD, Koll. Beih. **8**, 399 (1916). His investigations on the influence of dialysis of goldsols and its limit values (cf. fig. 15 and 16) are in striking accordance with this communication. The paper induces us to measure the potentials in the case of $HgCl_2$ solutions. Still more amazing is an investigation of BEANS and EASTLACK [Journ. of the Americ. chem. Soc. **37**, 2667 (1915)] on the best conditions for the preparation of highly dispersed gold sols. It gives the impression that the concentration of electrolytes necessary to get red sols coincide with those of the optimum charge of the glass capillary tube. I hope to revert to this subject before long.

Utrecht, VAN 'T HOFF-*Laboratory.*   December 1916.

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[1] Powis it is true made investigations on KCl and $K_4Fe(CN)_6$, but his conclusions probably hold as well for acids as for salts.

[2] Cf. FRENDLICH, Z. f. physik. Chem. **44**, 136 (1903).